

Interparticle friction and Rheology of Dense suspensions

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Outline

- **BACKGROUND ON THE RHEOLOGY OF DENSE SUSPENSIONS:**
Important but not well-understood role of **particle friction μ_p** .
- **AIM OF MY THESIS:**
Evidencing the relation between μ_p and **rheology**.
- **MATERIALS UNDER SCRUTINY:**
Polystyrene (PS) beads in various **matrix fluid**.
- **METHODS OF CHARACTERIZATION:**
Tuning-fork force microscope (TFM) and **Rheometry**.
- **RESULTS AND DISCUSSIONS:**
How different μ_p **profiles** explains different **rheological behaviors**.
- **CONCLUSION AND OUTLOOKS:**
The importance of studying μ_p in **rheology**.

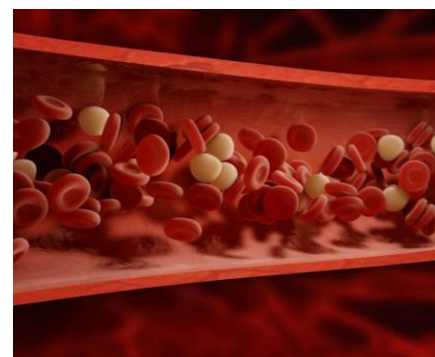


BACKGROUND

on the rheology of dense suspensions

What is a suspension?

‘Solid particles suspended in a liquid’

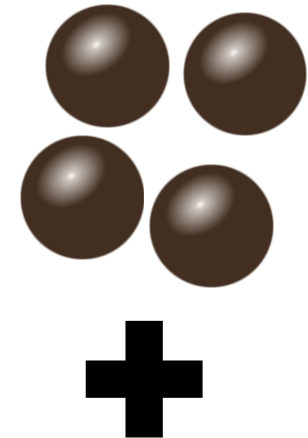


Credit: Google image
Handbook of Flexible Organic Electronics

Great interest in studying suspensions' flow

Simplification:

Smooth hard spheres

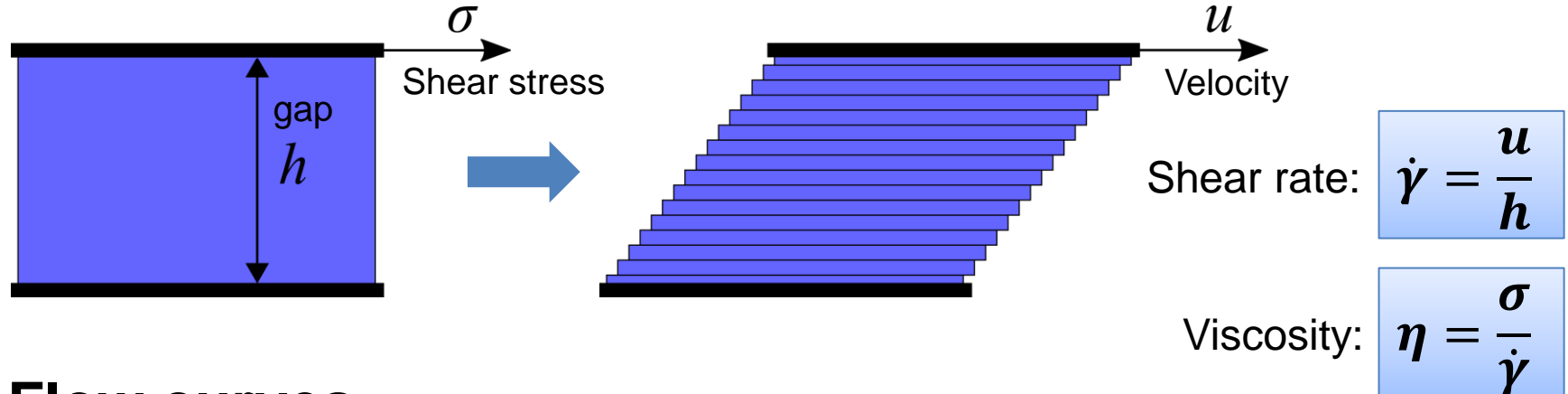


Newtonian fluid

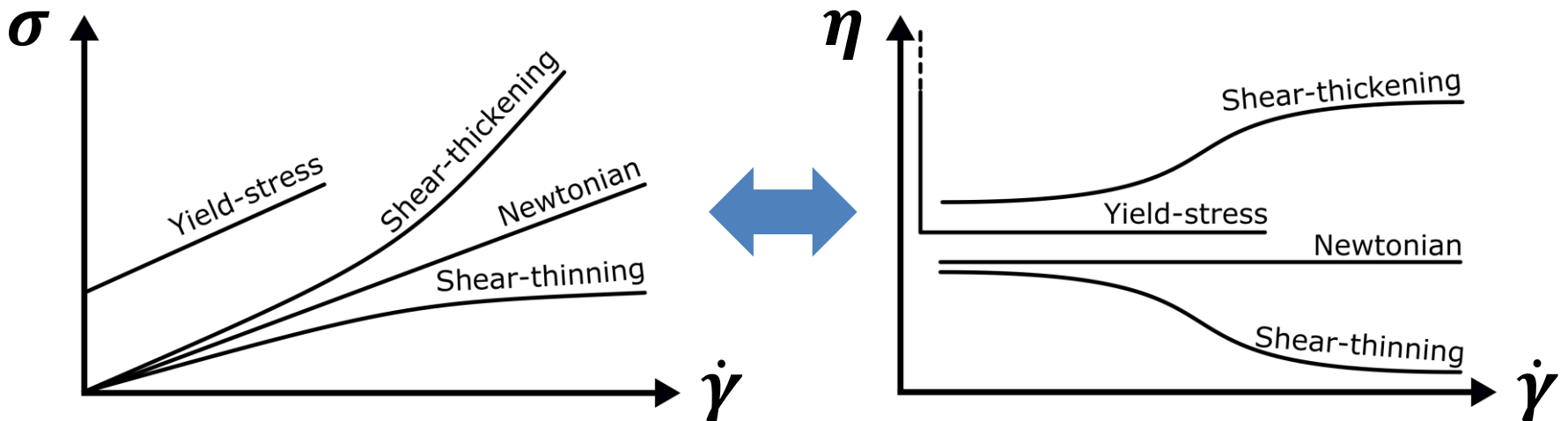
Dense suspension = high solid fraction $\phi = \frac{V_{solid}}{V_{total}}$

What is Rheology?

‘Study of flow’. How?

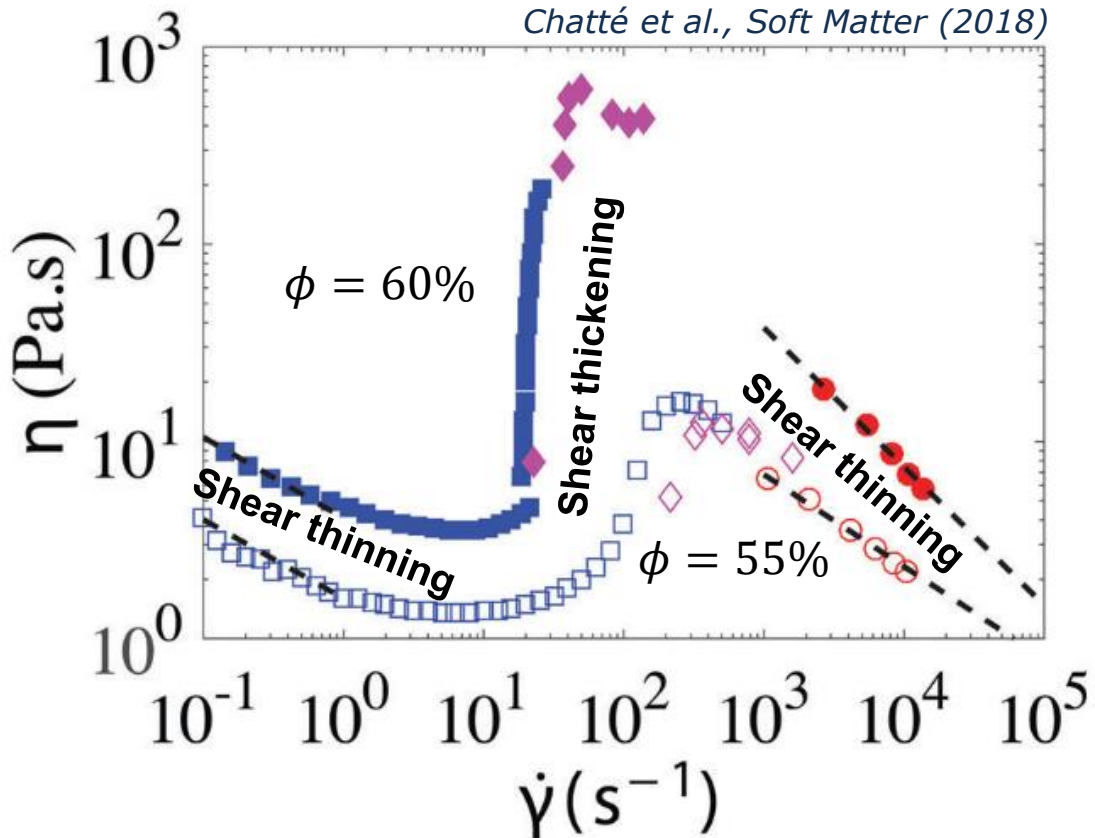


Flow curves

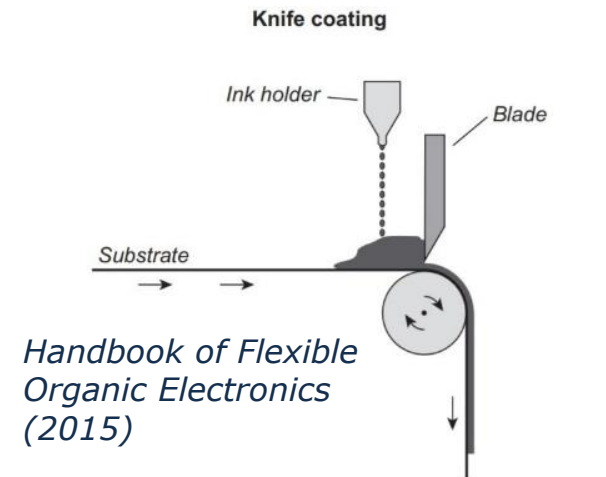


Non-Newtonian behaviors

An example: Flow curves of PVC particles suspended in DINCH plasticizer



Consequences:



What is the current understanding on non-Newtonian behaviors?



Dimensional analysis

Rheological parameters

- d : particle diameter
- ρ_p : particle density
- n : number concentration
- ρ_f : fluid density
- η_f : fluid viscosity
- $\dot{\gamma}$: shear rate
- $k_B T$: thermal energy

**7 variables
with 3 units:
[kg] [m] [s]**

Buckingham π theorem

Only $7 - 3 = 4$ dimensionless variables left:

$$Re = \frac{\rho_f \dot{\gamma} d^2}{\eta_f}$$

Viscous vs Inertial

$$Pe = \frac{3\pi \eta_f \dot{\gamma} d^3}{4k_B T}$$

Viscous vs Brownian

$$Sh = \frac{\eta_f \dot{\gamma}}{\Delta \rho g d}$$

Viscous vs Gravity

$$\phi = n \frac{\pi}{6} d^3$$

Solid fraction

Density-matched: $Sh \gg 1$

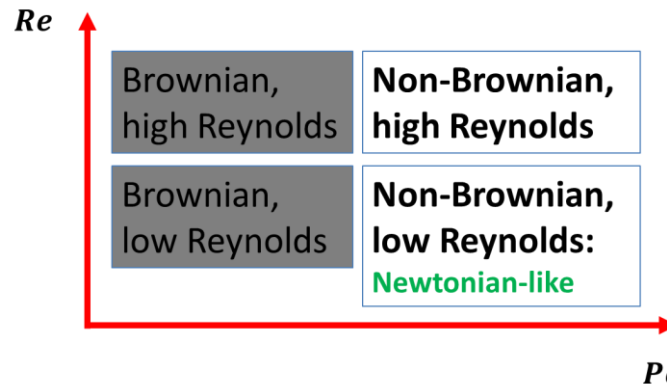
Non-Brownian: $Pe \gg 1$



$$\eta_s = f_\eta(Re, \phi)$$

with $\eta_s = \eta/\eta_f$

2 flow regimes:



Inertial regime

Viscous regime

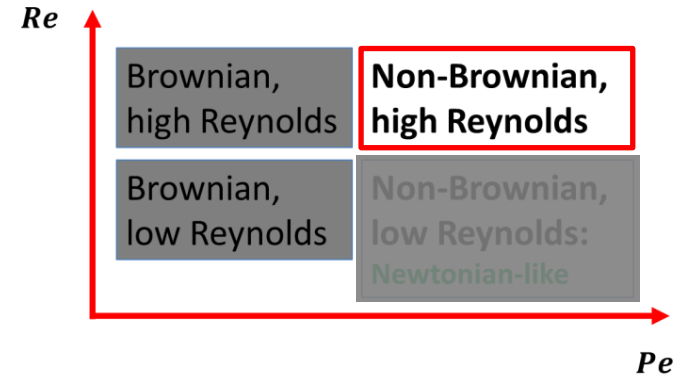


Inertial regime (high Re)

Inertia dominates:

Only 4 particle-related parameters:

$\rho_d, d, n, \dot{\gamma} \rightarrow$ 1 dimensionless number



The paradigm of dense granular matter:

Da Cruz et al., Phys. Rev. E (2005)

$$I = d\dot{\gamma} \sqrt{\frac{\rho_p}{\rho P}}$$

2 behavior laws:

$$\begin{cases} \phi = g(I) \\ \sigma = f(I)P^P \end{cases} \rightarrow \sigma = f(g^{-1}(\phi)) \frac{\rho_p d^2}{(g^{-1}(\phi))^2} \dot{\gamma}^2$$

$\sigma = A(\phi)\dot{\gamma}^2$: if ϕ is constant, σ varies as a function of $\dot{\gamma}^2$.

At high Re : Suspensions will shear thicken.

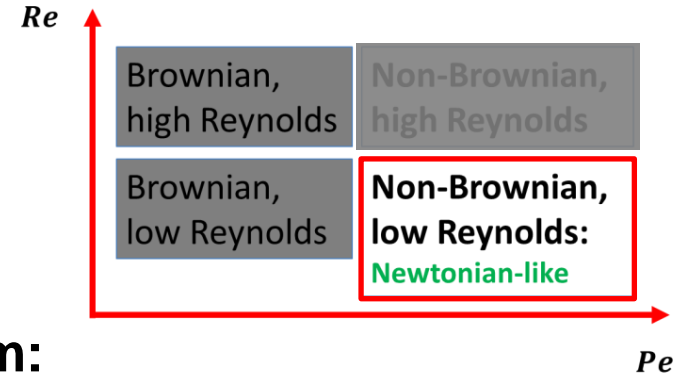


Viscous regime (low Re)

Viscous effects dominate:

Only 4 fluid-related parameters:

$d, \eta_f, n, \dot{\gamma} \rightarrow$ 1 dimensionless number



Borrowing from granular-matter paradigm:

Boyer et al., PRL (2011)

$$I_v = \frac{\eta_f \dot{\gamma}}{P^P}$$

2 behavior laws:

$$\begin{cases} \phi = g(I_v) \\ \sigma = f(I_v)P^P \end{cases} \rightarrow \sigma = f(g^{-1}(\phi)) \frac{\eta_f}{g^{-1}(\phi)} \dot{\gamma}$$

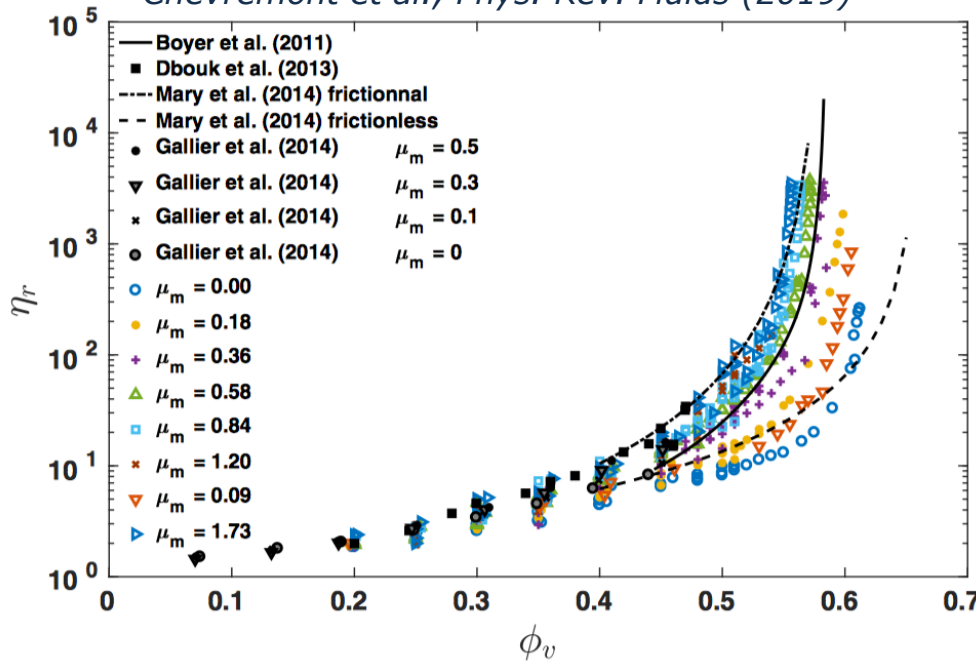
$\sigma = \eta_s(\phi) \eta_f \dot{\gamma}$: if ϕ is constant, σ will be proportional to $\dot{\gamma}$.

At low Re : Suspensions should behave as Newtonian fluid.

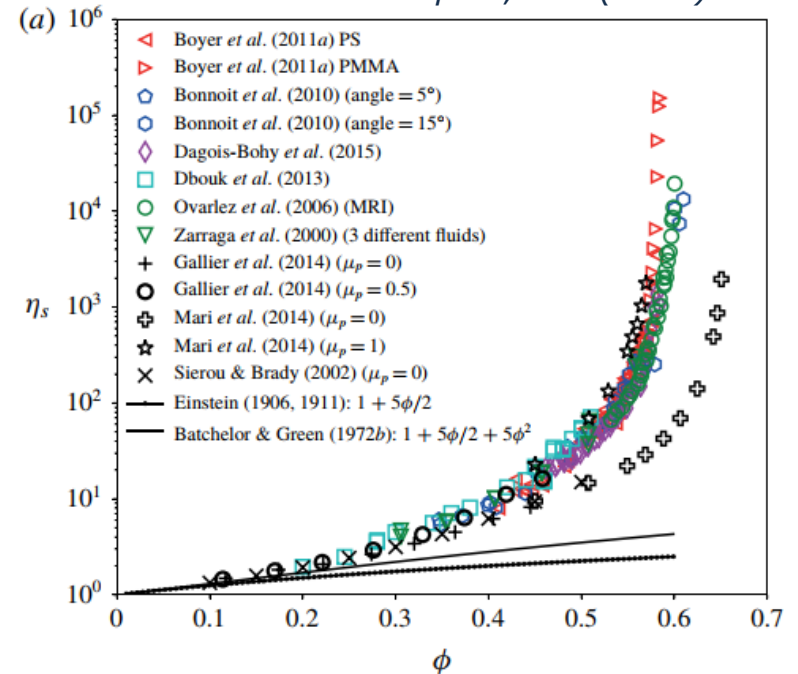
Dependence $\eta_s(\phi)$ on μ_p



Chèvremont et al., Phys. Rev. Fluids (2019)



Guazzelli & Pouliquen, JFM (2018)

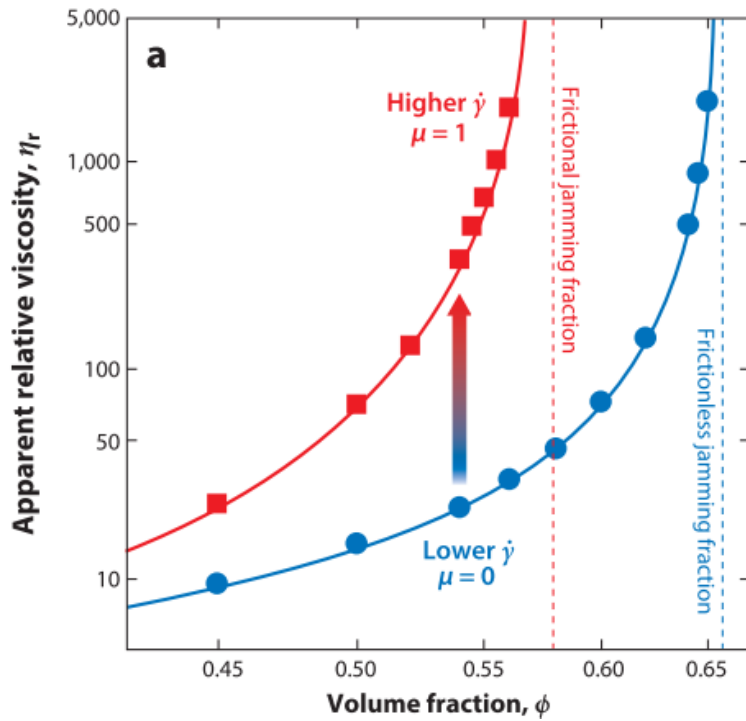


$\eta_s(\phi)$ curve shifts leftward when particle friction coefficient μ_p increases.

