Dense suspensions at the microscopic scale: characterizing and controlling interparticle interactions

Jean Comtet
Soft Matter Science and Engineering Laboratory
ESPCI, CNRS, Sorbonne University

jean.comtet@espci.fr

Lecture day GFR 2024 at IUSTI Laboratory

We are here

Jean Comtet (CNRS, ESPCI Paris)

Dense suspensions at the microscopic scale: characterizing and controlling interparticle interactions

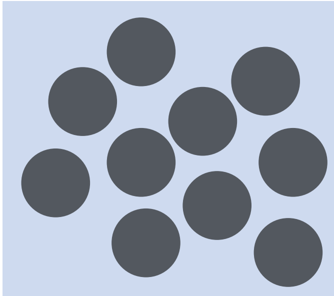
Francisco Melo da Rocha (IUSTI, Marseille)

Rheology of dense granular suspensions from microscopic considerations

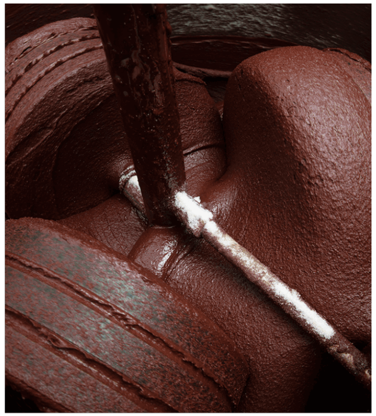
François Peters (InPhyNi, Nice)

What simulations tell us about granular suspension rheology?

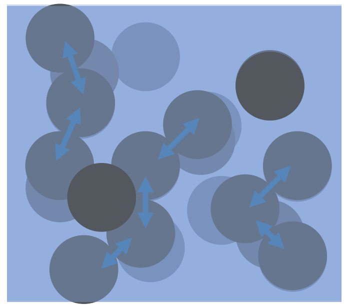
Dense suspensions



Solid particles
+ suspending fluid



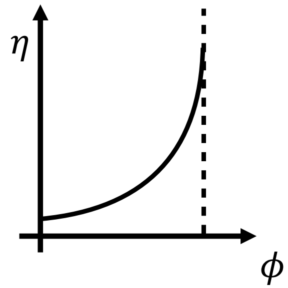
Dense suspension rheology - Light-speed review



1905 : Einstein, diluted regime

$$\eta = \eta_0(1 + 2.5\phi)$$

1970-1980 : semi-diluted regime, hydrodynamic interactions (Batchelor)



1990-today : Concentrated regime

(Cates, Wyart, Morris, Denn...)

2010 - ... : role of local contact forces and inter-particle friction

--> Necessary to rationalize complex non-newtonian flow behaviors

--> Allows to make the link with the specificity of the formulation/physicochemistry in industrial contexts

Can these local interaction forces be measured at the nanoscale and connected to macrosocopic material properties?

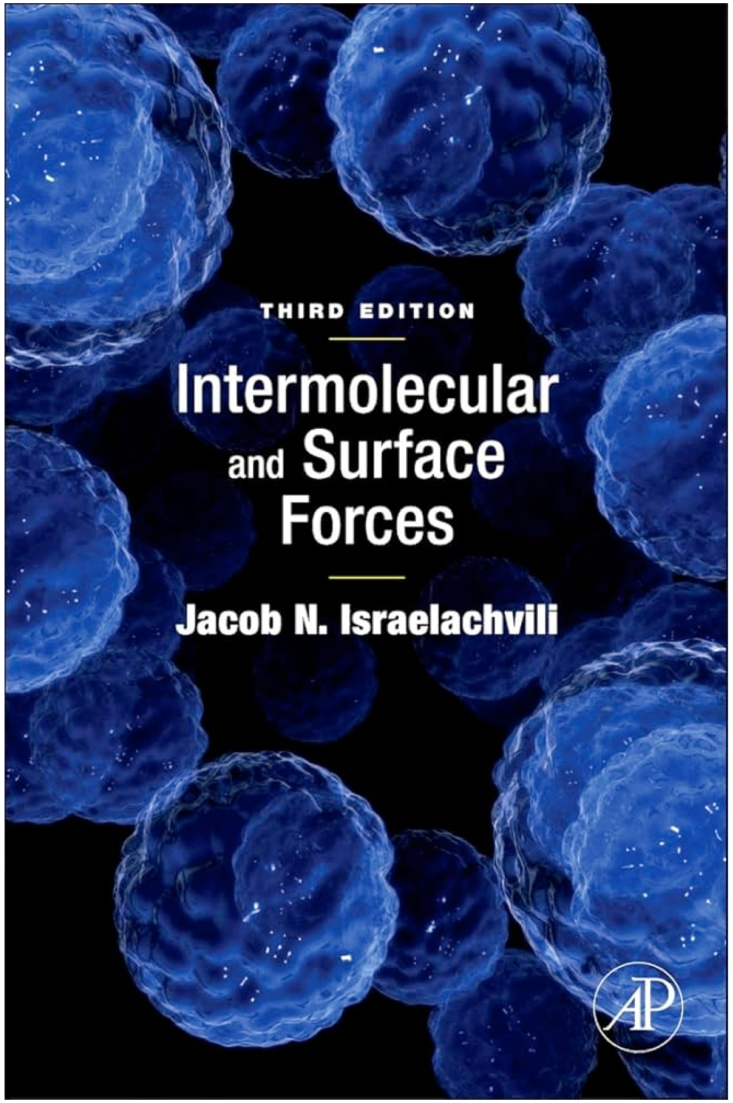
General Outline

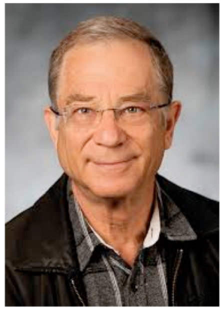
1. **Surface forces and friction – General Concepts**
    1. Surface forces
    2. Frictional forces
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Contact Aging
    2. Shear Thickening
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

General Outline

1. **Surface forces and friction – General Concepts**
    1. **Surface forces**
    2. Frictional forces
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Contact Aging
    2. Shear Thickening
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