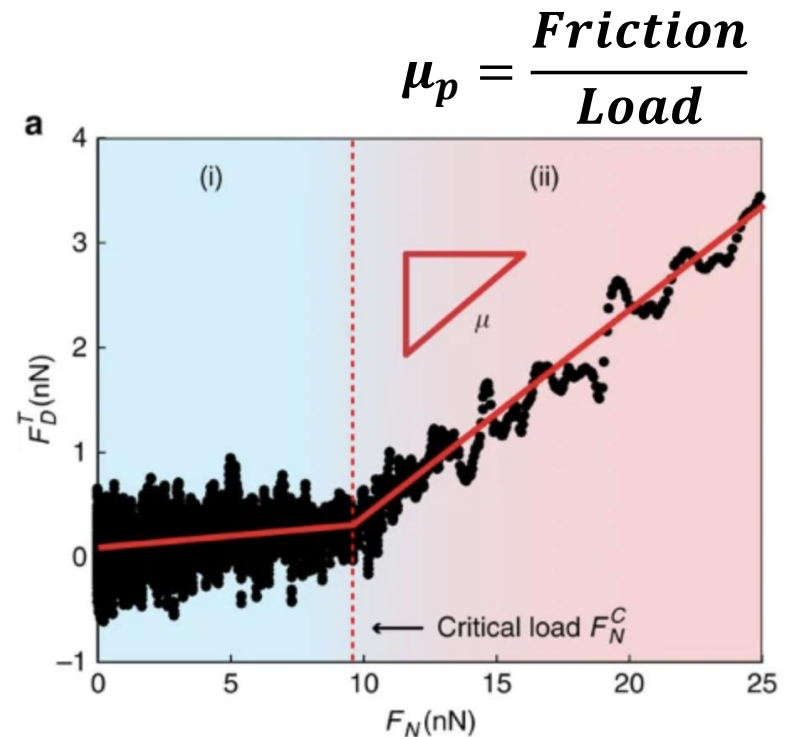
The role of μ_p is crucial
but experimental data on μ_p is still lacking.

Shear Thickening

Explanation: **Shear-induced transition**
 from **Low-friction profile** (soft/no contact)
 to **High-friction profile** (hard contact)



Morris, *Annu. Rev. Fluid Mech.* (2020)
 Mari et al., *J. Rheol.* (2011)



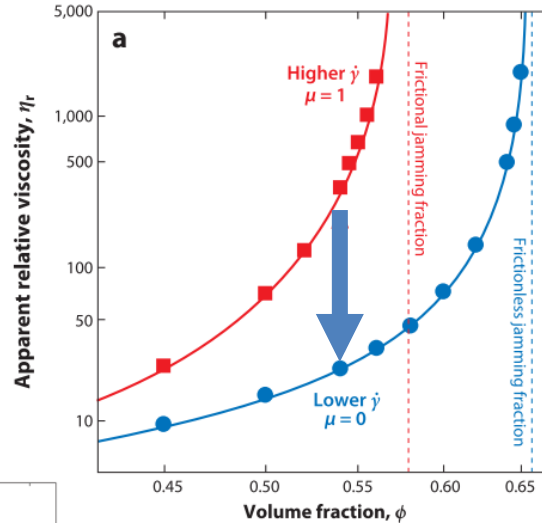
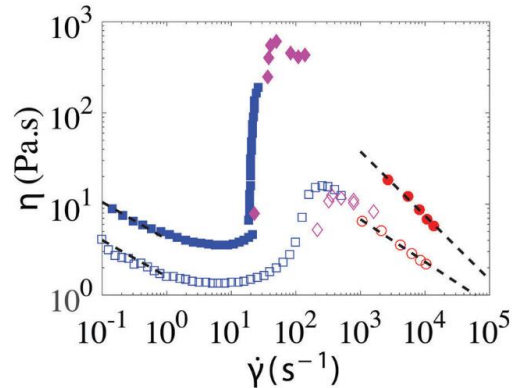
Comtet et al., *Nat. Comm.* (2017)

Shear Thinning

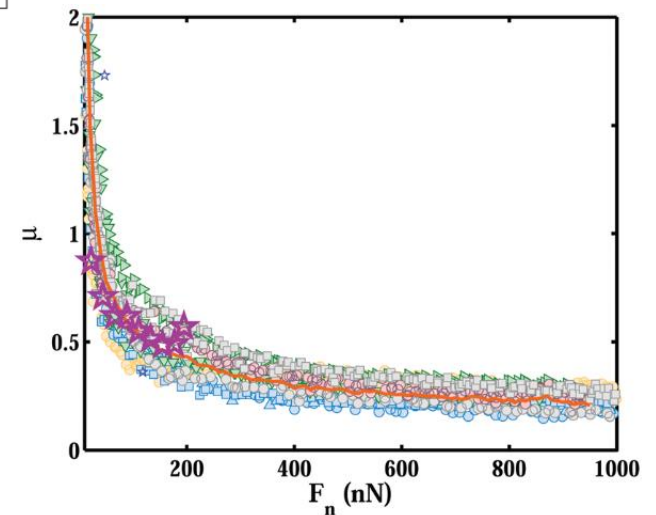
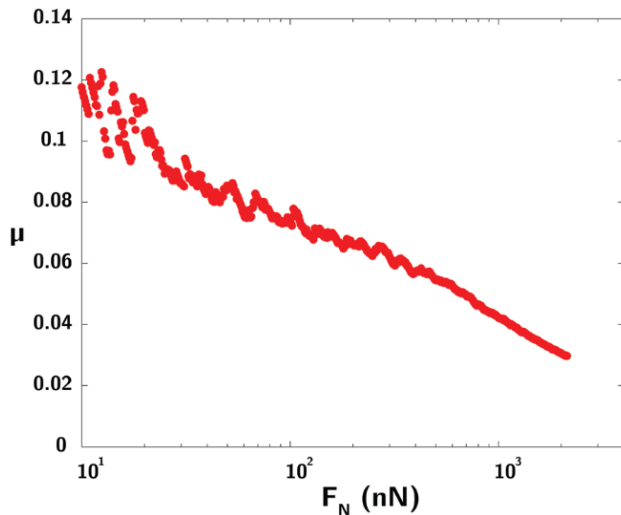
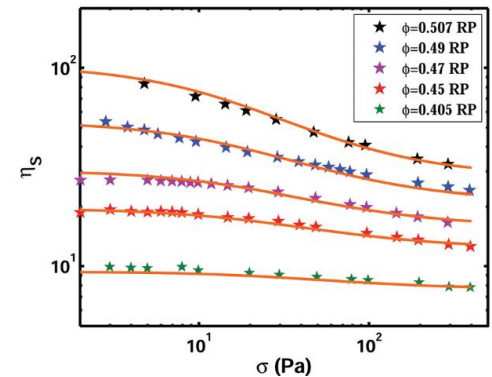


Explanation: **Decrease of μ_p with increasing normal load F_n**

Chatté et al., *Soft Matter* (2018)

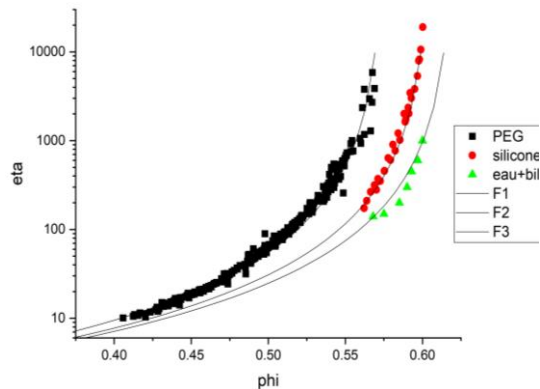


Arshad et al., *Soft Matter* (2021)



Open questions

1. Is something else missing in the rheological description?



- Well-established theoretical framework for suspension of smooth hard non-Brownian spheres.
- **But lack of experimental data on μ_p to explain their rheology.**

Ovarlez et al.: How to explain the lateral shift of the $\eta_s(\phi)$ curves as a function of the solvent?

2. How does shear-thickening occur even in the frictionless state?

3. How do shear-thickening suspensions flow in the frictional state?



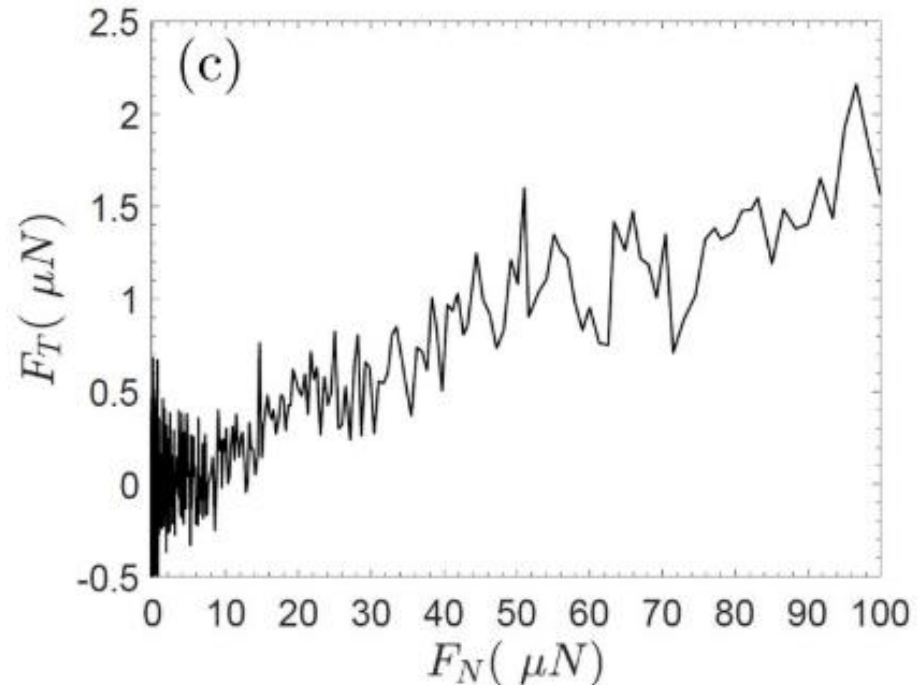
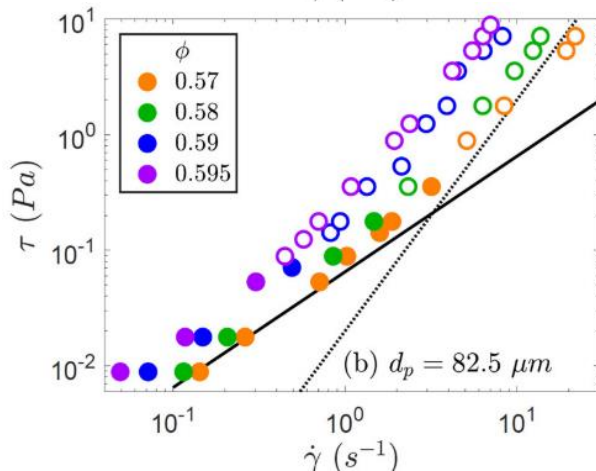
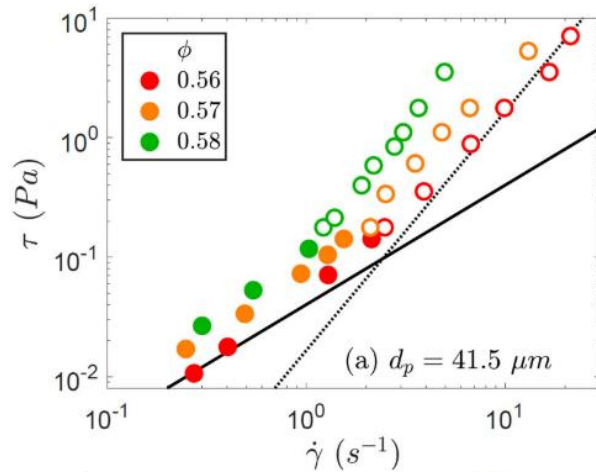
AIM OF MY THESIS

Response



2. FRICTIONLESS SHEAR-THICKENING OCCURS AT HIGH Re :

Madraki et al., JoR (2020)

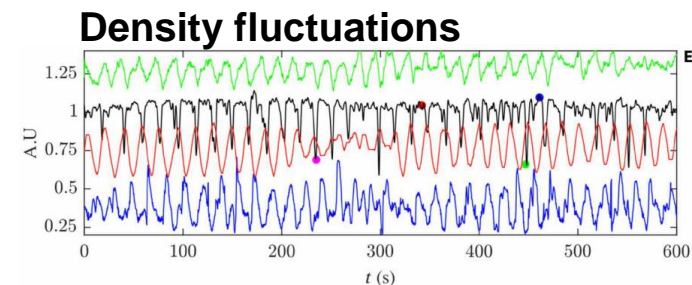
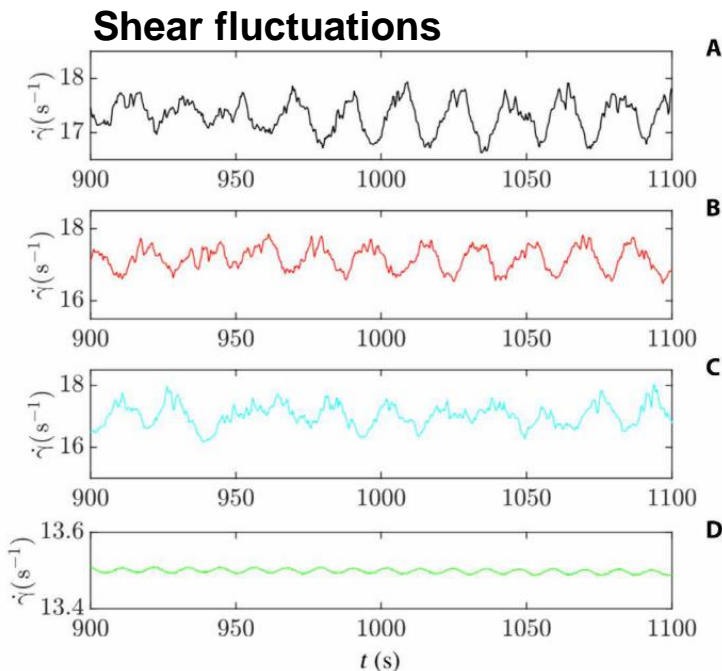


Viscous-to-inertial transition can occur before repulsive-to-frictional transition.

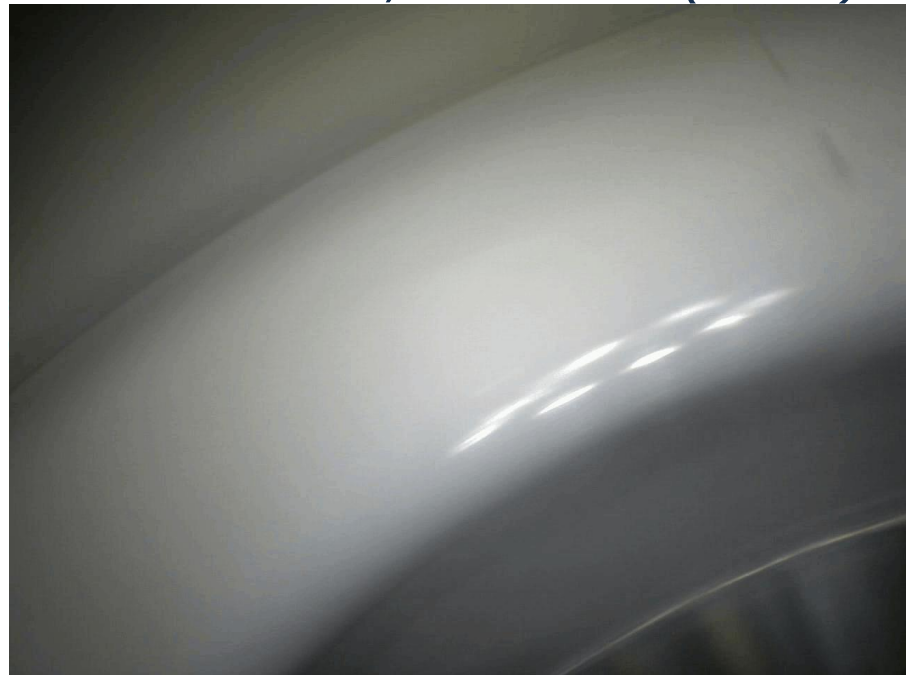
Response



3. INSTABILITY DURING SHEAR-THICKENING TRANSITION:



Ovarlez et al., Sci. Adv. (2020)



Density waves propagating in the velocity direction generate shear instabilities.



Response

1. THE ROLE OF SOLVENT ON THE RHEOLOGICAL BEHAVIORS :

What is the influence of solvent on the $\eta_s(\phi)$ curves?

What is the description at the microscopic level (F_N^C , F_T^D , and μ_p)

How the dependence of μ_p on normal load results in shear thinning?



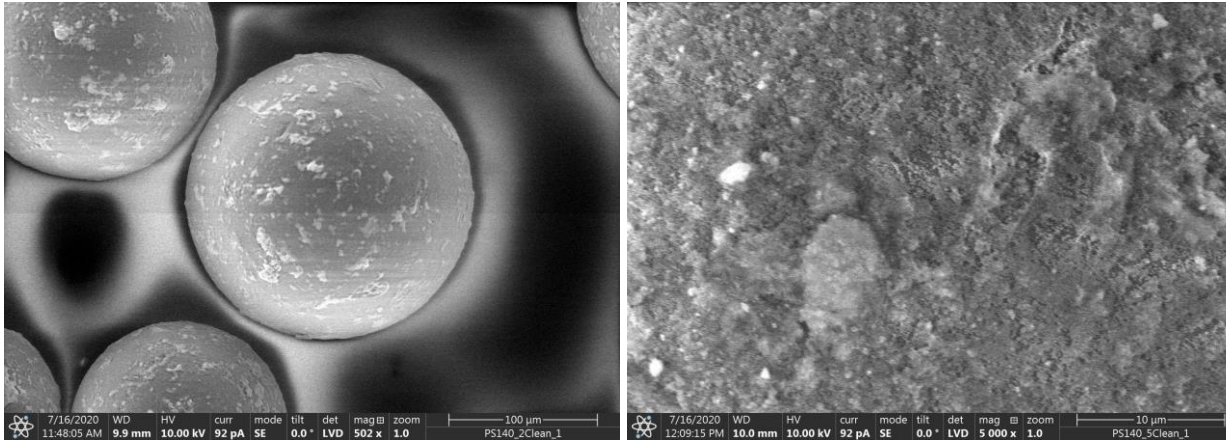
MATERIALS

under scrutiny

Particle cleaning



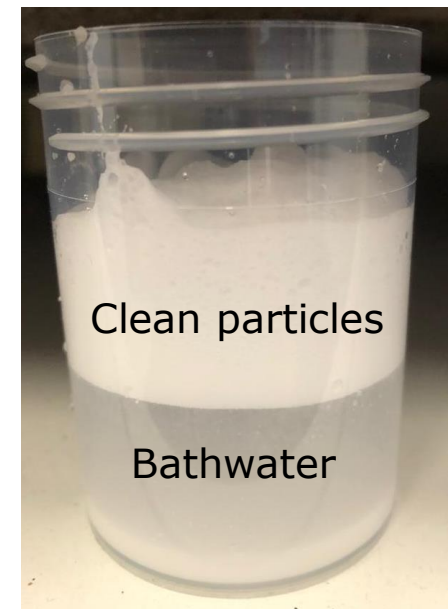
Polystyrene (PS) spheres, $R = 20 \mu\text{m}$



SEM micrograph of washed PS spheres

Washing process:

- Sonicate the raw beads in deionized water.
- Replace regularly the bathwater.
- Filter out the 'creamed' beads. (Pickering emulsion).
- Dry at 70°C until becoming powder-like.



Suspension preparation



Solvents

Nal solution, $\eta_f \approx 1 \text{ mPa s}$

(density-matched)

Silicone oil, $\eta_f \approx 20 \text{ mPa s}$

PEG, $\eta_f \approx 2000 \text{ mPa s}$

(Poly(ethylene glycol-ran-propylene glycol) mono-butyl ether)

} Newtonian fluids

Preparation protocol:

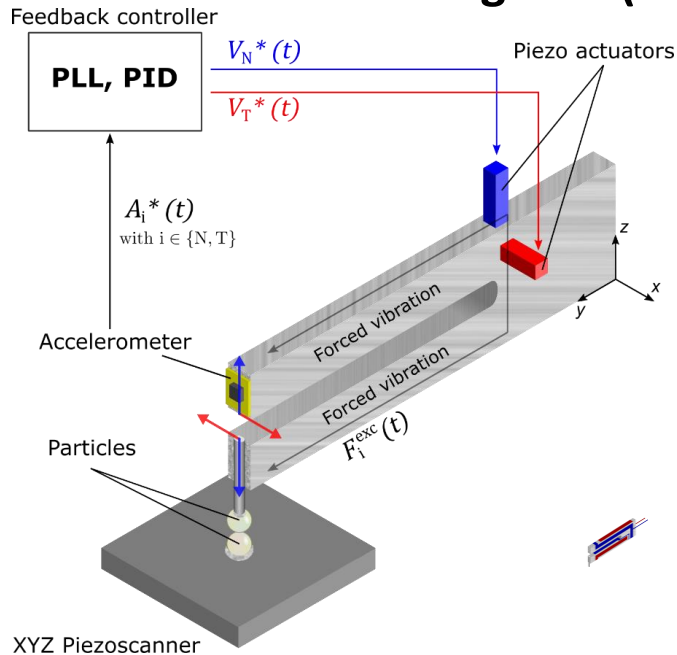
- Weigh the particles.
- Add the solvent.
- Homogenize the mixture
- Degas the mixture using vacuum (if not water-based)
- Homogenize the mixture before each rheometric measurement.



METHODS of characterization

2 setups for 2 force scales:

With aluminum tuning fork (TF):

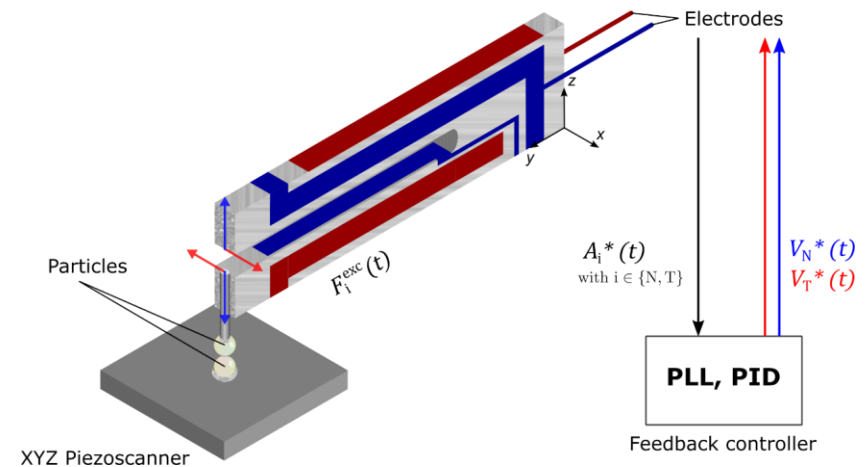


Prongs' dimension:

$$L = 75 \text{ mm}, W = 6.8 \text{ mm},$$

$$T = 12 \text{ mm}$$

With quartz tuning fork (TF):



Prongs' dimension:

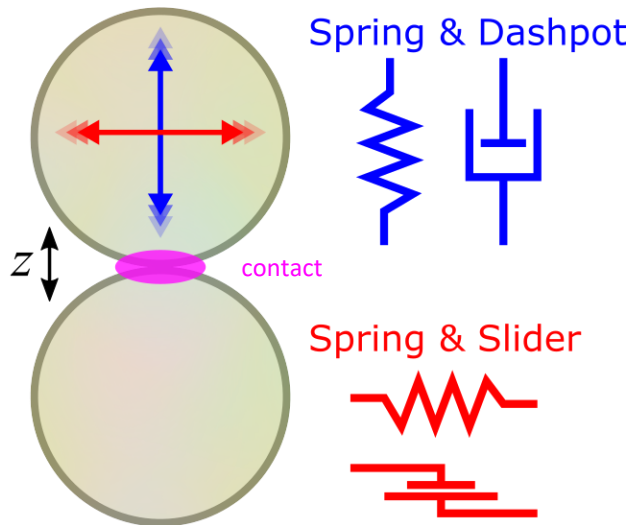
$$L = 3.75 \text{ mm}, W = 0.34 \text{ mm},$$

$$T = 0.6 \text{ mm}$$

Quartz TF is 20 times smaller than aluminum TF.

Principle of TFM

Models:



WITHOUT interactions between particles:

- Resonate at a frequency f_0
- Require an excitation voltage E_0 (to maintain a constant oscillation amplitude A)

WITH interactions between particles:

- Resonate at a frequency $f(z)$
- Require an excitation voltage $E(z)$ (to maintain the same amplitude A)

F_N^C : Normal conservative force
(elastic force)

$$F_N^C(z) = -2 \frac{k_0^N}{f_0^N} \int \delta f^N(z) dz$$

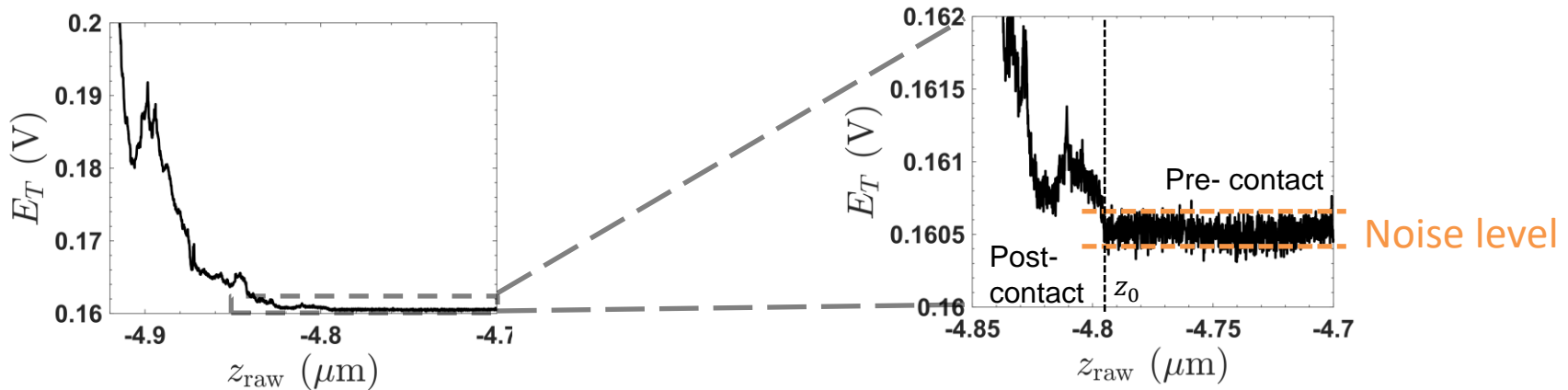
F_T^D : Tangential dissipative force
(frictional force)

$$F_T^D(z) = \frac{4}{\pi} C^T \left(E^T(z) - E_0^T \right)$$

2 modes
are
decoupled

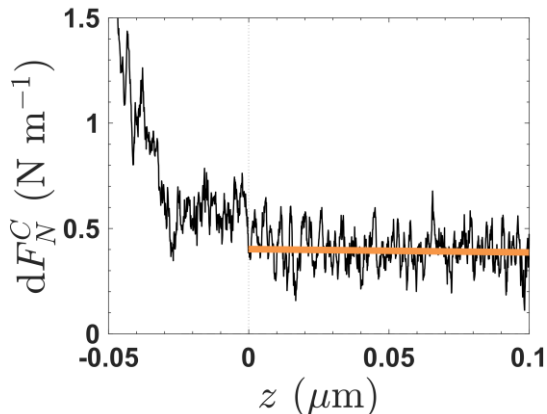
Determination of $z = 0$

$z = z_{\text{raw}} - z_0$. z_0 is the raw separation where E_T rises out of the noise.



Incorrect $z = 0$ results in artifacts on repulsive force before contact, but no effect on μ_p .

Thermal drift correction: for $\delta F_N^C(z)$ and $E_T(z)$

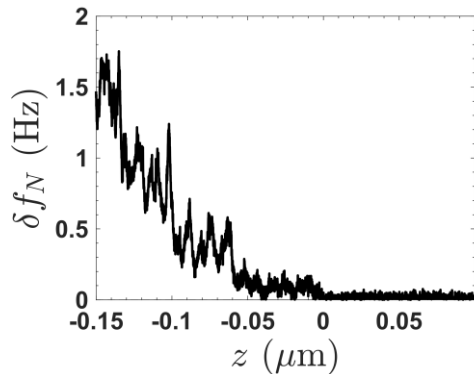


- Apply a **linear fit** for the signals before contact.
- Subtract the fit value from raw data.
- Calculate the forces using the resulting value.

Raw signal of TFM (air)



Aluminum TF:



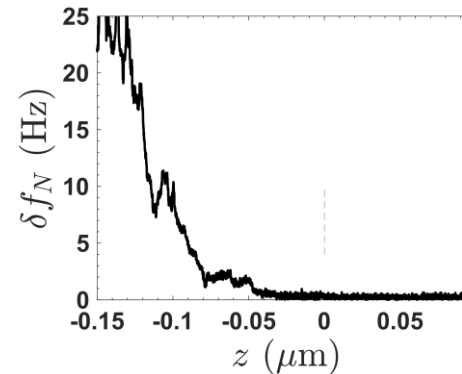
Sensitivity:

$$s_N^C = \frac{2k_0^N}{f_0^N} \approx 700 \text{ N m}^{-1} \text{ Hz}^{-1}$$

Noise level
 $\approx 0.01 \text{ Hz}$

Minimal stiffness shift $\approx 7 \text{ N m}^{-1}$

Quartz TF:

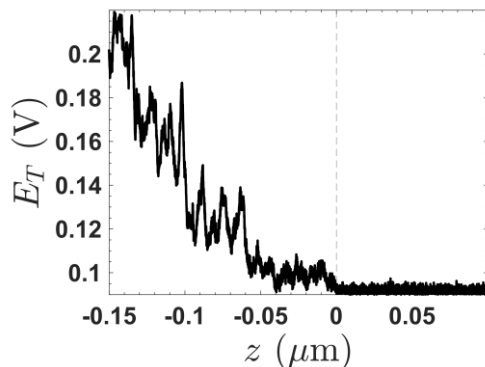


Sensitivity:

$$s_N^C = \frac{2k_0^N}{f_0^N} \approx 1 \text{ N m}^{-1} \text{ Hz}^{-1}$$

Noise level
 $\approx 0.1 \text{ Hz}$

Minimal stiffness shift $\approx 0.1 \text{ N m}^{-1}$

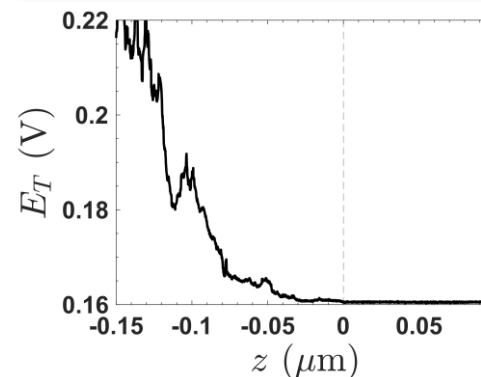


Sensitivity:

$$C_T = \frac{k_0^T}{Q_0^T} C_{\text{drive}}^T \approx 30 \mu\text{N V}^{-1}$$

Noise level
 $\approx 1 \text{ mV}$

Minimal force $\approx 30 \text{ nN}$



Sensitivity:

$$C_T = \frac{k_0^T}{Q_0^T} C_{\text{drive}}^T \approx 10 \mu\text{N V}^{-1}$$

Noise level
 $\approx 0.1 \text{ mV}$

Minimal force $\approx 3 \text{ nN}$

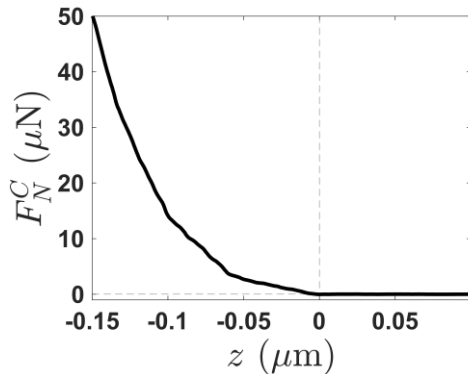
More stable versus high normal load

More sensitive to small forces

Force measurement (air)



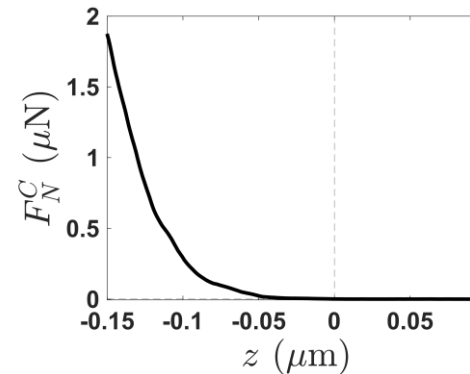
Aluminum TF:



Normal load
(FCN):

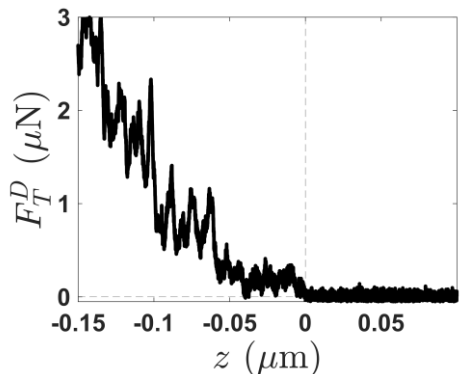
$$F_N^C = s_N^C \int \delta f^N(z) dz$$

Quartz TF:



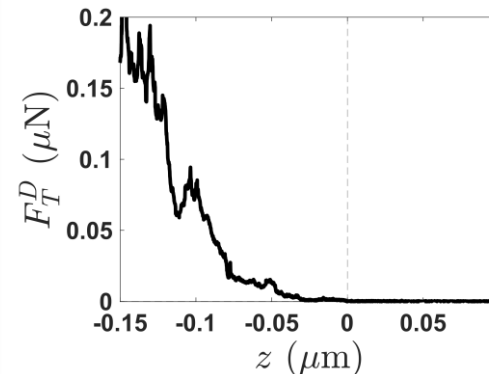
Normal load
(FCN):

$$F_N^C = s_N^C \int \delta f^N(z) dz$$



Tangential
friction (FDT):

$$F_T^D = \frac{4}{\pi} C_T (E^T(z) - E_0^T)$$

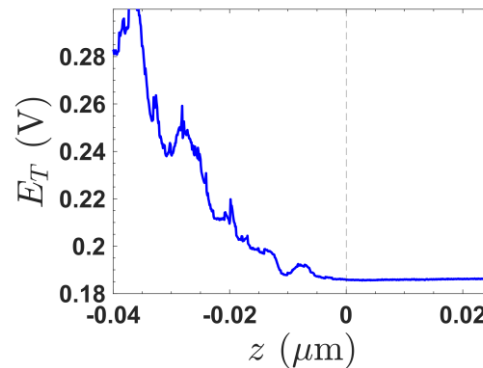
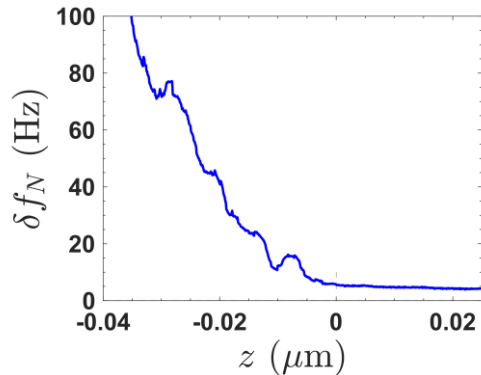


Tangential
friction (FDT):

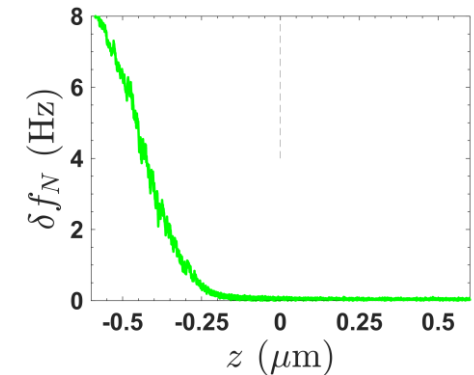
$$F_T^D = \frac{4}{\pi} C_T (E^T(z) - E_0^T)$$



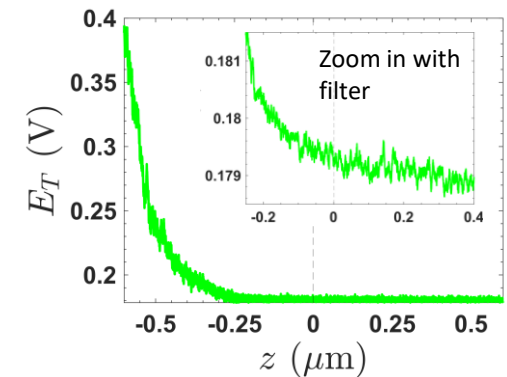
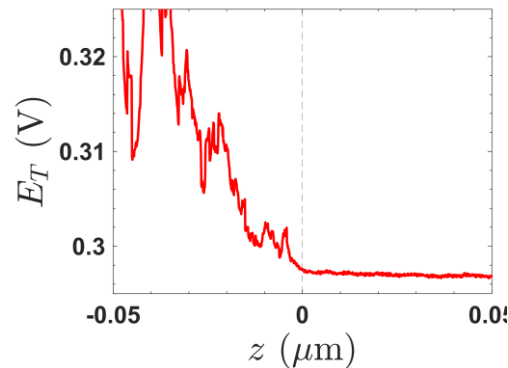
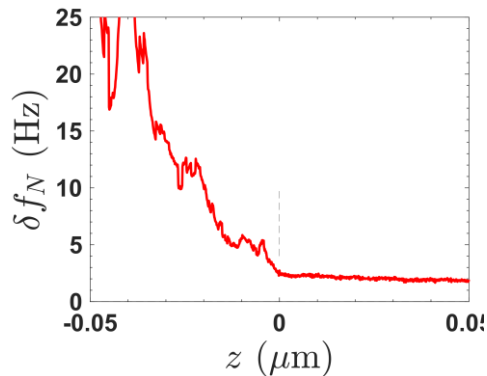
Nal solution (Quartz)



PEG (Aluminum)



Silicone oil (Quartz)



No significant change in noise level at $\eta_f \leq 20$ mPa s.
 For $\eta_f = 2000$ mPa s, $E_T(z)$ is roughly 2 times noisier.

Noise and measure bias



Possible source of noise:

- **High humidity**
→ Counteracted by placing dehydrator in the measuring chamber.
- **Acoustic and mechanical vibration**
→ Counteracted by using acoustic box, anchor, and anti-vibration table.
- **Electronic noise**
→ Negligible compare the force scale of interest.
- **Thermal noise** (negligible at our scale).
- **Noise from motors** inside the chamber (negligible at our scale).