1.1 Surface Forces

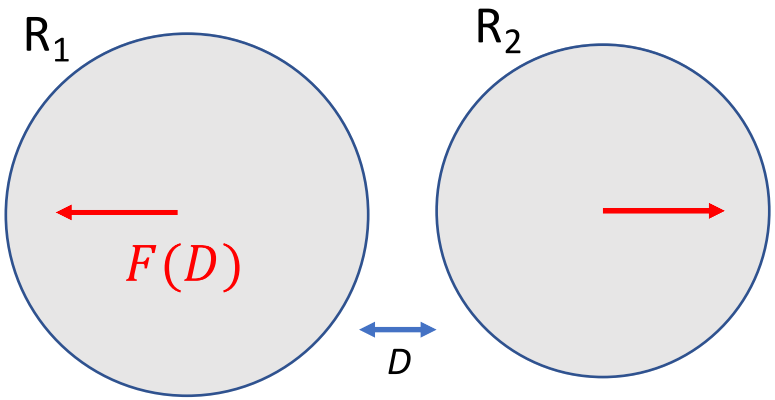




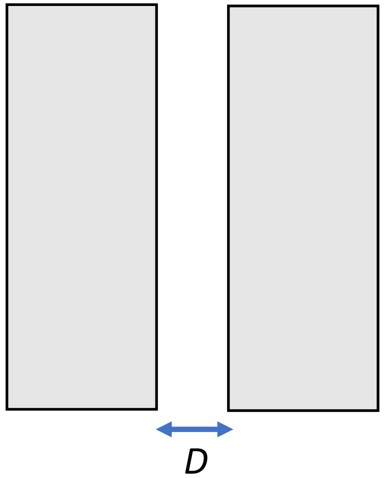
1944 - 2018

1.1 Surface Forces

The Derjaguin Approximation



Forces F(D) between two particles



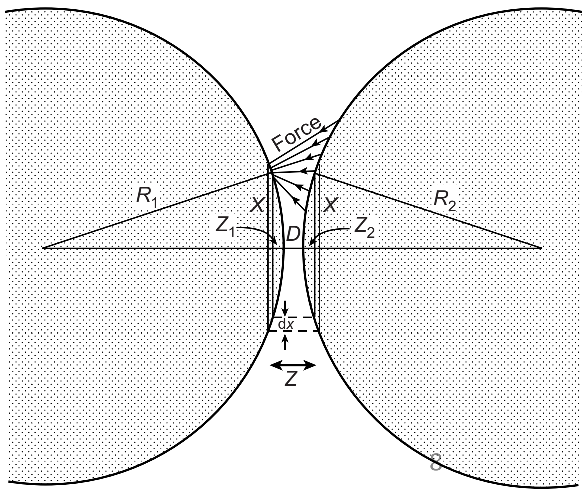
Interaction energy per unit area

$\mathrm{D} \ll R_1, R_2$

$$\boldsymbol{F(D) = 2\pi R_{\mathrm{eff}} W(D)}$$

with $$\frac{1}{R_{\mathrm{eff}}} = \frac{1}{R_1} + \frac{1}{R_2}$$

$\boldsymbol{W(D)}$ **[J.m^{-2}]**



- Interaction forces can be extrapolated from various experimental situations
- Simplifies estimation of interaction forces based on analytical calculation of the interaction energy

1.1 Surface Forces

Van Der Waals Forces

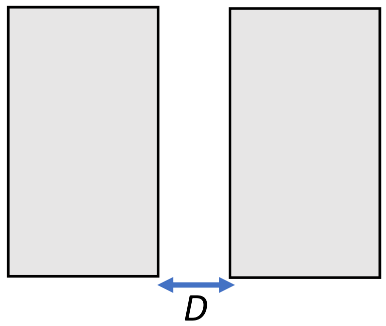
”Dispersive forces”: exist between all bodies
Originate from interactions between fluctuating dipoles in the material

Interaction energy between two particles

universal scaling

$$V_{\mathrm{vdw}} \sim -\frac{1}{r^6}$$

Interaction energy per unit area between two surfaces



Hamaker constant A [J]

$$W(D) = -\frac{A}{12\pi D^2}$$

Lifshitz theory for symmetric interfaces

$$A = \frac{3}{4}kT\left(\frac{\epsilon_{\mathrm{S}} - \epsilon_{\mathrm{L}}}{\epsilon_{\mathrm{S}} - \epsilon_{\mathrm{L}}}\right)^2 + \frac{3h\nu_{\mathrm{e}}}{16\sqrt{2}}\frac{\left(n_{\mathrm{S}}^2 - n_{\mathrm{L}}^2\right)^2}{\left(n_{\mathrm{S}}^2 + n_{\mathrm{L}}^2\right)^{3/2}}$$

$A > 0$ → Van Der Waals interactions are always attractive
and depend on the dielectric/optical index contrast

Order of magnitude : in air : $A \sim 10^{-19}$ J
in liquid : $A \sim 10^{-21} - 10^{-20}$ J

Example of experimental situations :
solid particles in an organic solvent

1.1 Surface Forces

Van Der Waals Forces

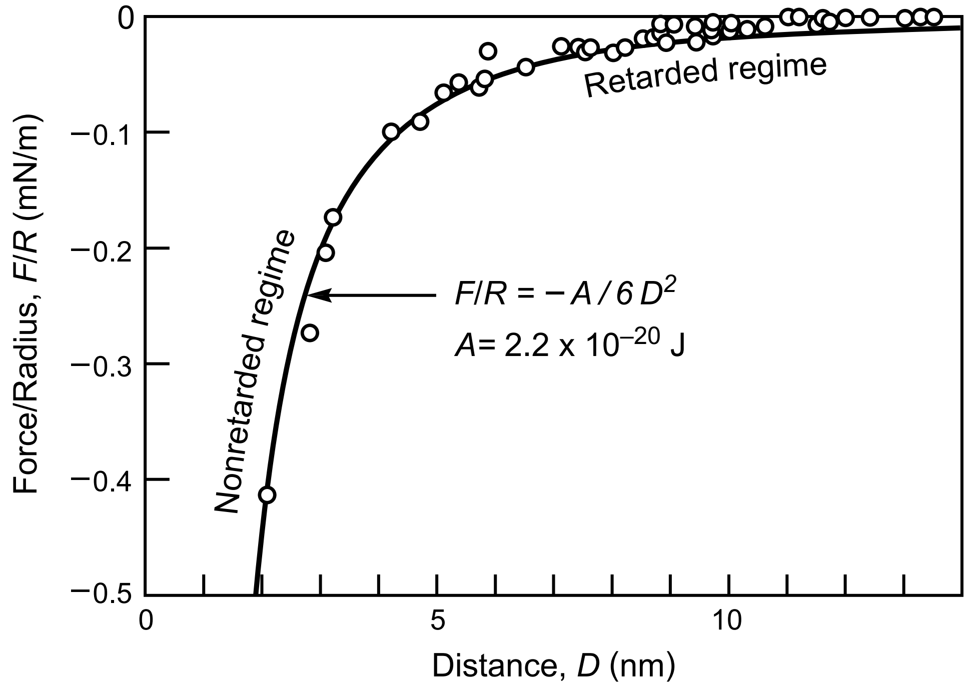
Autumn, Kellar, et al. "Evidence for van der Waals adhesion in gecko setae." *Proceedings of the National Academy of Sciences* 99.19 (2002): 12252-12256.