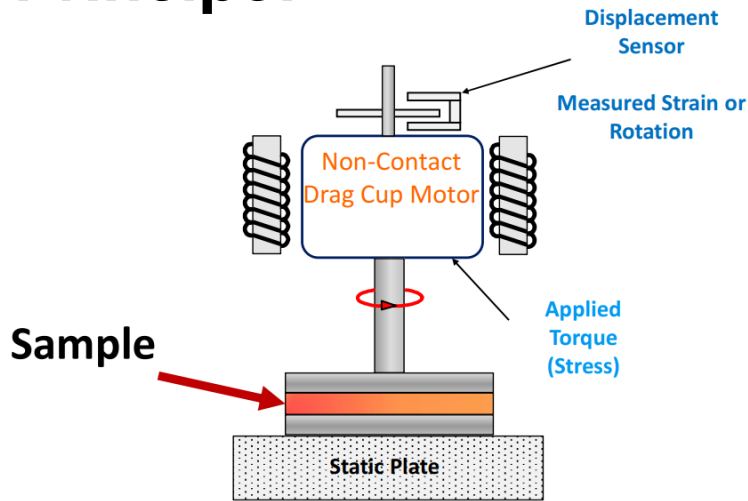
Possible bias:

- Starting and ending point of the linear fit for the thermal drifts.

Rheometry



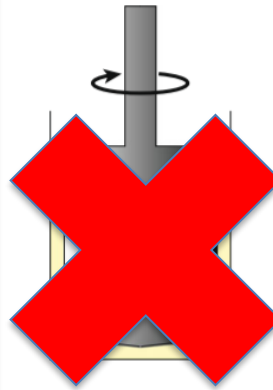
Principe:



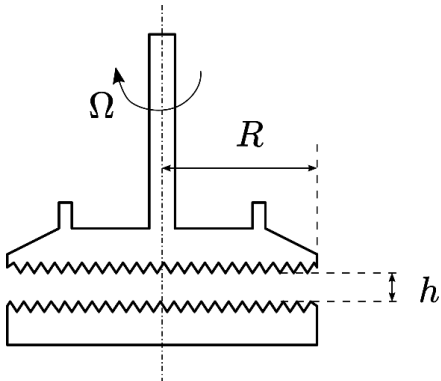
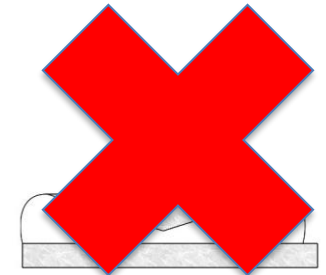
TA instruments (2019)

Geometries:

Severe migration to the bottom and the exterior

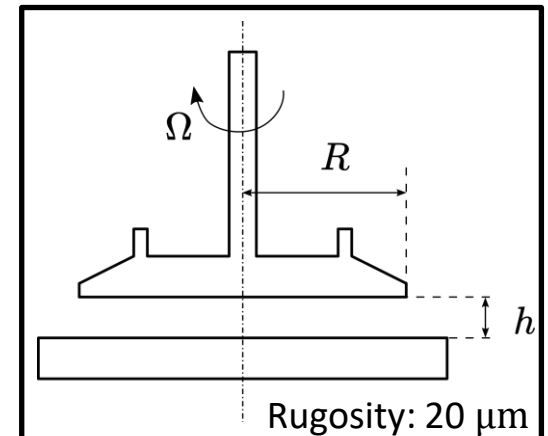


Not suitable for large particles



Help to avoid wall slip. No migration.

Might have sedimentation and drainage problem.

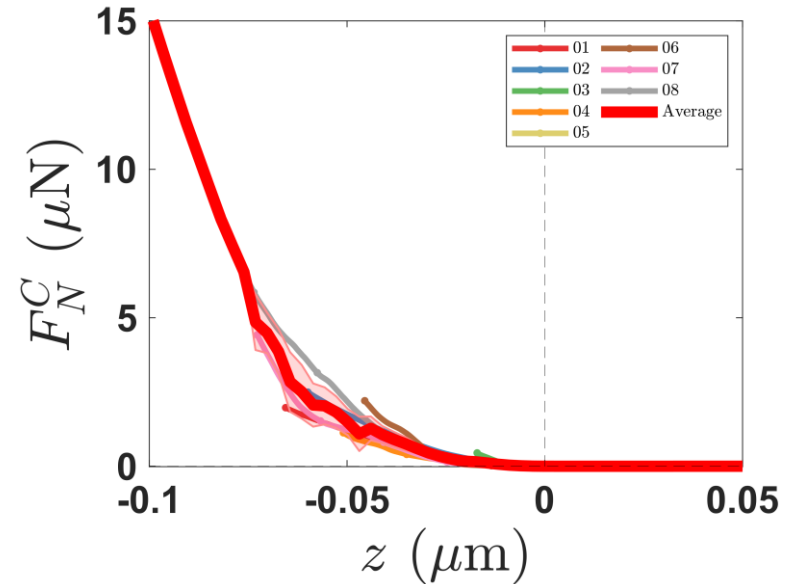
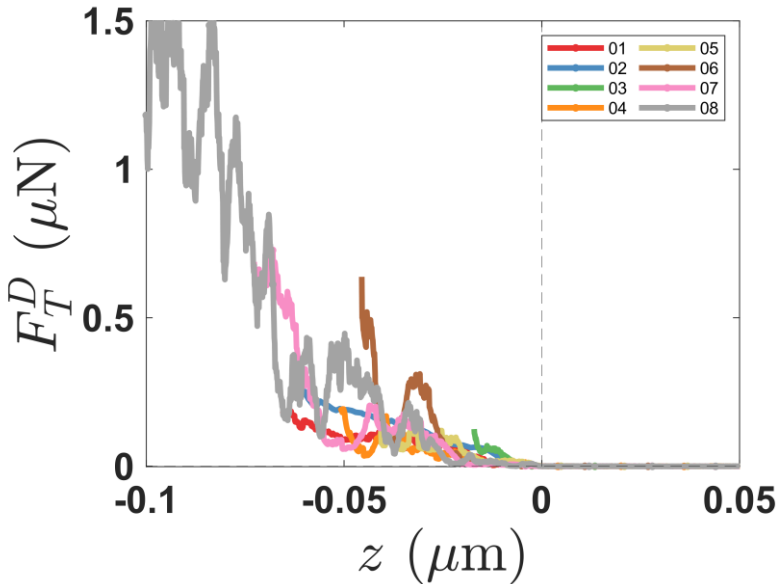




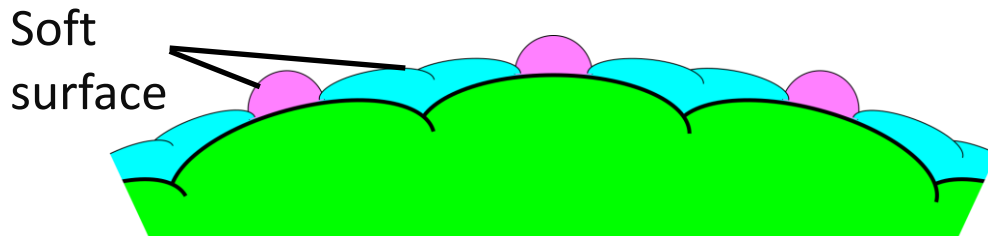
RESULTS & DISCUSSION

Contact force profiles

Silicone oil



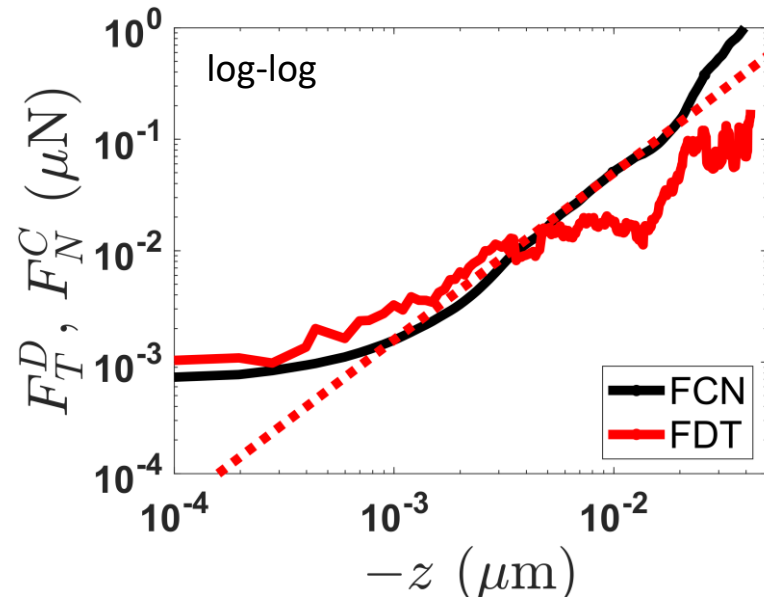
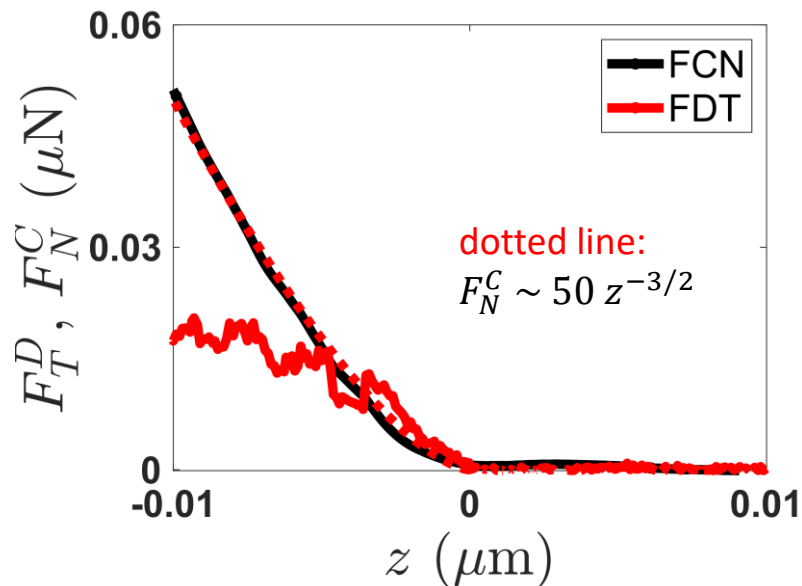
$F_N(z)$ model: $F_N^C = f(z, E_0, h_r)$



z	E_0	h_r
0 nm - 15 nm	1 GPa	15 nm
15 nm - 50 nm	1 GPa	90 nm
50 nm - center	3 GPa	530 nm

Contact force profiles

Silicone oil



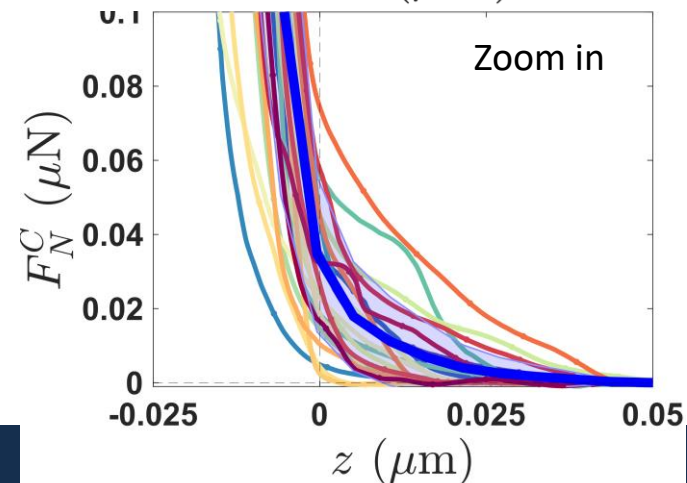
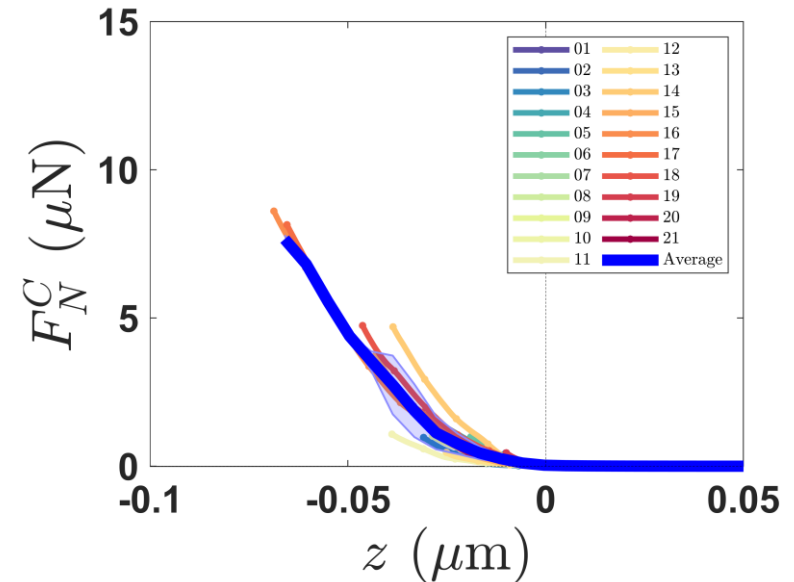
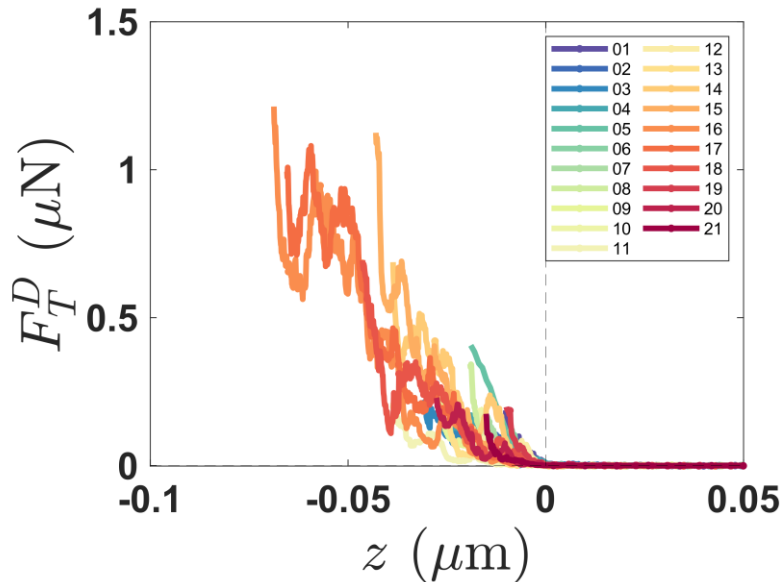
No sign of repulsive force

→ Quasi-unstable suspension (with very low yield stress)

Close to $z = 0$, Hertz model with either low contact radius (from asperities) or low Young modulus.

Contact force profiles

Nal solution

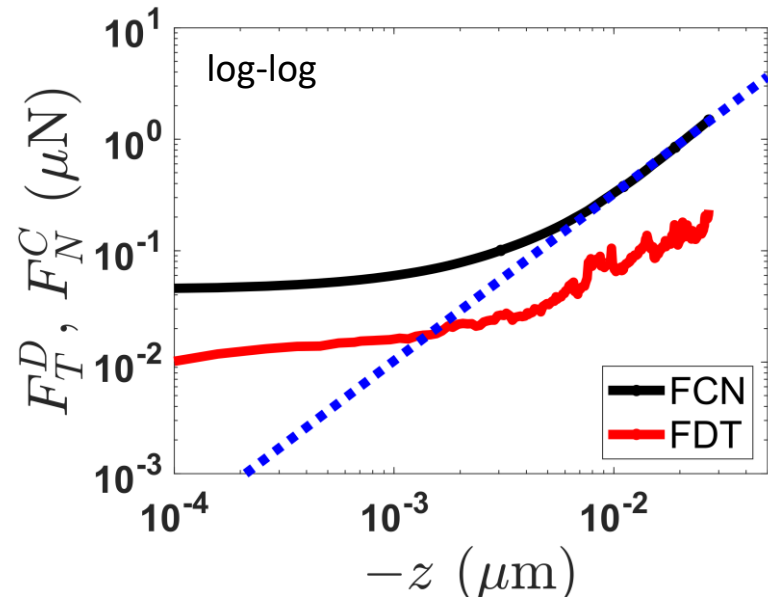
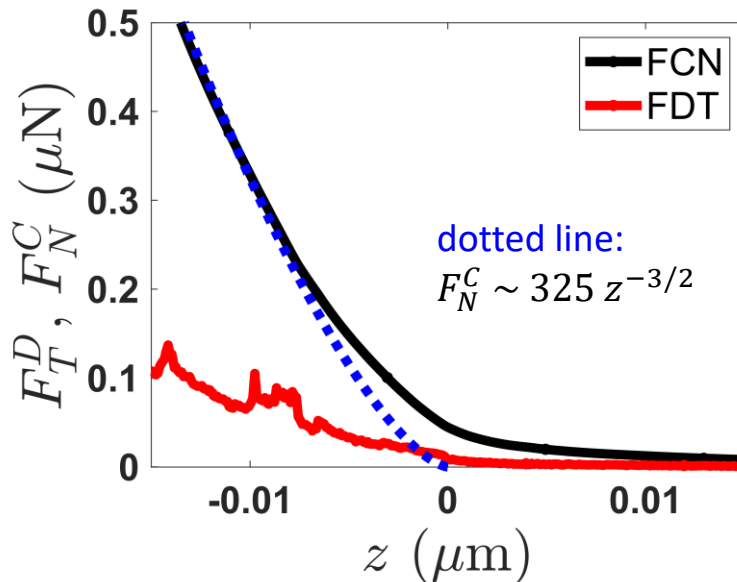


Presence of repulsive forces.

Repulsion added to the force profile after contact.

Contact force profiles

Nal solution

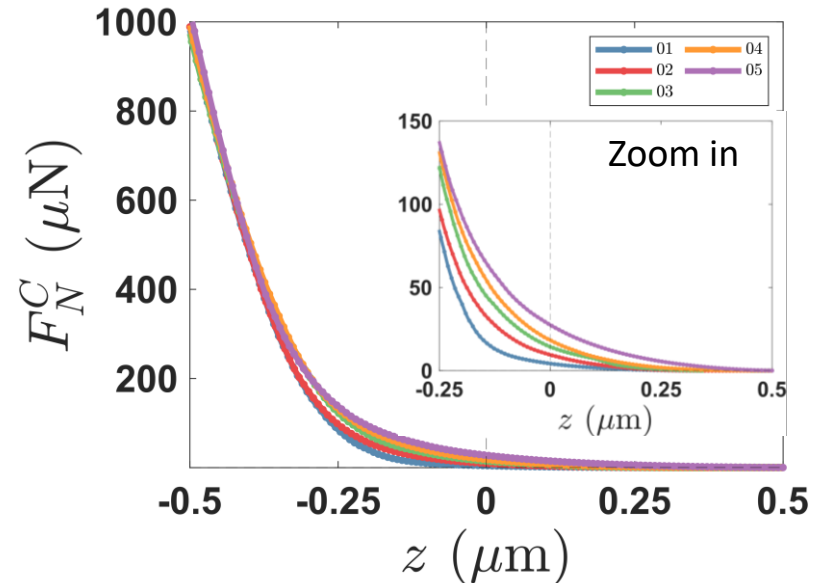
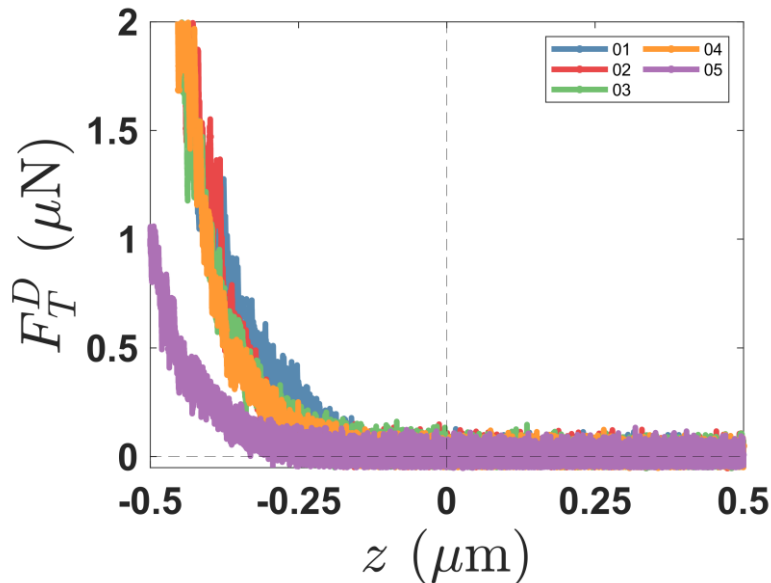


Debye length $\lambda_D = 0.4$ nm for solution of $I = 0.5136$ M
 → Not ionic repulsion. Must be of steric origin.