Typical adhesion energy *in air :*

$$W(a) = -\frac{A}{12\pi a^2} \approx 60\ \mathrm{mJ.m^{-2}}$$

Molecular distance $a \approx 0.2$ nm

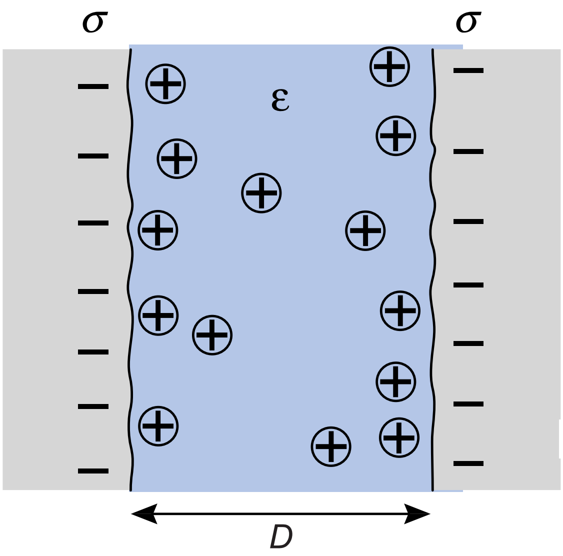
Measurements of Van Der Waals forces in water,
(between two mica surfaces with R = 1 cm)



1.1 Surface Forces

Electrostatic/double layer forces

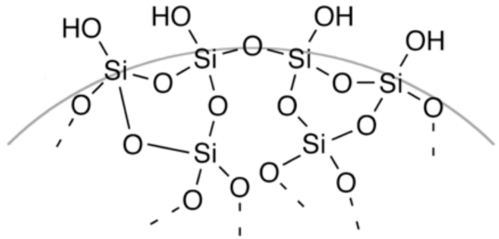
Interactions between charged surfaces in solution

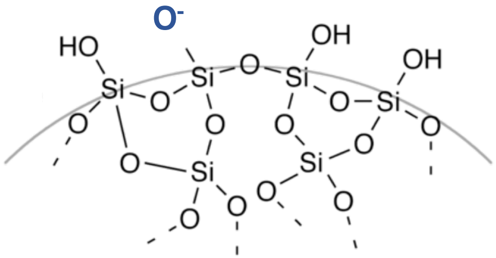


Why do surfaces get charged?

Ionizable surface

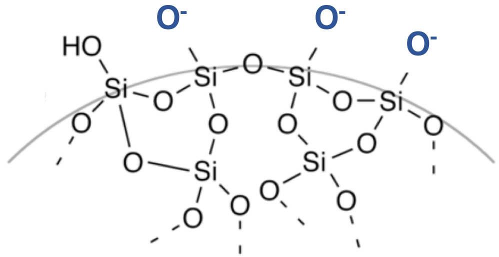
Silica/glass surface in air





Low pH

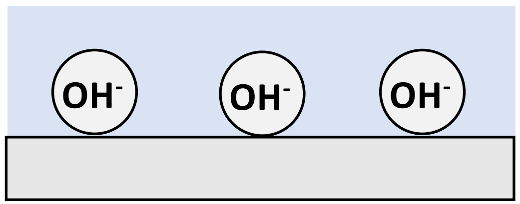
silanol deprotonation :
SiOH/SiO-



High pH

Polyelectrolytes

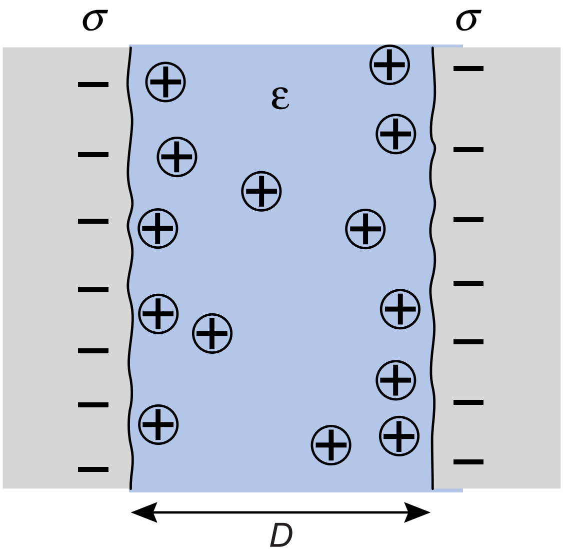
Hydrophobic surfaces



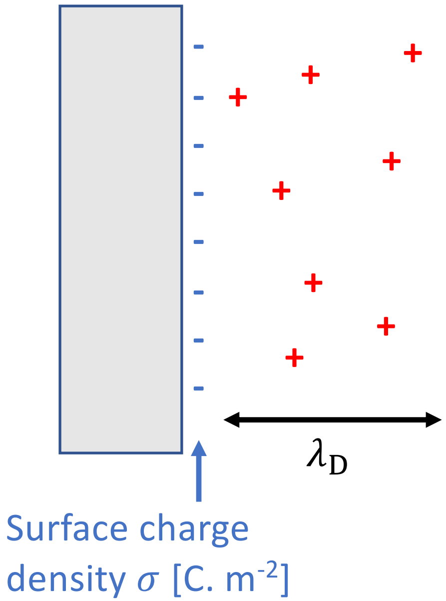
1.1 Surface Forces

Electrostatic/double layer forces

Interactions between charged surfaces in solution



Counterion distribution is given by Poisson-Boltzman distribution



Debye Screening length

$$\lambda_D = \left(\frac{k_B T \epsilon \epsilon_0}{2 q^2 N_A c}\right) \approx \frac{0.3\ \mathrm{nm}}{\sqrt{c\ (\mathrm{mol.\,L^{-1}})}}$$

≈ 100 nm in DI water
≈ 10 nm in 1 mM salt
≈ 1 nm in 100 mM salt

$\sigma \approx$ 10 mC.m^{-2} for silica in water

Electric Double Layer interaction energy

(linearized form)

$$W_{\mathrm{EDL}}(h) = \frac{2\sigma^2 \lambda_D}{\epsilon_0 \epsilon_r} \exp\left(-\frac{h}{\lambda_D}\right)$$

Experimental situations : particles in water

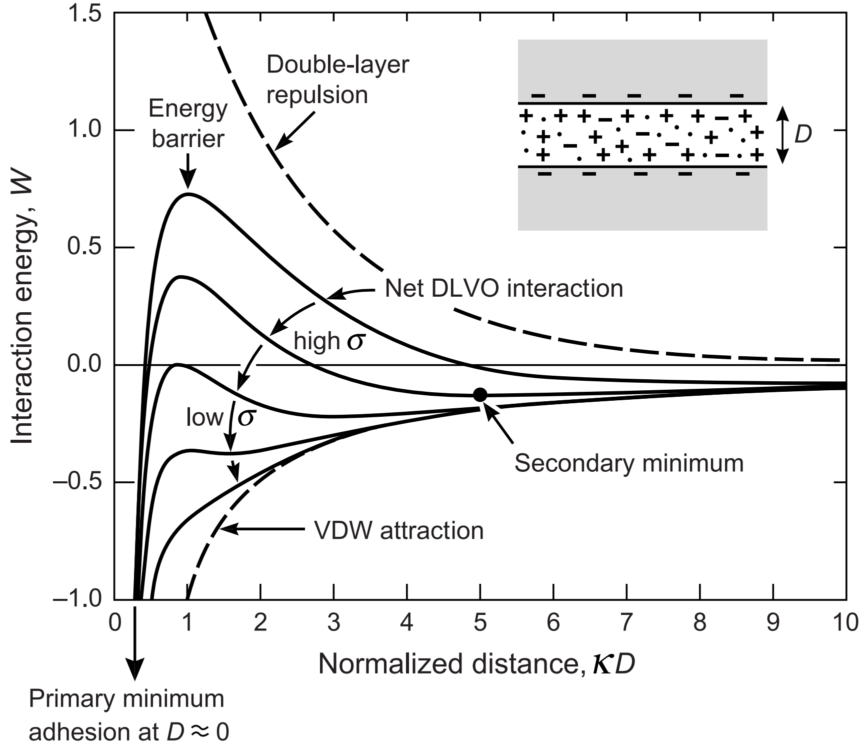
Tuning the screening length → salt concentration
Tuning the surface charge → pH

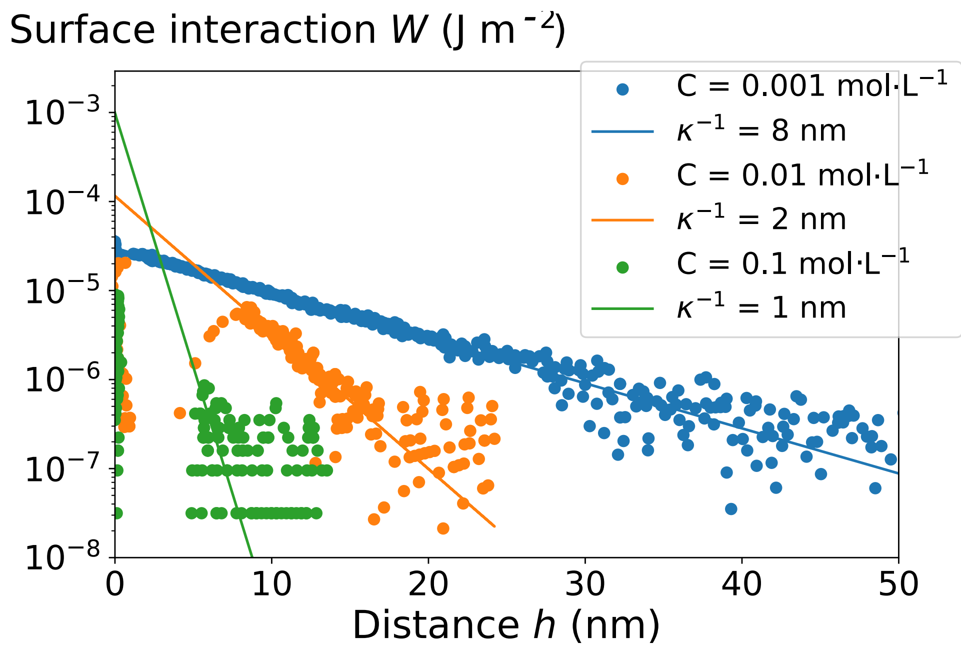
1.1 Surface Forces

Electrostatic/double layer forces

"DLVO" surface forces (Derjaguin, Landau, Verwey, Overbeek)