At high overlap, Hertz model with the Young modulus of PS.

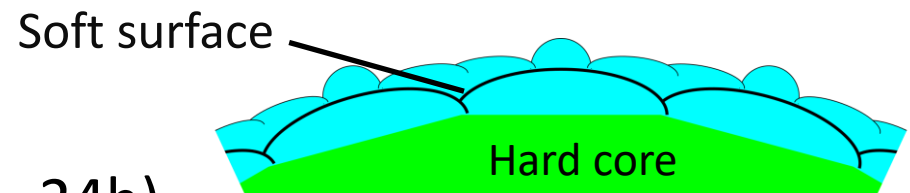
Contact force profiles

PEG



PS particles swell in PEG.

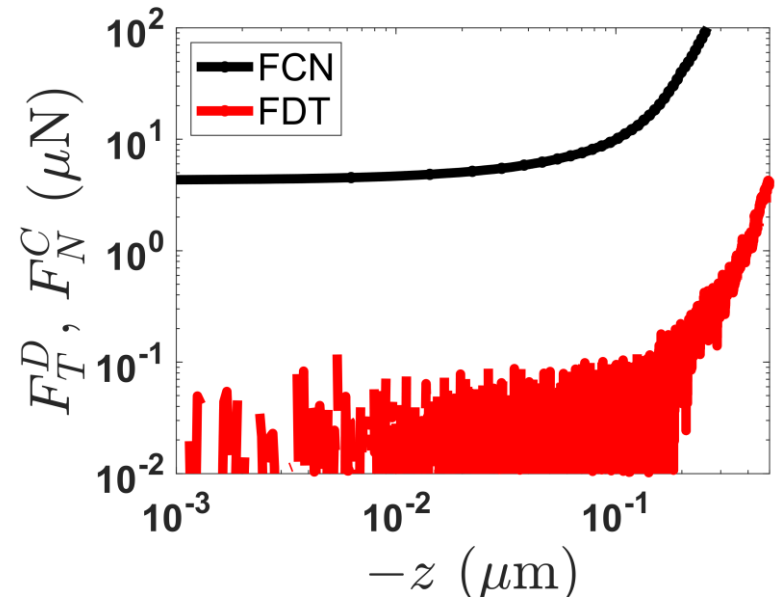
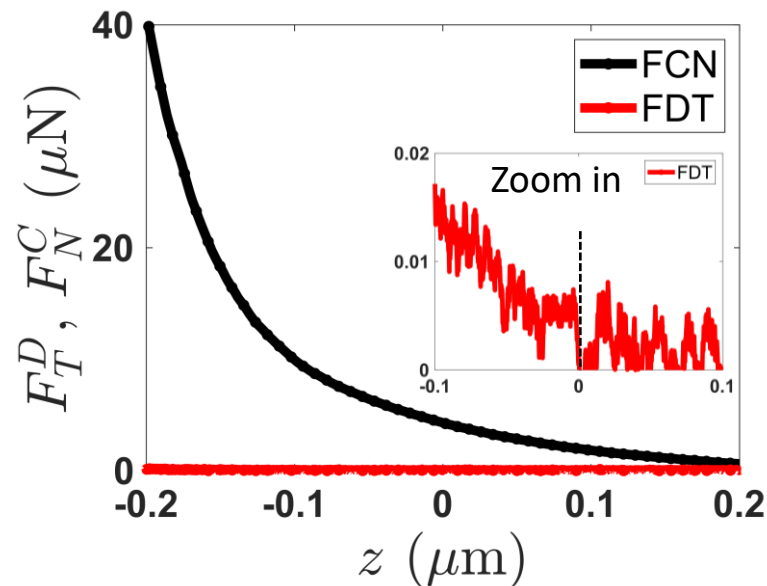
Swelling increases with the submerged duration (1h – 24h).



Swelling modifies the solid fraction: $\phi_{\text{eff}} = \beta \phi$.

Contact force profiles

PEG

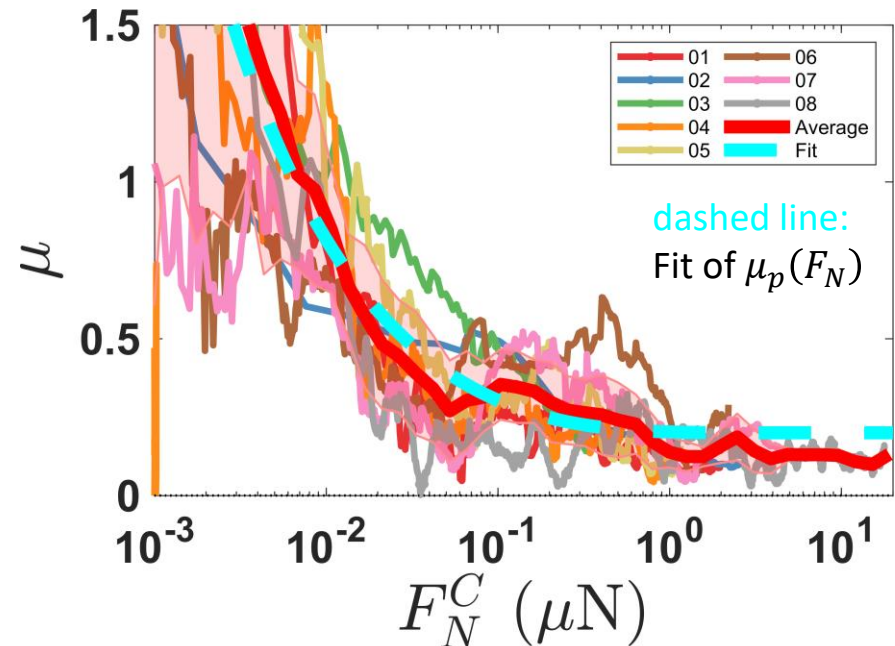
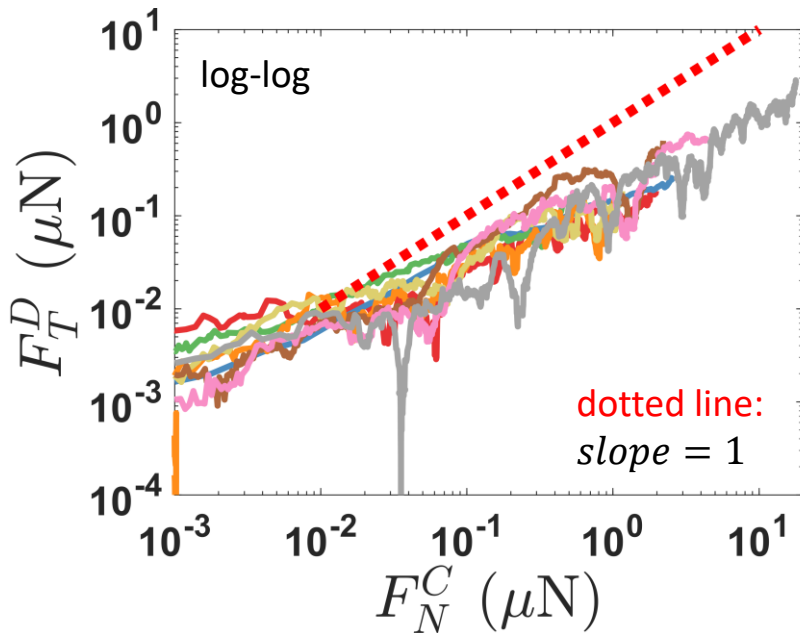


$z = 0$ is determined by the same method as before.

Normal load are more 2 orders of magnitude higher than Friction.

$\mu_p(F_N)$ -profile in oil

Silicone oil



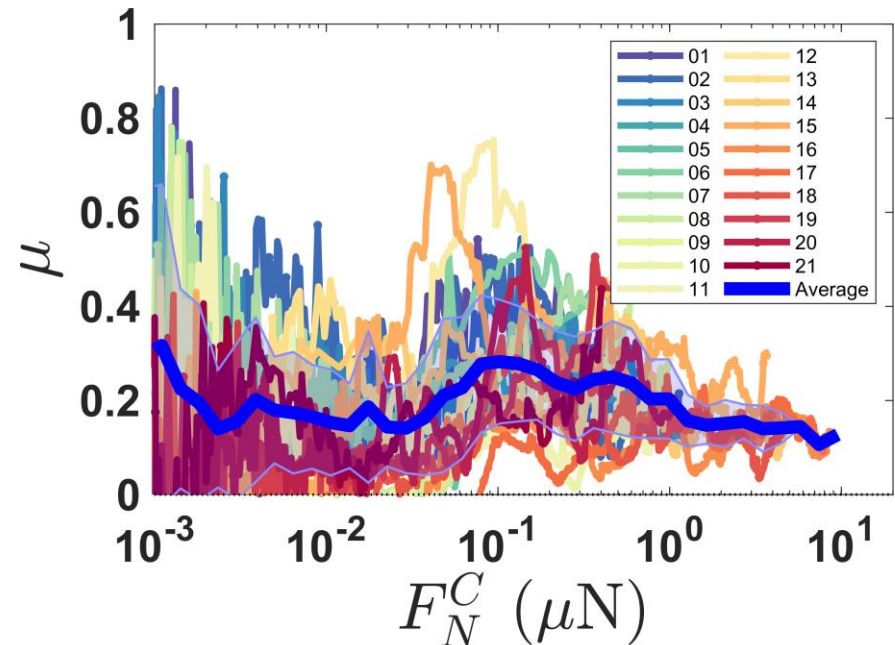
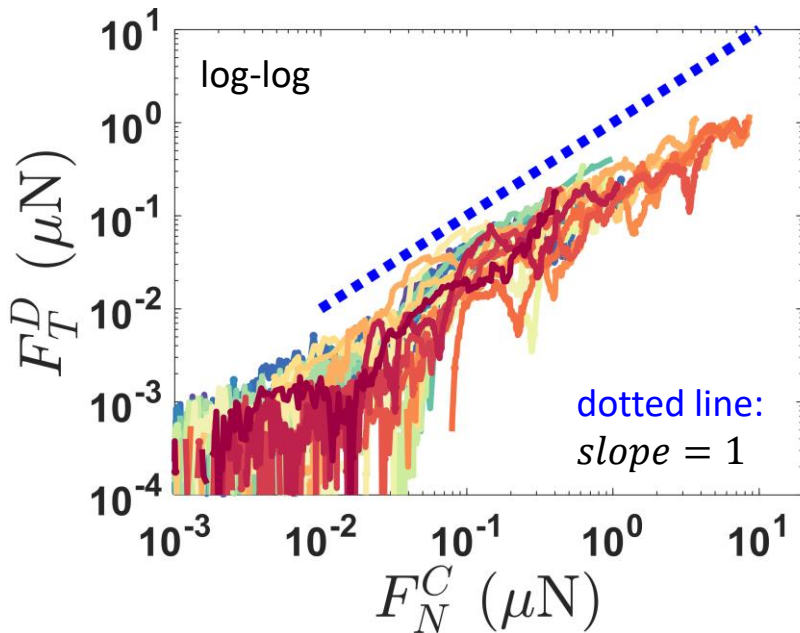
μ_p decreases with increasing F_N .

Fit for the dependence of $\mu_p(F_N)$:

$$\mu_p = 0.2 \coth(2.5 F_N^{0.5})$$

$\mu_p(F_N)$ -profile in NaI

NaI solution



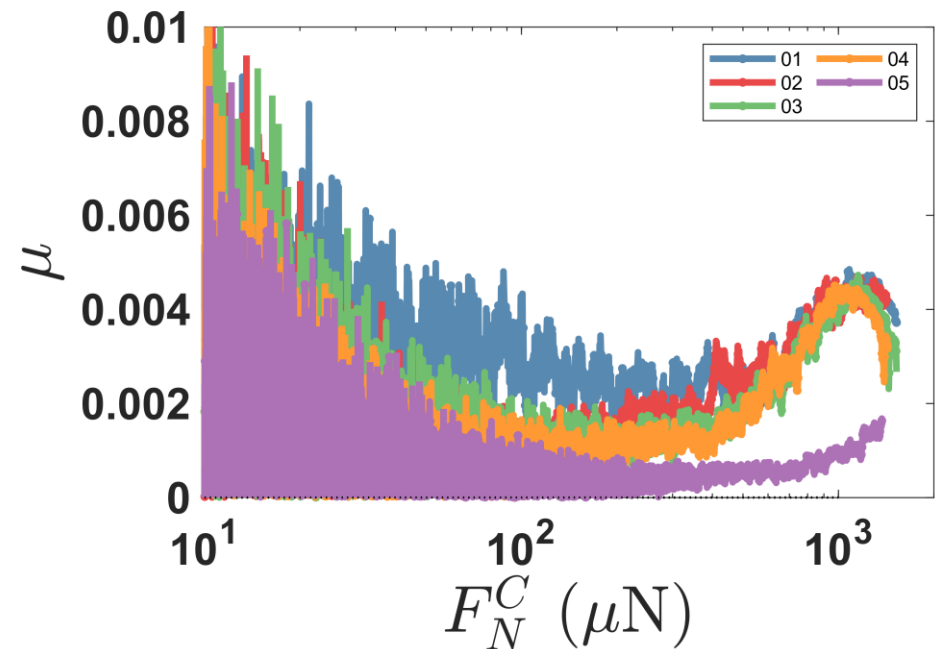
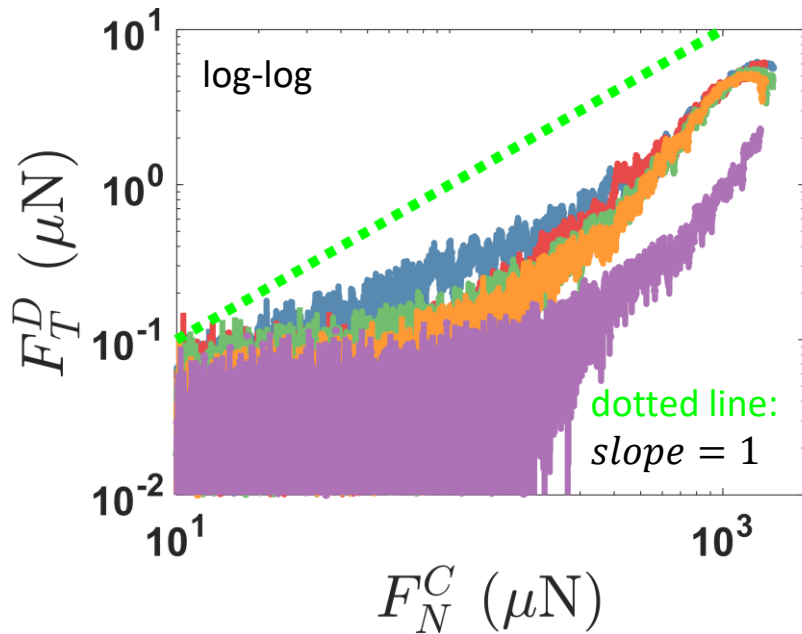
μ_p is constant despite of increasing F_N .

→ The small repulsive forces must have plateaued $\mu_p(F_N)$ profile.

$\mu_p \approx 0.2$.

$\mu_p(F_N)$ -variation in PEG

PEG

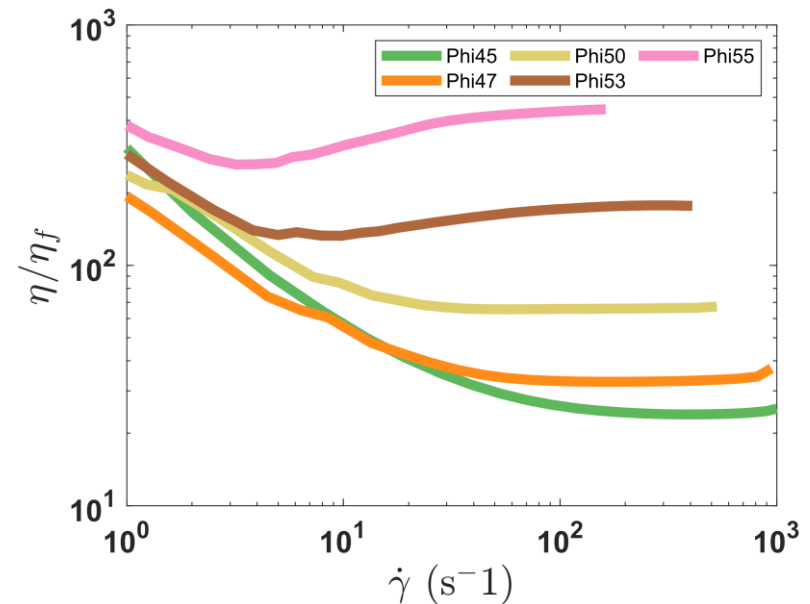
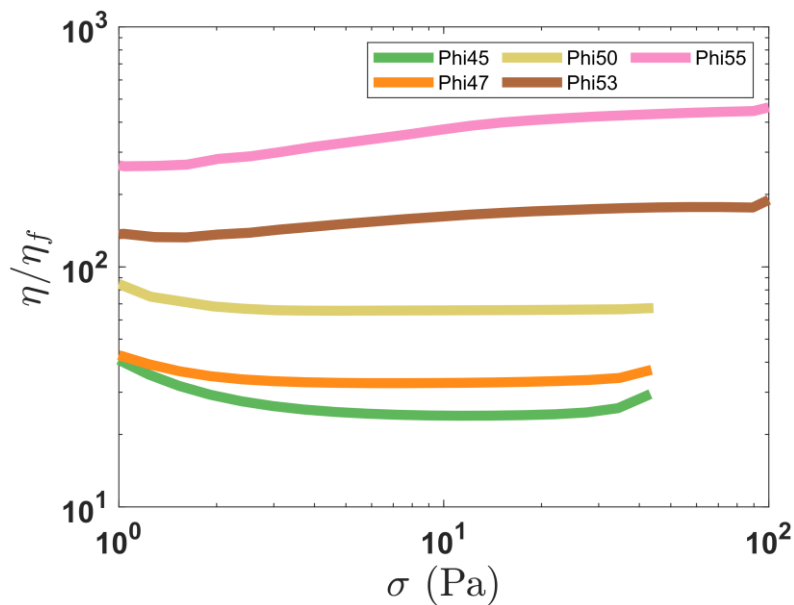


$\mu_p \approx 0$ at all F_N .

Flow curves



Nal solution



Inertial regime starts from $\dot{\gamma} \approx 3 s^{-1}$.

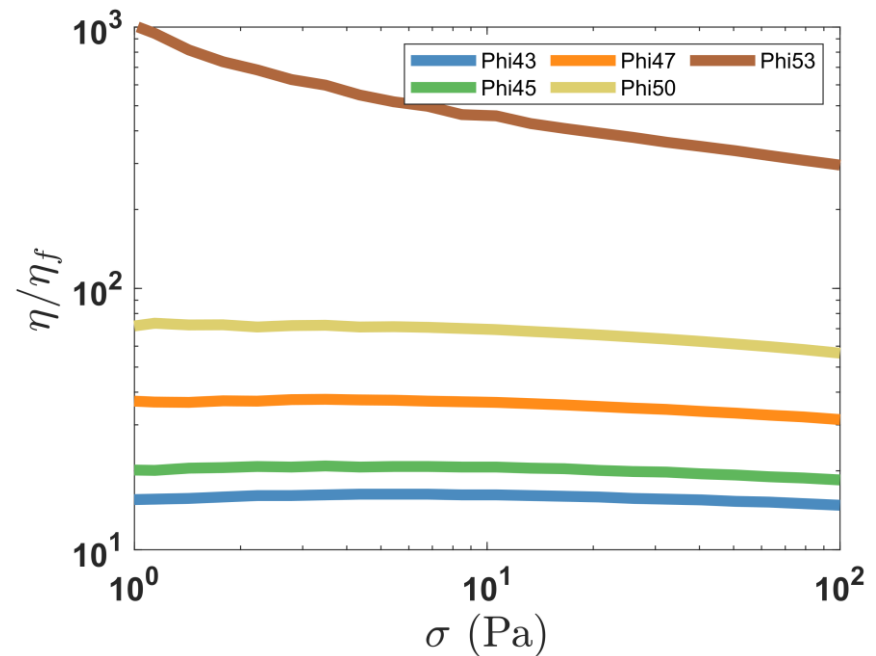
In the inertial regime: Newtonian behavior.