$$W_{\mathrm{DLVO}} = W_{\mathrm{VdW}} + W_{\mathrm{EDL}}$$



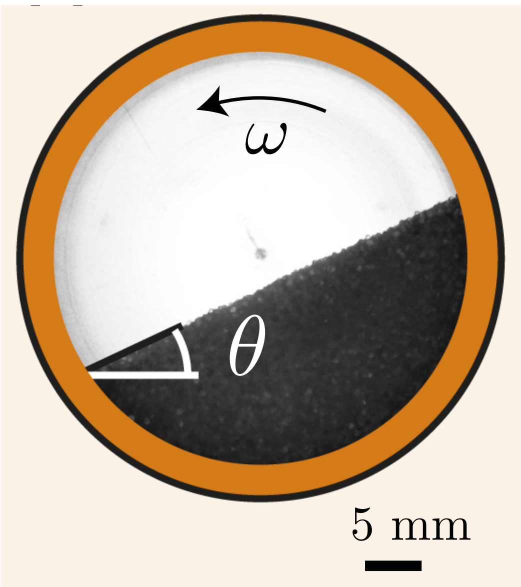


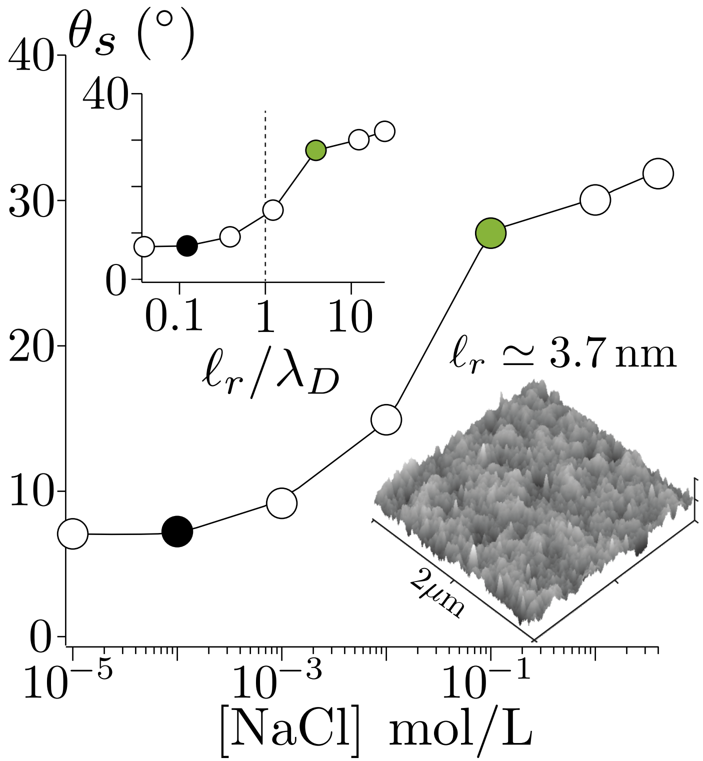
(AFM data from *Guilhem Mariette*)

1.1 Surface Forces

Electrostatic/double layer forces

Relevance of electrostatic double layer forces at the macroscopic scale of the suspension





Clavaud, C., Bérut, A., Metzger, B., & Forterre, Y. (2017). Revealing the frictional transition in shear-thickening suspensions. *Proceedings of the National Academy of Sciences*, *114*(20), 5147-5152.

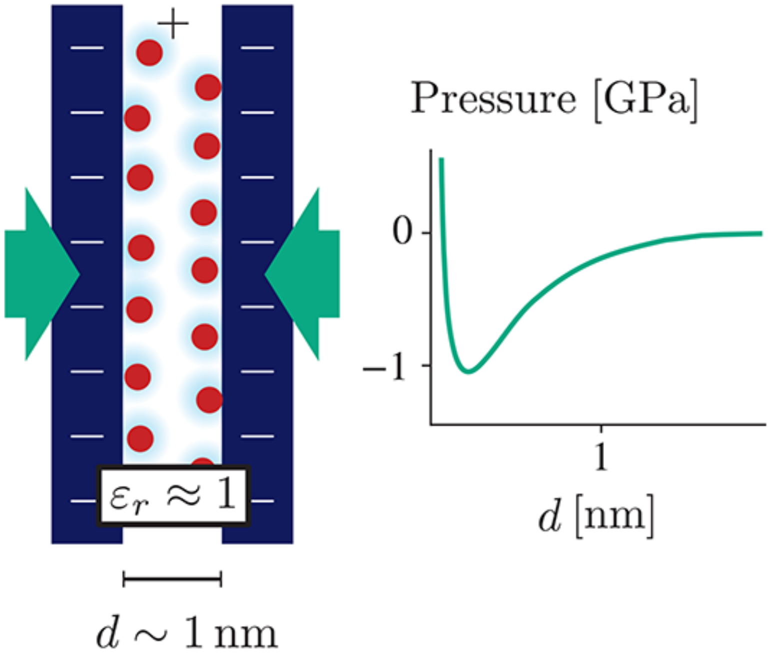
1.1 Surface Forces

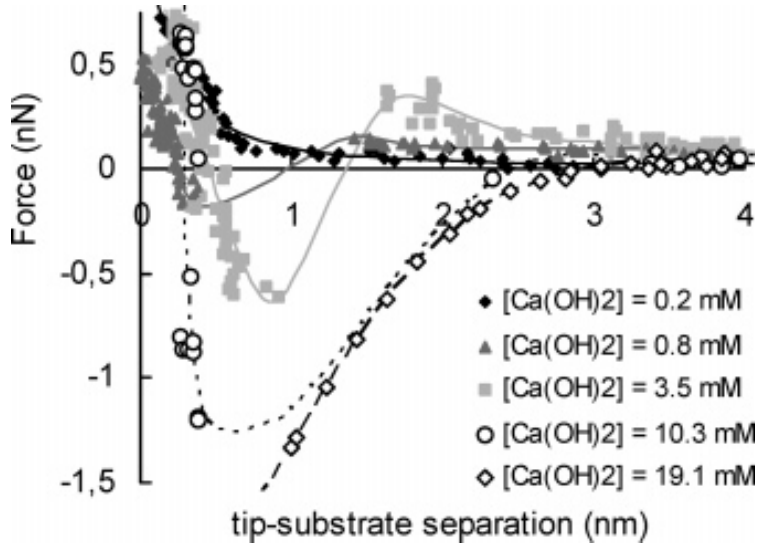
Ionic correlation forces

Ionic correlations can lead to the emergence of attractive forces between same-charge surfaces

→ Necessary to explain cement cohesion (high surface charge/high salinity/divalent ions like Ca^{2+})

"Bjerrum Length" $\lambda_B = \dfrac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \approx 0.7$ nm in bulk water





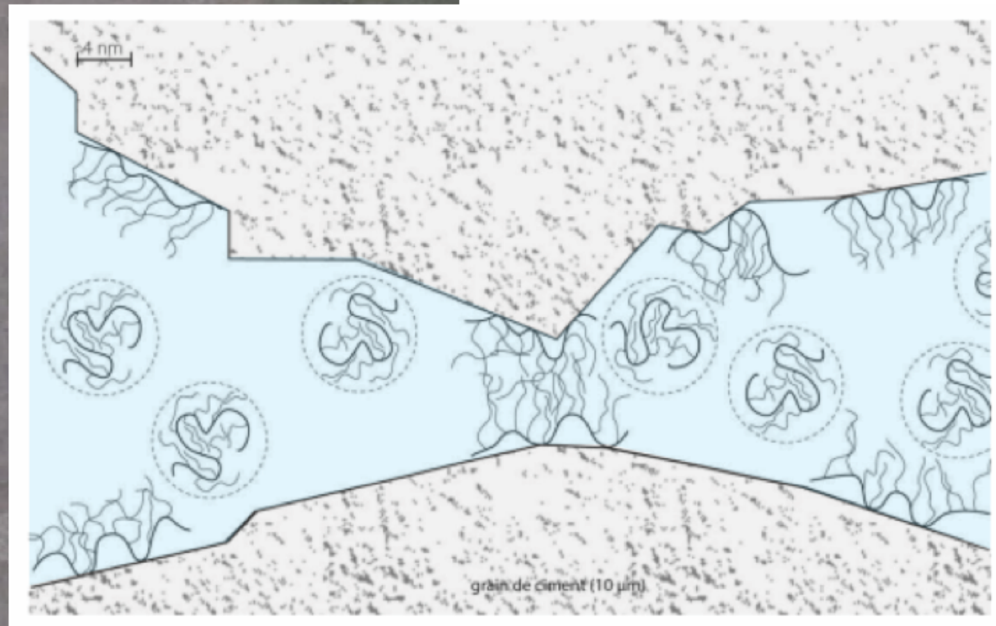
Palaia, Ivan, et al. "Like-charge attraction at the nanoscale: ground-state correlations and water destructuring." *The Journal of Physical Chemistry B* 126.16 (2022): 3143-3149.

Plassard, Cédric, et al. "Nanoscale experimental investigation of particle interactions at the origin of the cohesion of cement." *Langmuir* 21.16 (2005): 7263-7270.

1.1 Surface Forces

Polymer induced steric forces

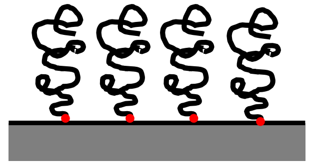
Example of the effect of superplasticizer on cement rheology



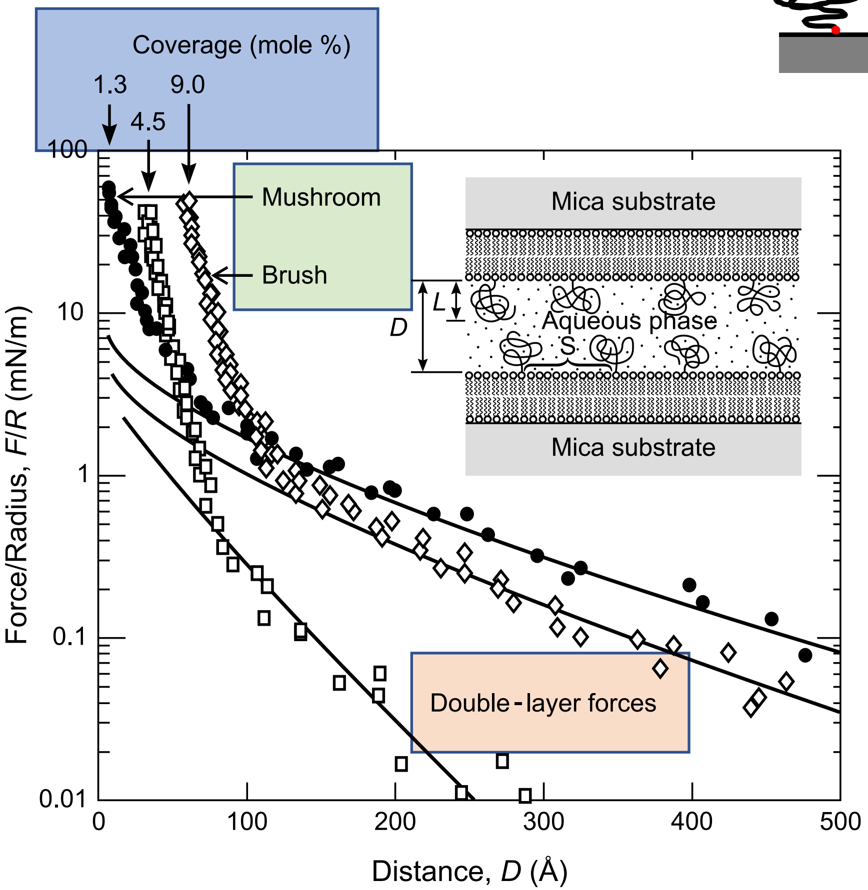
1.1 Surface Forces

Polymer induced steric forces – grafted chains

« Mushroom »



« Brush »



Grafted PEO in water

Steric repulsion of entropic origin.

Approximate interaction energy for mushrooms:

$$W(D) \approx 36.\Gamma.\mathrm{k_B T}.\mathrm{e}^{-D/R_g}$$

Surface coverage density Γ (m^{-2})

Characteristic distance R_g

For polymer brushes

$$P(D) \approx \mathrm{k_B T}.\Gamma^{\frac{3}{2}}.\left[\left(\frac{2L}{D}\right)^{\frac{9}{4}} - \left(\frac{D}{2L}\right)^{\frac{3}{4}}\right]$$

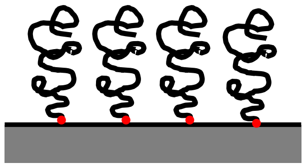
$$\approx 32 \cdot \Gamma^{\frac{3}{2}} \cdot kT.e^{-\pi D/L}$$

"Alexander-de Gennes"

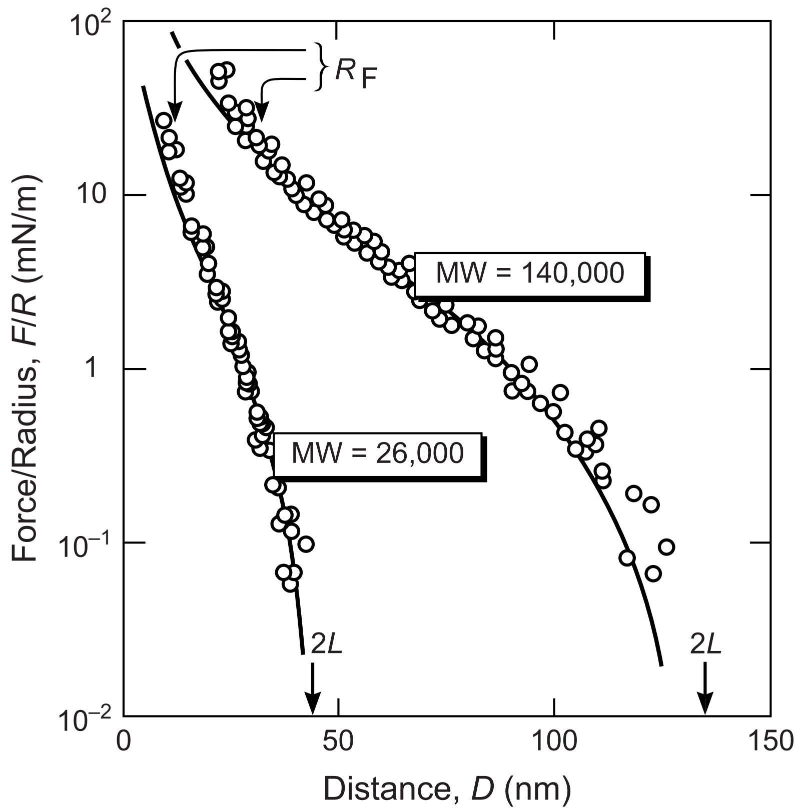
1.1 Surface Forces

Polymer induced steric forces – grafted chains

« Mushroom »



« Brush »



Polystyrene in toluene

Steric repulsion of entropic origin.