Flow curves



PEG, between 2 cross-hatched plates

Old sample (>24h)



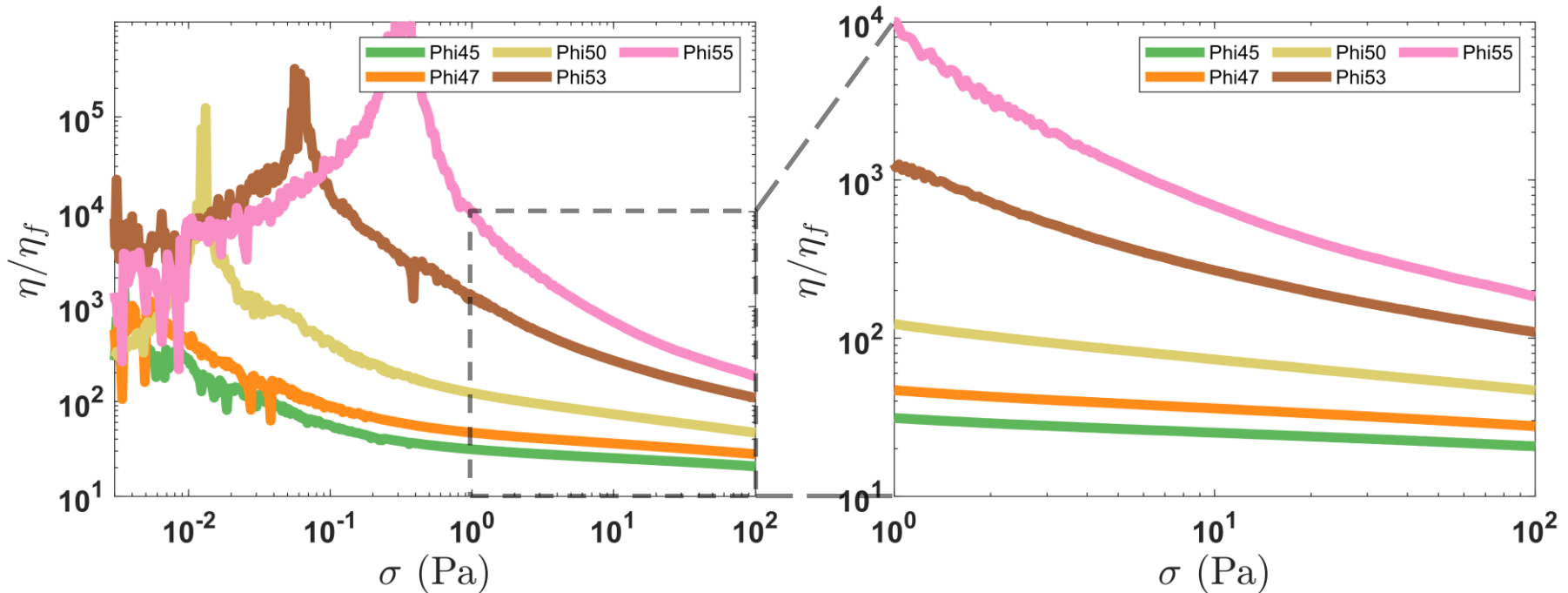
Aged **PEG** suspension is elastic-like: proof of swelling effect.

Apparent shear thinning: NOT from the variation of μ_p ,
but from squeezing effect of the shear of the swelled layer.

Flow curves



Silicone oil



Presence of a small yield stress: quasi-unstable suspension
 \rightarrow data at $\sigma < 10 \sigma_{\text{yield}}$ are not valid for force analysis.

Shear thinning originates from the reducing of μ_p with F_N .

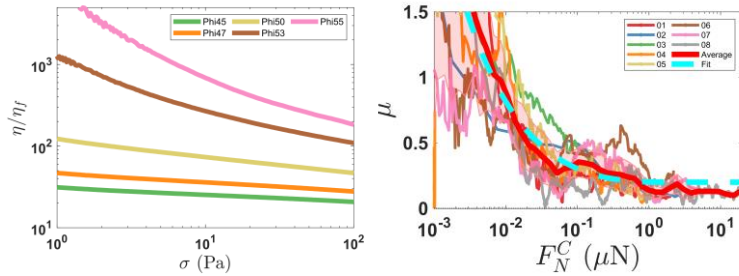
Rheology vs AFM Si. Oil



From $\eta_s(\sigma)$ and $\mu_p(F_N)$

to $\eta_s(\phi)$

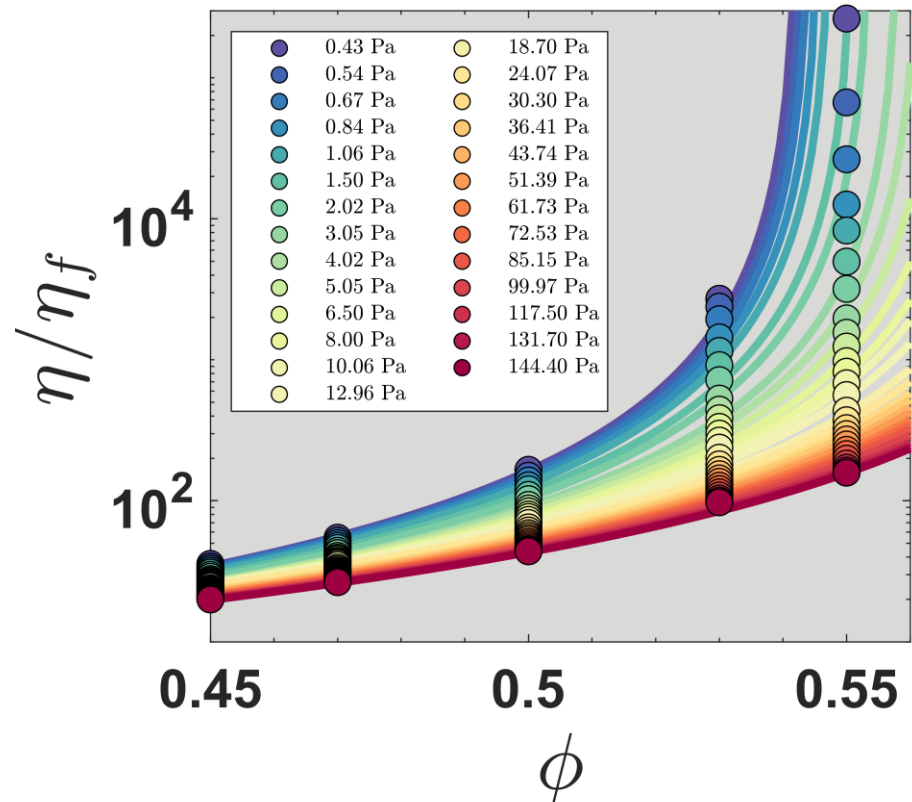
showing the dependence ϕ_j on μ_p



Model:

$$\left\{ \begin{array}{l} \sigma = \frac{1.69 F_N}{6\pi R^2} \\ \mu_p = 0.2 \coth(2.5 F_N^{0.5}) \\ \eta_s(\phi, \mu_p) = \frac{\alpha(\mu_p(F_N))}{\left(1 - \frac{\phi}{\phi_m(\mu_p(F_N))}\right)^2} \end{array} \right.$$

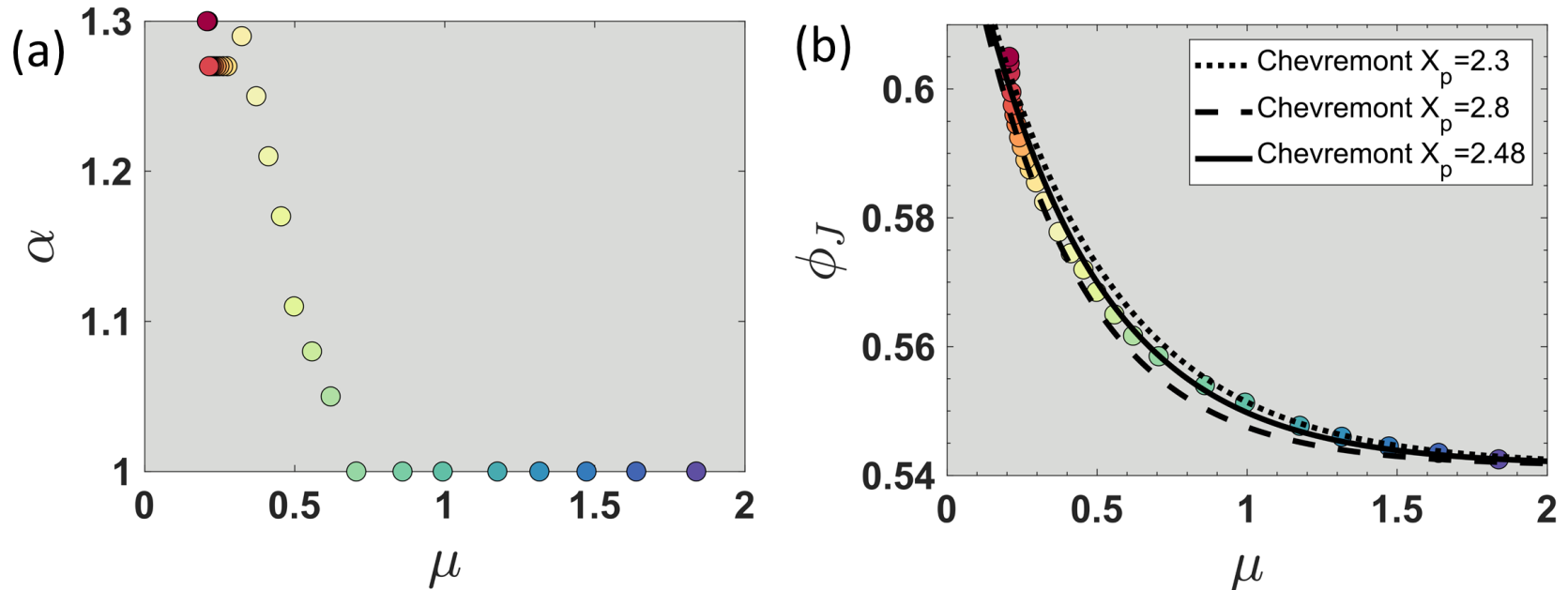
Arshad et al., *Soft Matter* (2021)



Rheology vs AFM Si. Oil



The dependence of ϕ_m on μ_p



Fit from Chevremont et al., PRF (2020):

$$\phi_J = \phi_J^{\mu_p=0} - \left(\phi_J^{\mu_p=0} - \phi_J^{\mu_p=\infty} \right) \left[1 - \exp(-X_p \mu_p) \right]$$

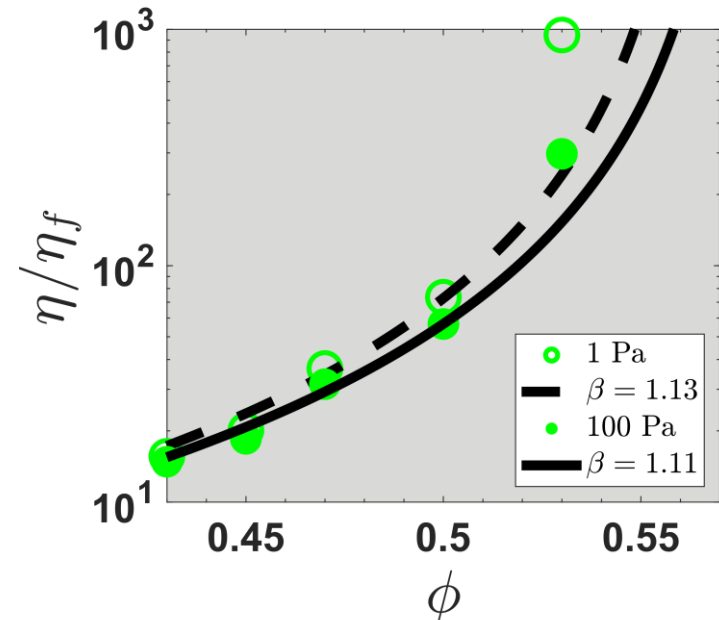
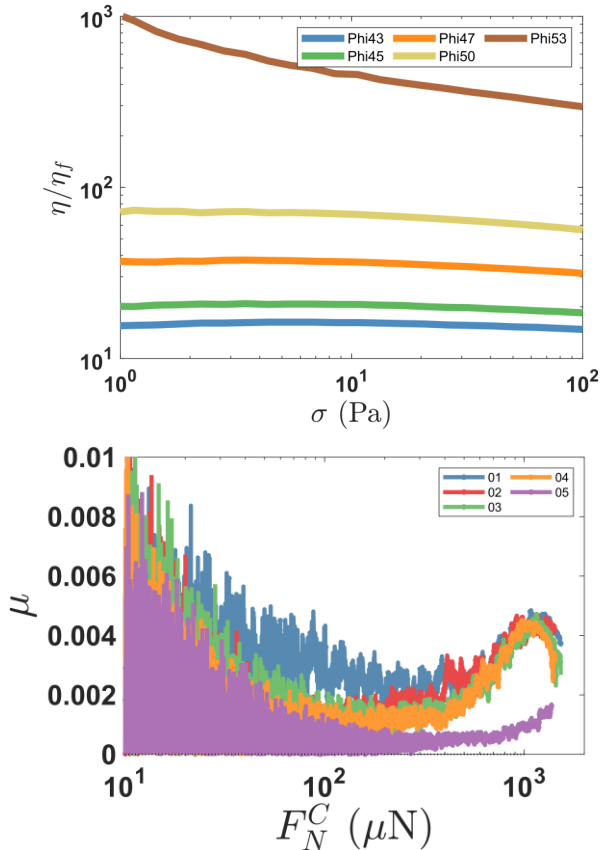
$$\text{with } \phi_J^{\mu_p=0} = 0.64, \phi_J^{\mu_p=\infty} = 0.5415, X_p = 2.8$$



Rheology vs AFM PEG

From $\eta_s(\sigma)$ and $\mu_p(F_N)$

to $\eta_s(\phi)$



$$\eta_s(\phi, \mu_p) = \frac{1}{\left(1 - \frac{\beta \phi}{0.64}\right)^2}$$

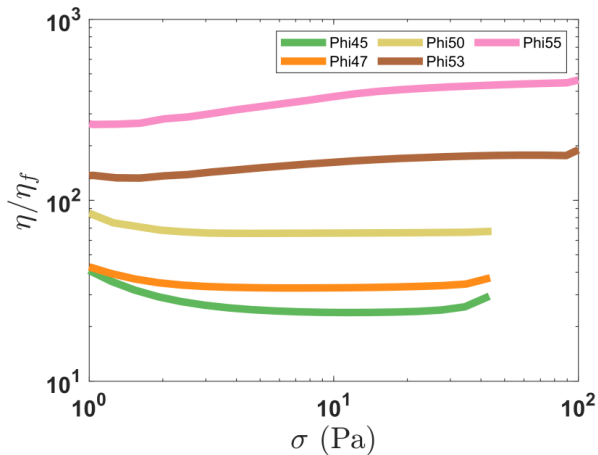
High shear stresses reduce β
 \rightarrow shear forces squeeze the swelled layer.

Max shear force = 0.4 N
 where $\mu_p = 0$

Rheology vs AFM NaI sol.



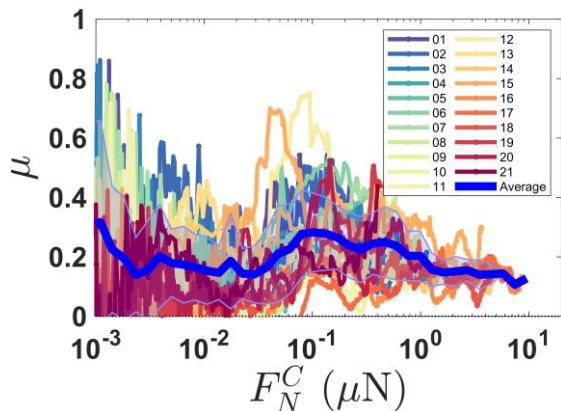
From $\eta_s(\sigma)$ and $\mu_p(F_N)$



Inertial from the start.

In inertial regime, there is no role of contact.

There is no-known fit for $\eta_s(\phi)$.





CONCLUSION & OUTLOOKS

Conclusion: the importance of μ_p



Solvents heavily impact the characteristics of particle contact, via F_N^C , F_T^D , and μ_p .

Experimental evidence of the role of decreasing μ_p on shear thinning behavior.

By transitioning from frictionless to inertial regime, shear thickening can occur even without friction.

During the transition from frictionless state to frictional state, dense suspensions flow inhomogeneously in the form of density waves.



Outlooks: Vibrations

Particles force profiles under vibrations:

Will the added vibrations generate repulsive forces before contact?

Will they alter the force profile during contact?

Rheological behaviors under vibrations:

Low amplitude – High frequency
for colloidal suspension

High amplitude – Low frequency
for granular suspension

} Reducing viscosity:
What is interplay
between vibrations
and friction force.

(collaboration with LoF, Bordeaux)

MERCI DE VOTRE ATTENTION!



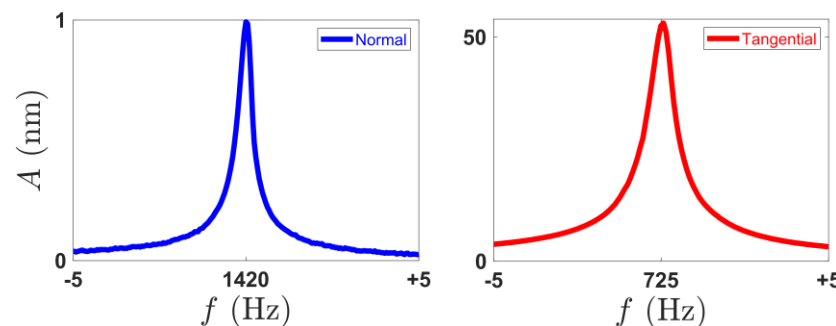
Aluminum TF:

Parameters	Normal mode	Tangential mode
Static stiffness k_0	480000 N m ⁻¹	154000 N m ⁻¹
typical Resonating frequency f_0	1400 Hz	700 Hz
typical Q factor Q_0 (in air)	3000 – 2000	600 – 400
Typical Accelerometer factor C_{accel}	0.430 μm V ⁻¹	1.720 μm V ⁻¹
typical Driving factor C_{drive}	50 nm V ⁻¹	100 nm V ⁻¹
typical Force transduction factor C	10 μN V ⁻¹	30 μN V ⁻¹

2 modes are decoupled

$$C = \frac{k_0}{Q_0} C_{\text{drive}}$$

**typical
Resonance curves:**





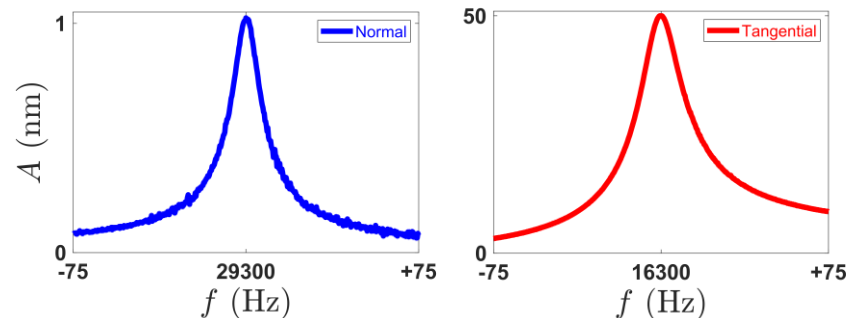
Quartz TF:

Parameters	Normal mode	Tangential mode
Static stiffness k_0	26630 N m ⁻¹	8550 N m ⁻¹
typical Resonating frequency f_0	29000 Hz	16000 Hz
typical Q factor Q_0 (in air)	3000 – 2000	600 – 400
Typical Accelerometer factor C_{elect}	50 nm V ⁻¹	2950 nm V ⁻¹
typical Driving factor C_{drive}	300 nm V ⁻¹	300 nm V ⁻¹
typical Force transduction factor C	5 μN V ⁻¹	10 μN V ⁻¹

2 modes are decoupled

$$C = \frac{k_0}{Q_0} C_{\text{drive}}$$

**typical
Resonance curves:**



Effect of changing Q and k

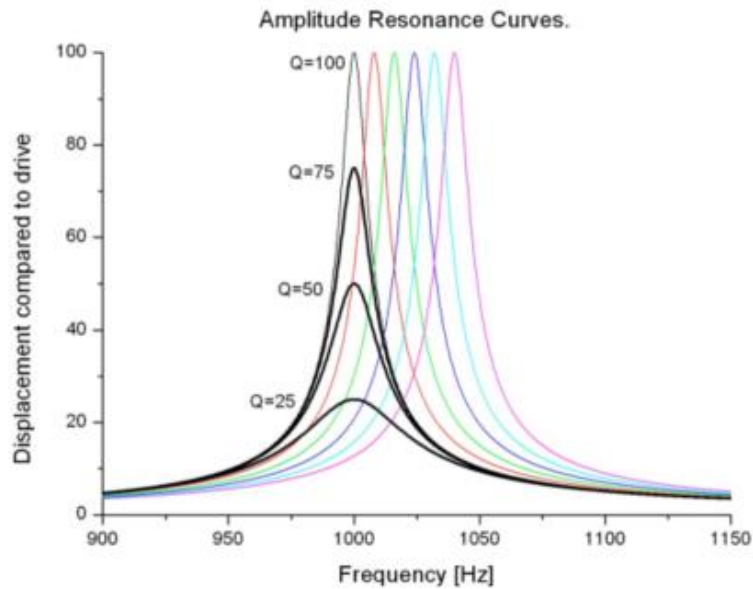


Fig. 2. Amplitude resonance curves for four values of Q (same k) and six values of k (same Q) increasing from left to right.