Approximate interaction energy for mushrooms:

$$W(D) \approx 36.\Gamma.\mathrm{k_B T}.\mathrm{e}^{-D/R_g}$$

Surface coverage density Γ (m^{-2})

Characteristic distance R_g

For polymer brushes

$$P(D) \approx \mathrm{k_B T}.\Gamma^{\frac{3}{2}}.\left[\left(\frac{2L}{D}\right)^{\frac{9}{4}} - \left(\frac{D}{2L}\right)^{\frac{3}{4}}\right]$$

$$\approx 32 \cdot \Gamma^{\frac{3}{2}} \cdot kT.e^{-\pi D/L}$$

"Alexander-de Gennes"

Polymer induced steric forces – adsorbed chains

Additional complexity

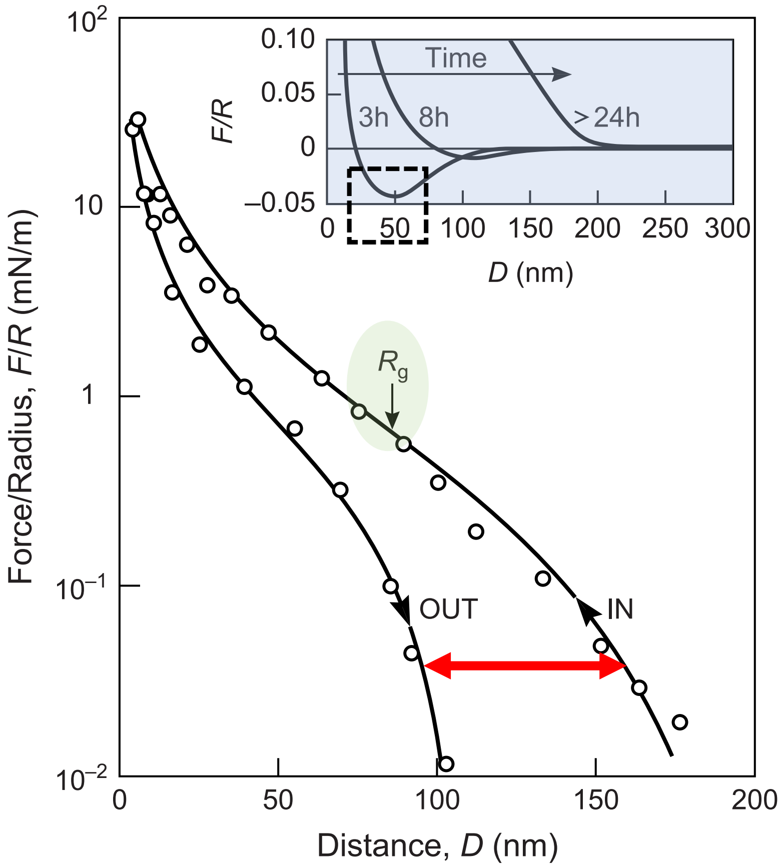
(i) Unit repeats of the polymer chains attach and detach from the surface

(ii) Polymer chains can exchange with the volume acting as reservoir.

→ The number of anchoring sites is not known.

1.1 Surface Forces

Polymer induced steric forces – adsorbed chains



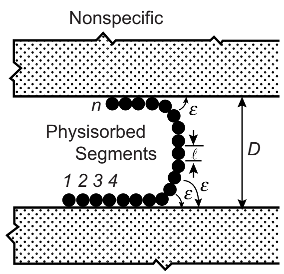
High MW PEO (10^6 g.mol^{-1}) adsorbed on mica surfaces

Additional complexity

(i) Unit repeats of the polymer chains attach and detach from the surface

(ii) Polymer chains can exchange with the volume acting as reservoir.

→ The number of anchoring sites is not known.



Range of the steric forces higher than the giration radius of the adsorbed polymer chain

Forces dependent of the adsorption time

Hysteresis

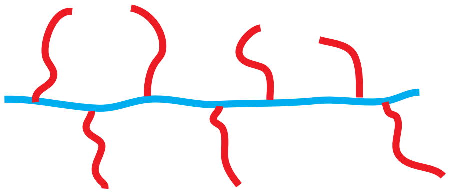
Attractive "bridging" interactions

1.1 Surface Forces

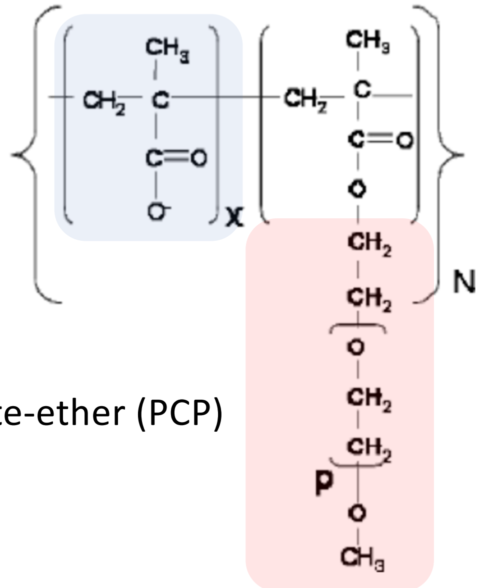
Polymer induced steric forces – adsorbed chains

Case of superplastifying molecules

Negatively charged backbone



Non adsorbing hydrophilic side chains



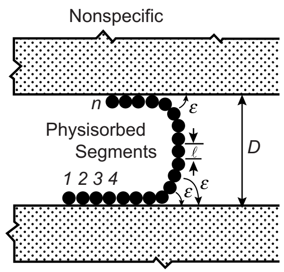
Polycarboxylate-ether (PCP)

Additional complexity

(i) Unit repeats of the polymer chains attach and detach from the surface

(ii) Polymer chains can exchange with the volume acting as reservoir.

→ The number of anchoring sites is not known.