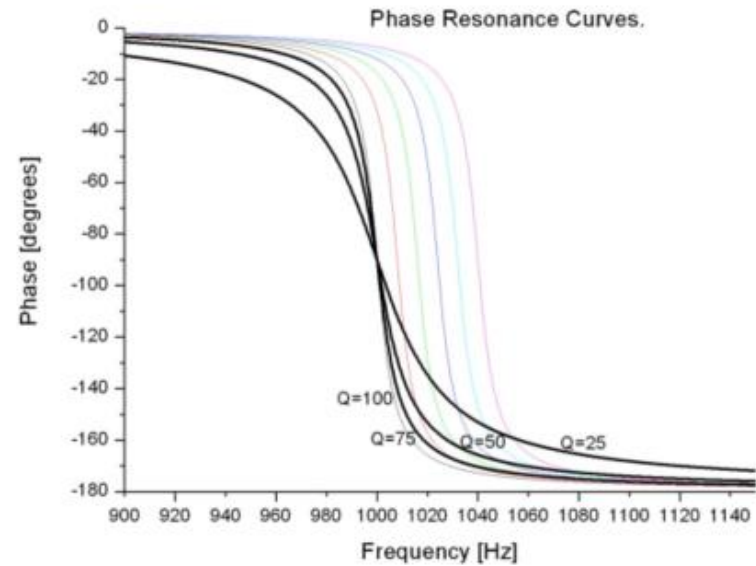
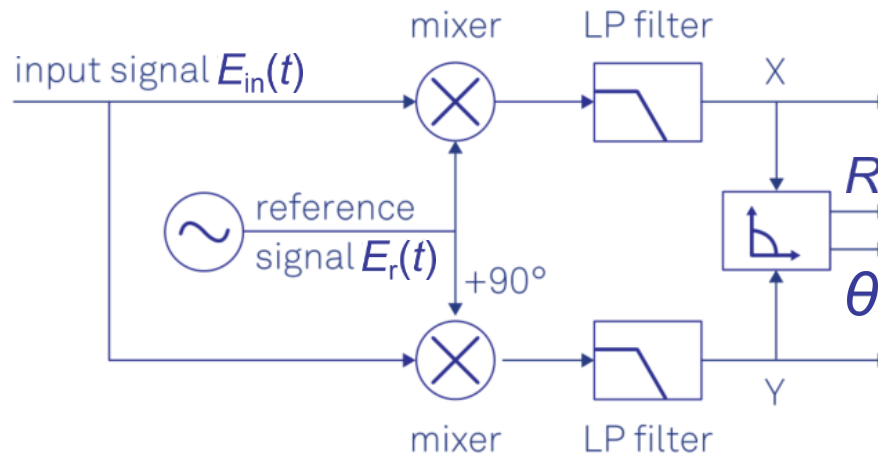
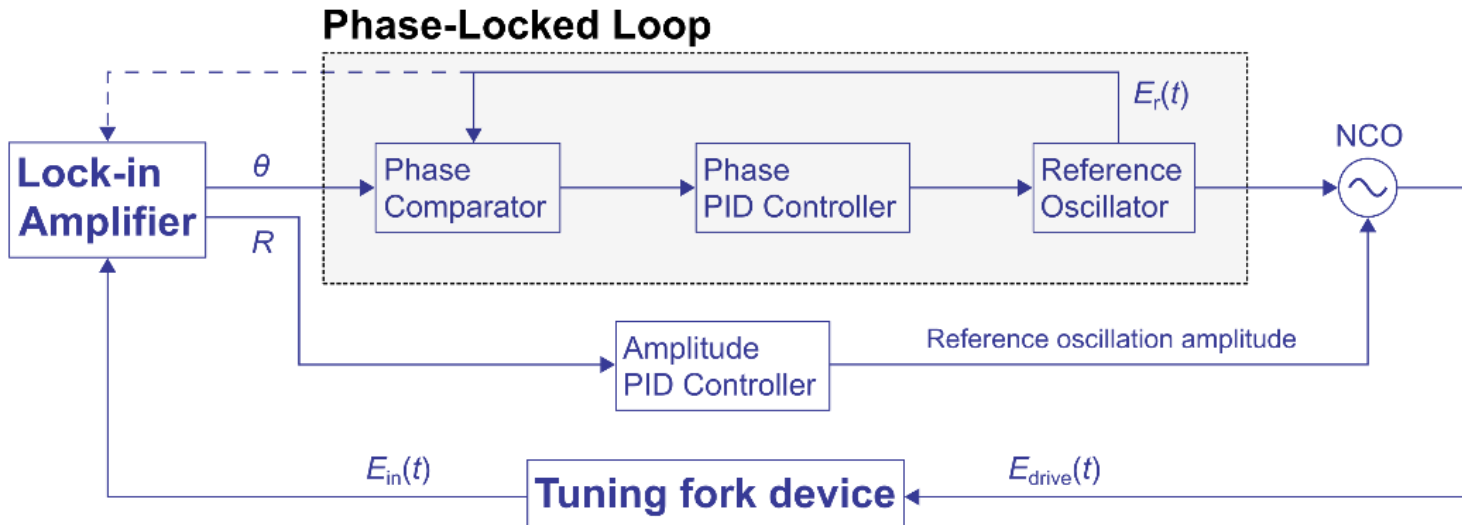


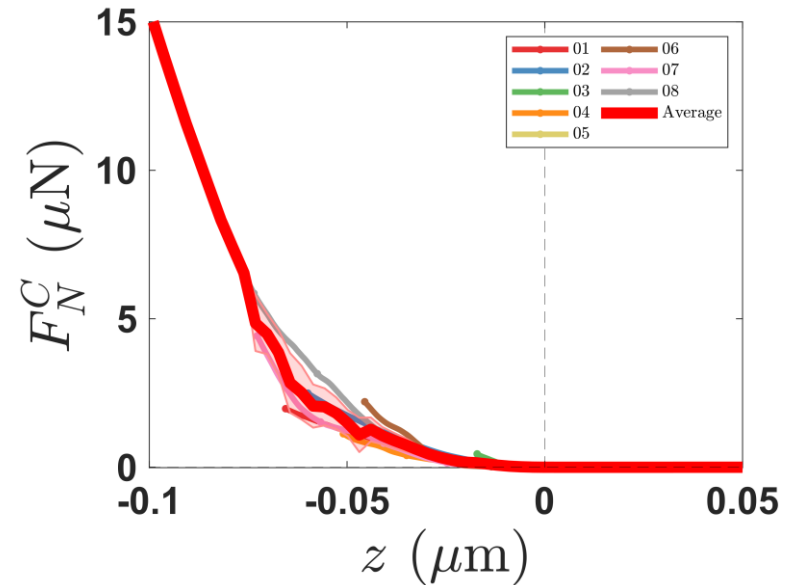
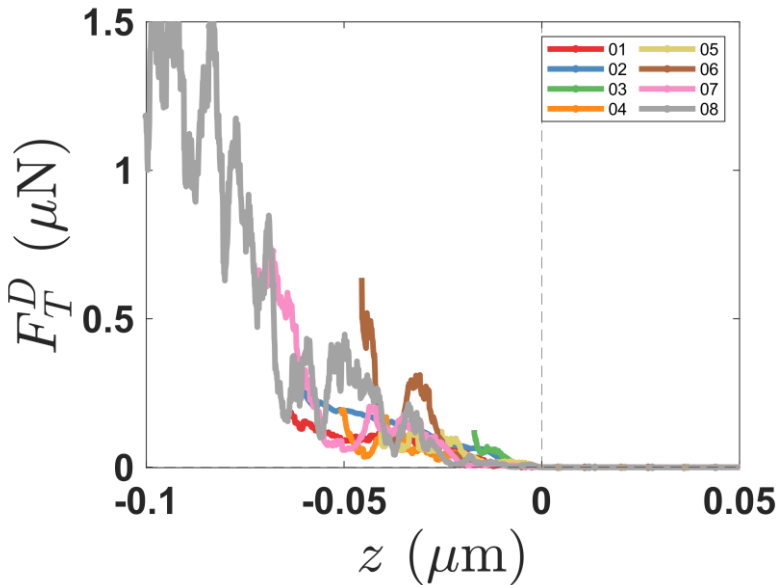
Fig. 3. Phase resonance curves for four values of Q (same k) and six values of k (same Q) increasing from left to right.

Principe of PLL

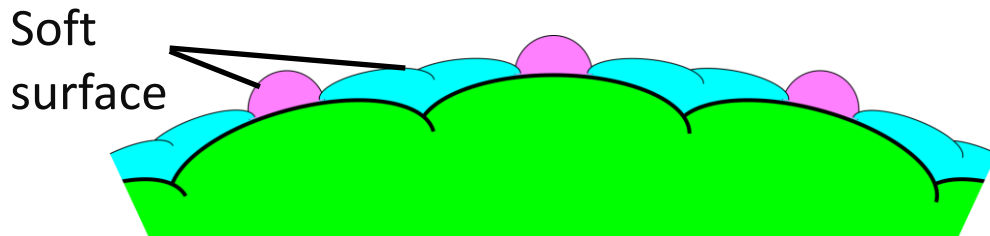


Contact force profiles

Silicone oil



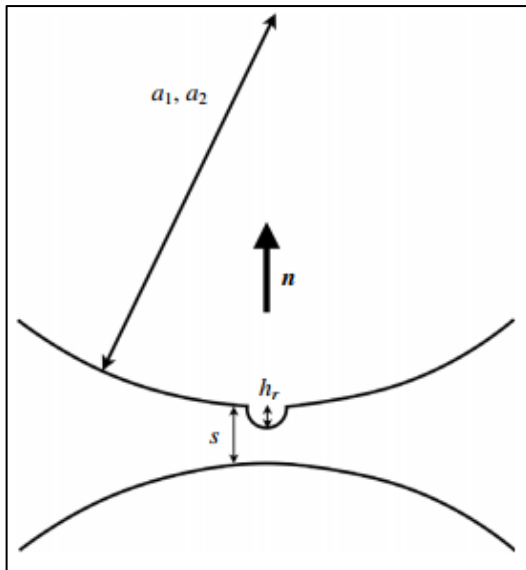
$F_N(z)$ model: $F_N^C = f(z, E_0, h_r)$



z	E_0	h_r
0 nm - 15 nm	1 GPa	15 nm
15 nm - 50 nm	1 GPa	90 nm
50 nm - center	3 GPa	530 nm

The aims:

Measure Load-dependent variation of Friction coefficient
 Compare with the simulation of Lemaire's group



Lobry et al.,
J. Fluid Mech. (2019)

Contact between a single asperity
 and a smooth surface

$F_N(z)$ model :

$$F_n = -L_c \left(\frac{\delta}{\delta_c} \right)^{3/2} \left[1 - \exp \left(\frac{1}{1 - \left(\frac{\delta}{\delta_c} \right)^\beta} \right) \right] n,$$

Stokes force:

$$F_N = \frac{1}{1.69} 6\pi\eta_0\eta_s R^2 \dot{\gamma}$$

$$= \frac{1}{1.69} 6\pi R^2 \sigma$$

with

η_0, η_s : fluid viscosity, relative viscosity

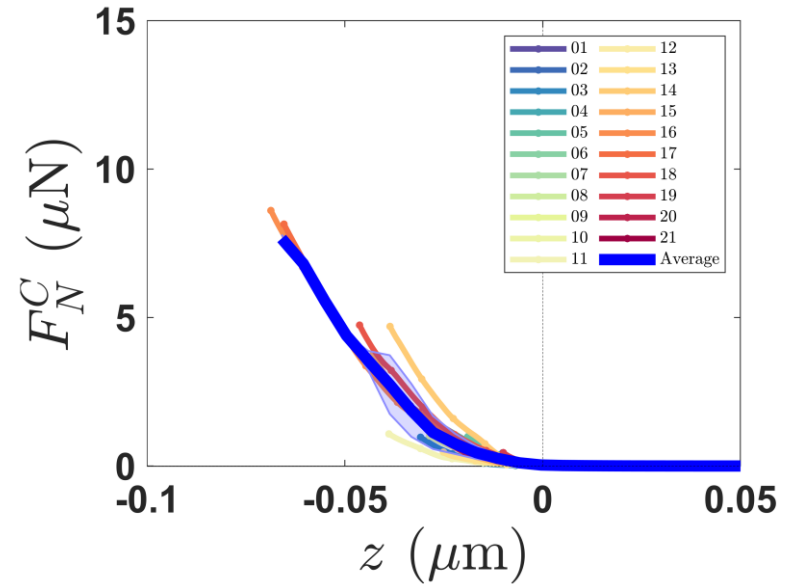
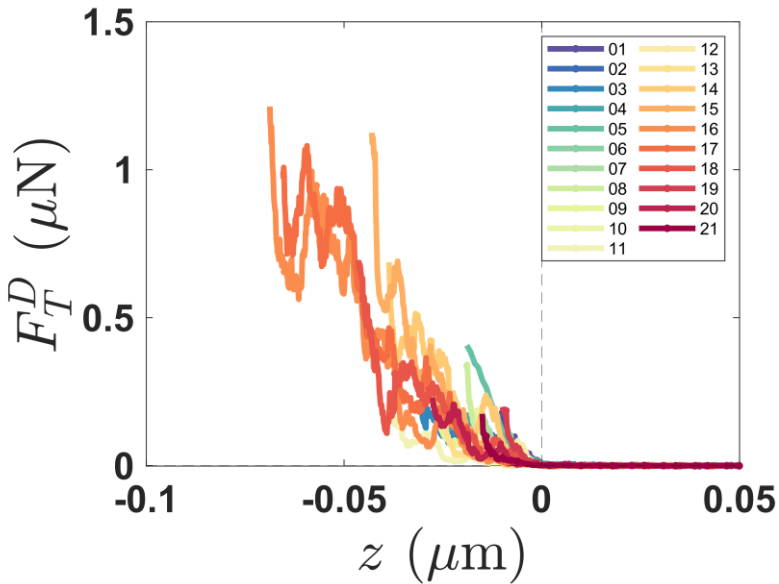
L_c, δ_c : critical load and overlap

(which are functions of E_0 and h_r)

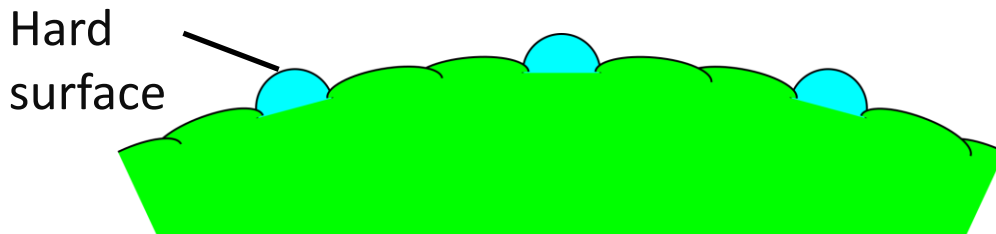
E_0 : elastic modulus, h_r : asperity height.

Contact force profiles

Nal solution



$F_N(z)$ model $F_N^C = f(z, E_0, h_r)$

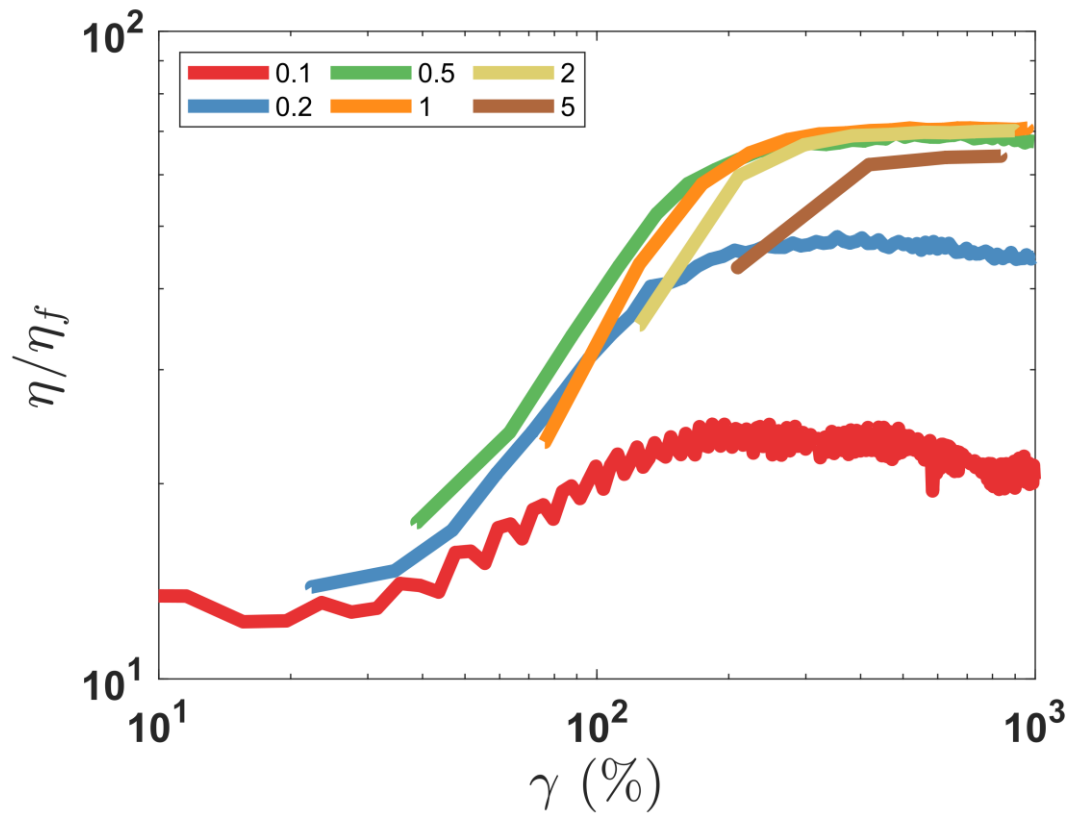


z	E_0	h_r
0 nm - 23 nm	3 GPa	20 nm
23 nm - center	3 GPa	300 nm

Shear reversal



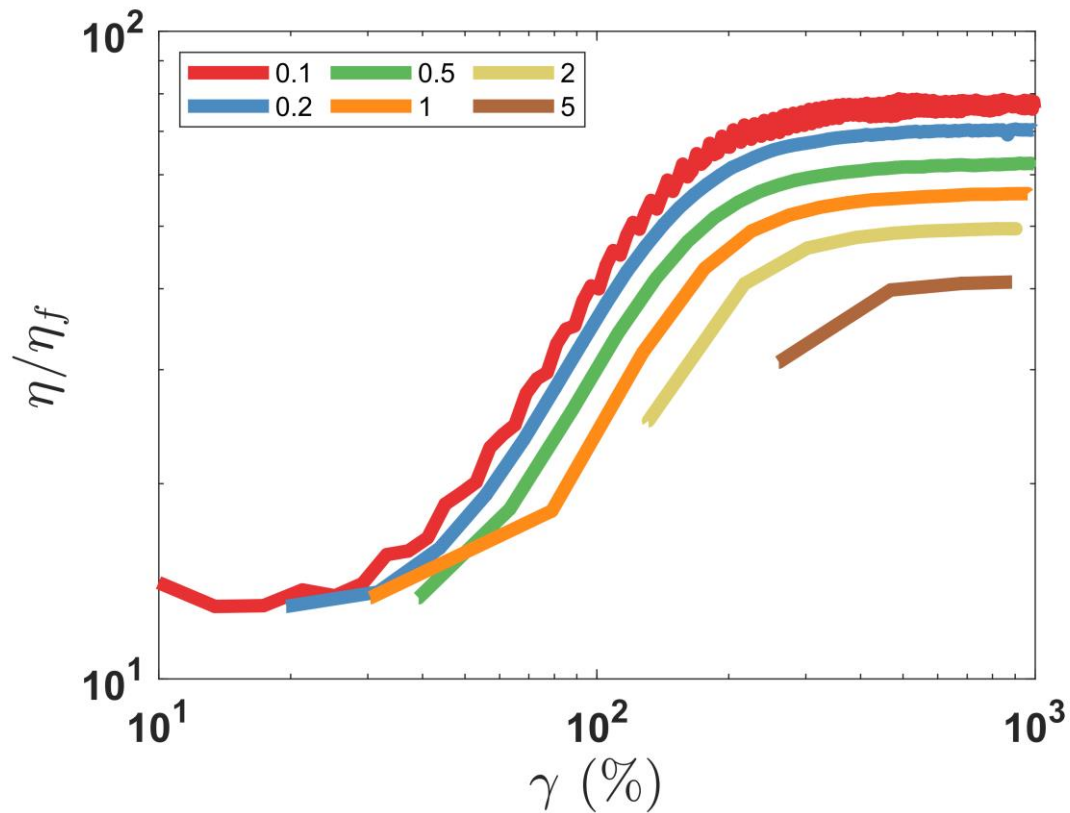
PS particles in **Silicone oil**



Shear reversal



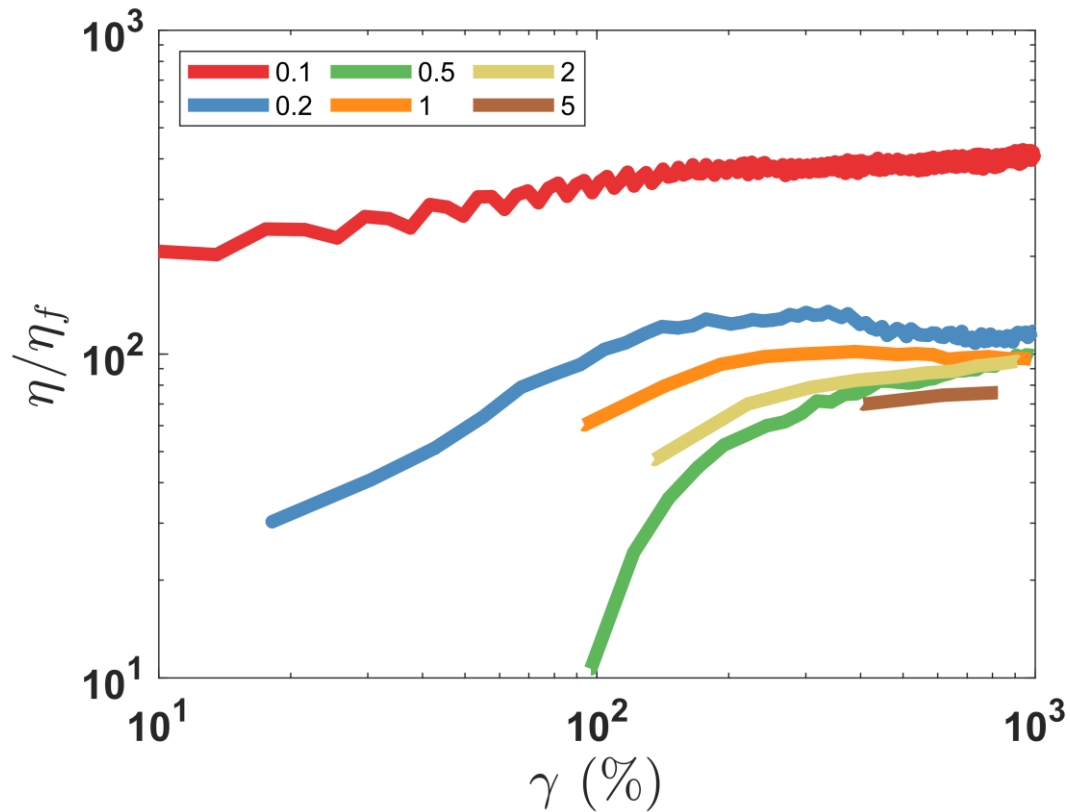
PS particles in PEG



Shear reversal

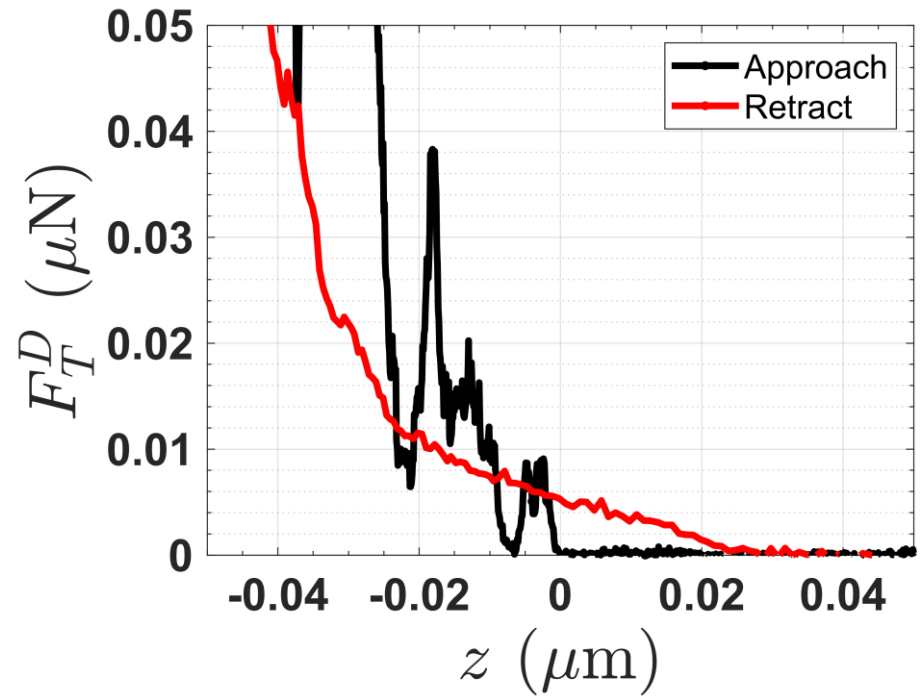
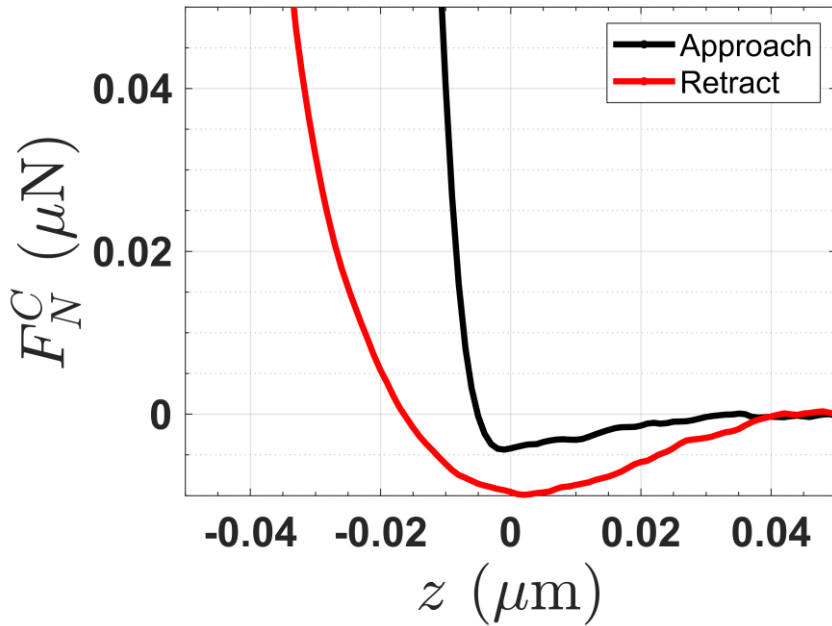


PS particles in NaI solution



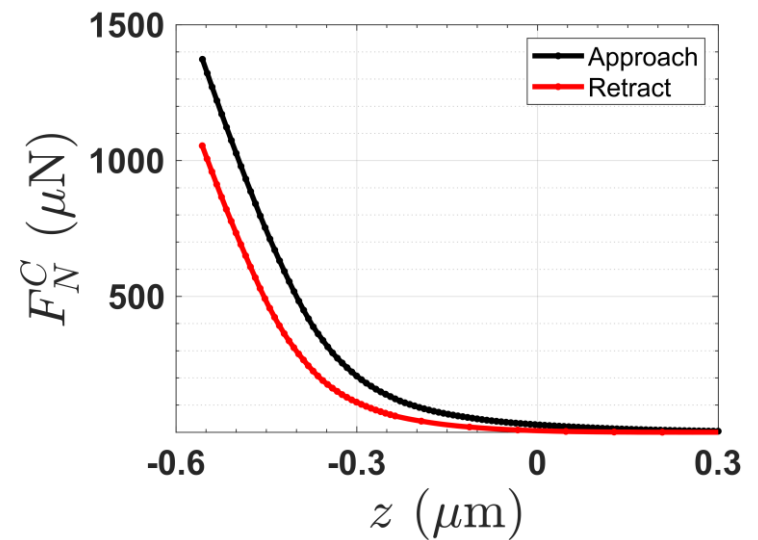
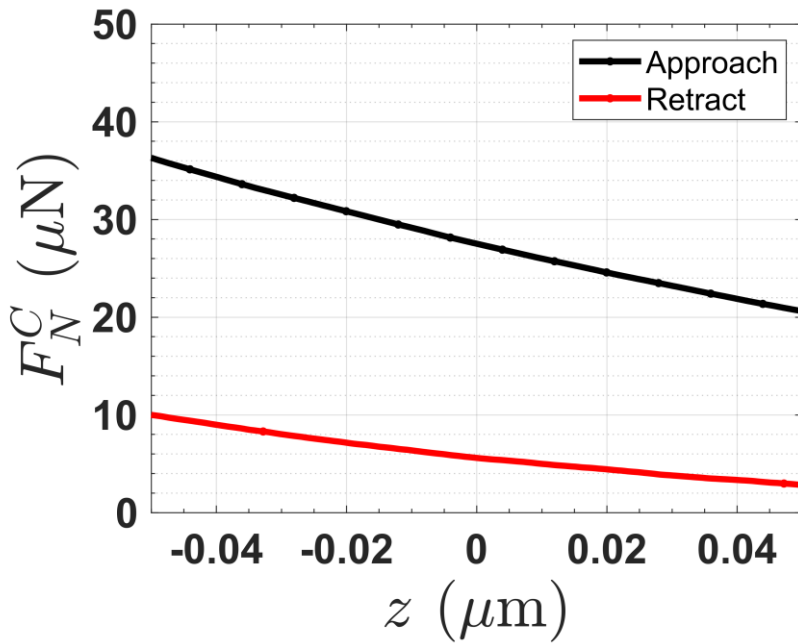
Approach-Retract

PS particles in **Silicone oil**



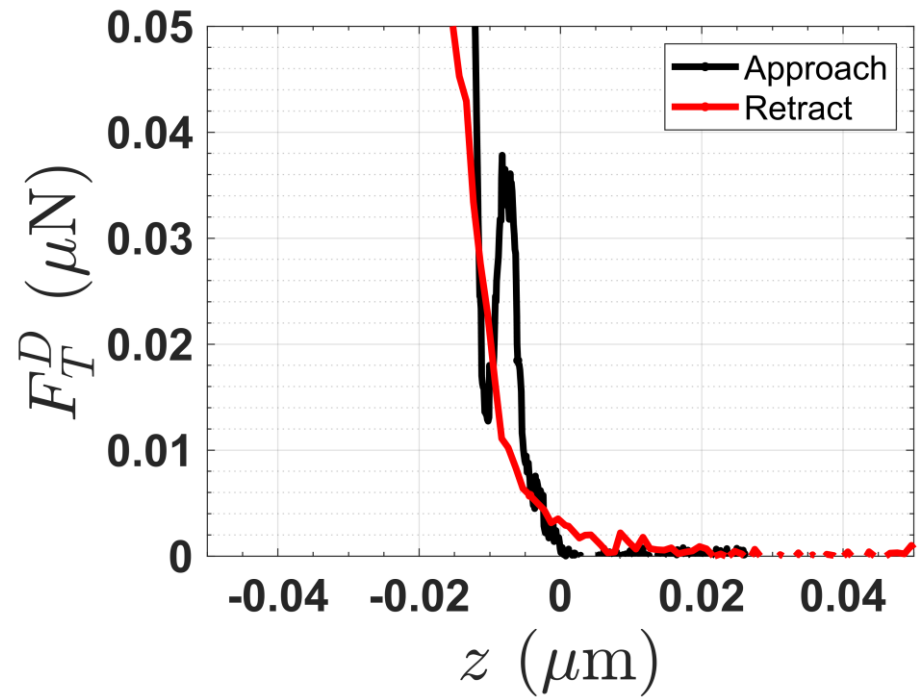
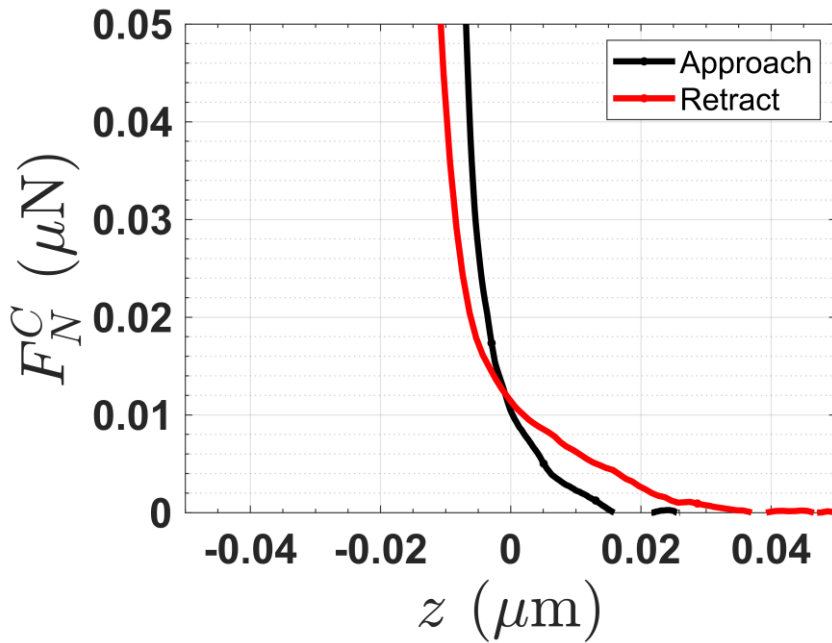
Approach-Retract

PS particles in PEG



Approach-Retract

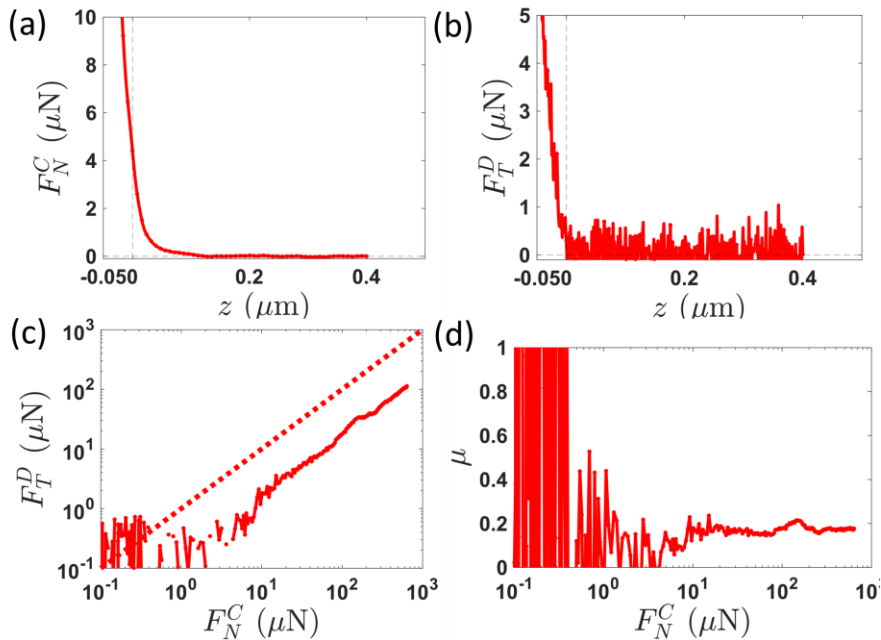
PS particles in NaI solution



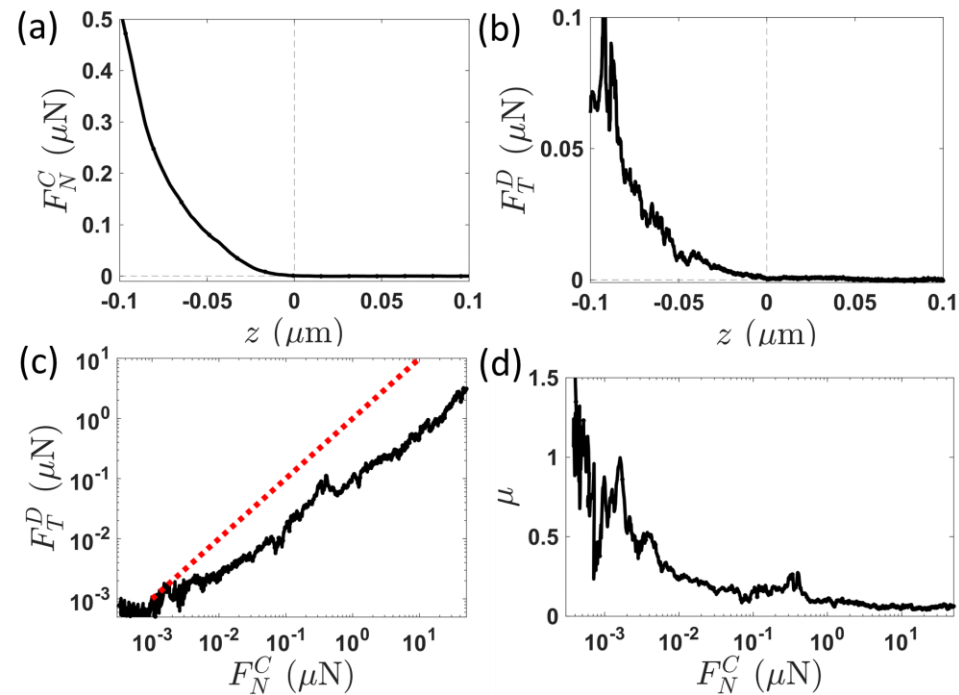
Raw-Clean differences



PS particles in **Silicone oils**



Raw d140 in Oil20



Clean d40 in Oil5

Raw-Clean differences



PS particles in NaI