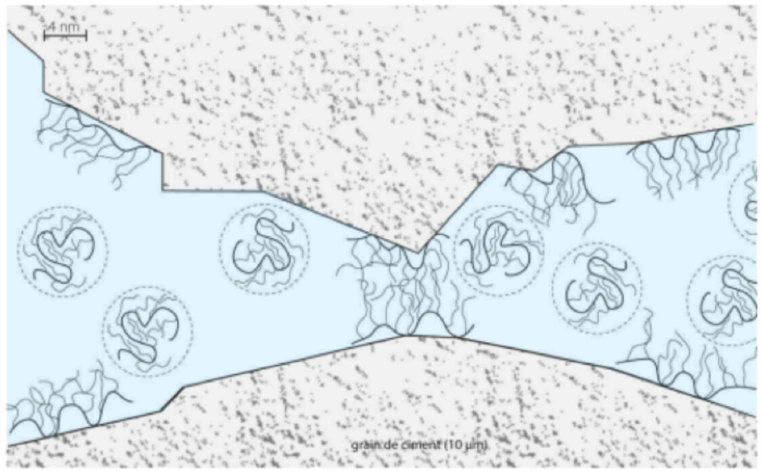


Range of the steric forces higher than the giration radius of the adsorbed polymer chain

Forces dependent of the adsorption time

Hysteresis

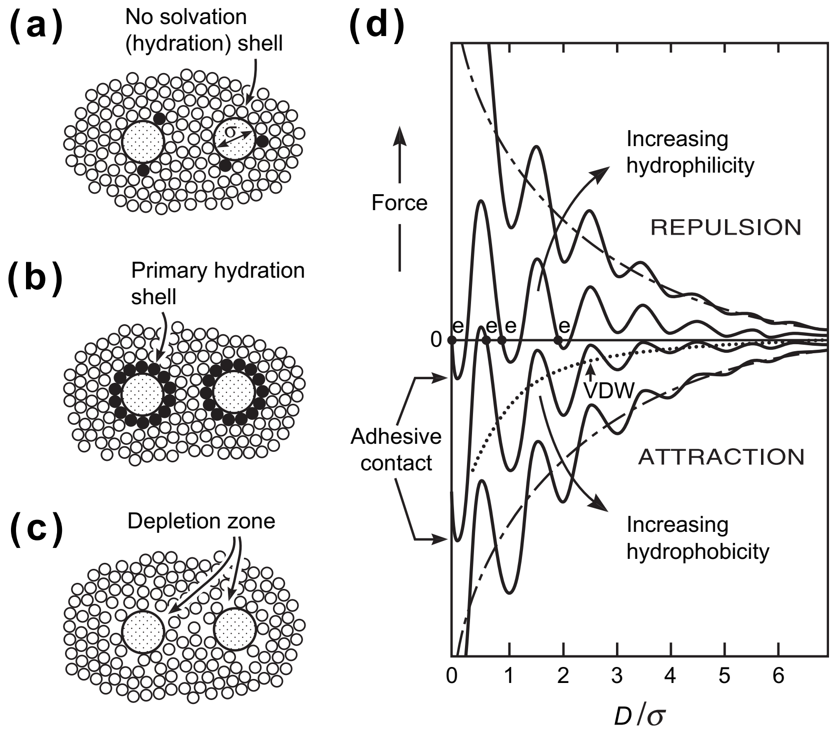
Attractive "bridging" interactions

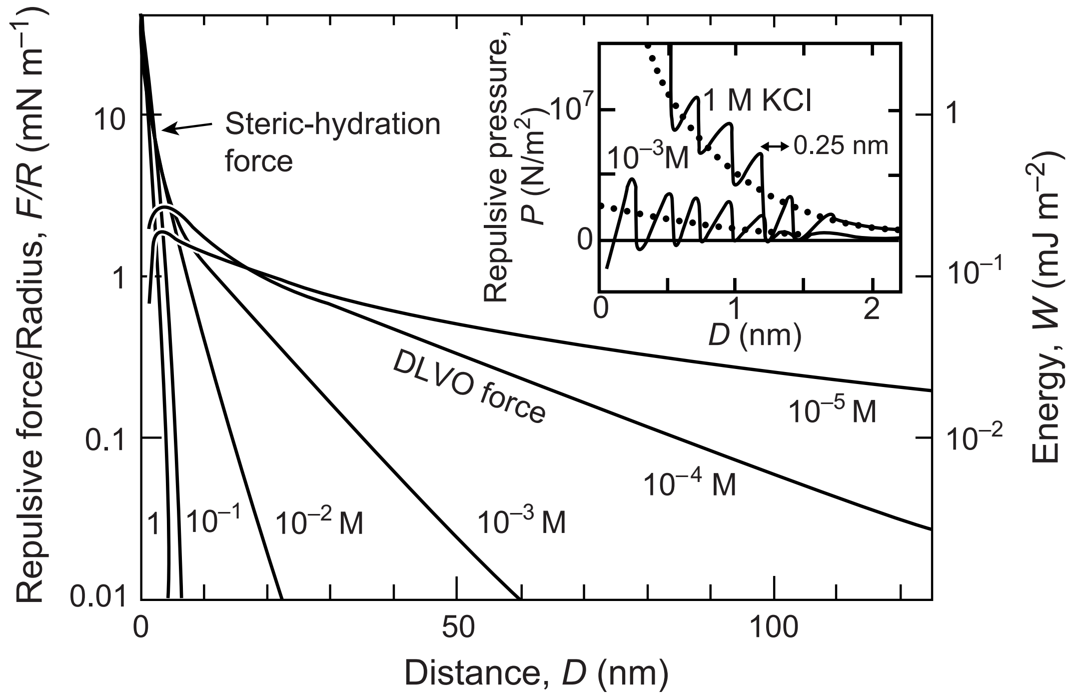


Other near-surface forces

hydrophobic interactions, solvation forces…

Solvent and surface specific near-surface forces





General Outline

1. **Surface forces and friction – General Concepts**
    1. Surface forces
    2. **Frictional forces**
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Shear Thickening
    2. Contact Aging
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

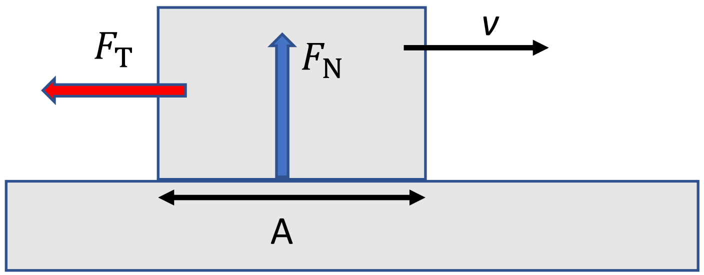
1.2 Solid Friction

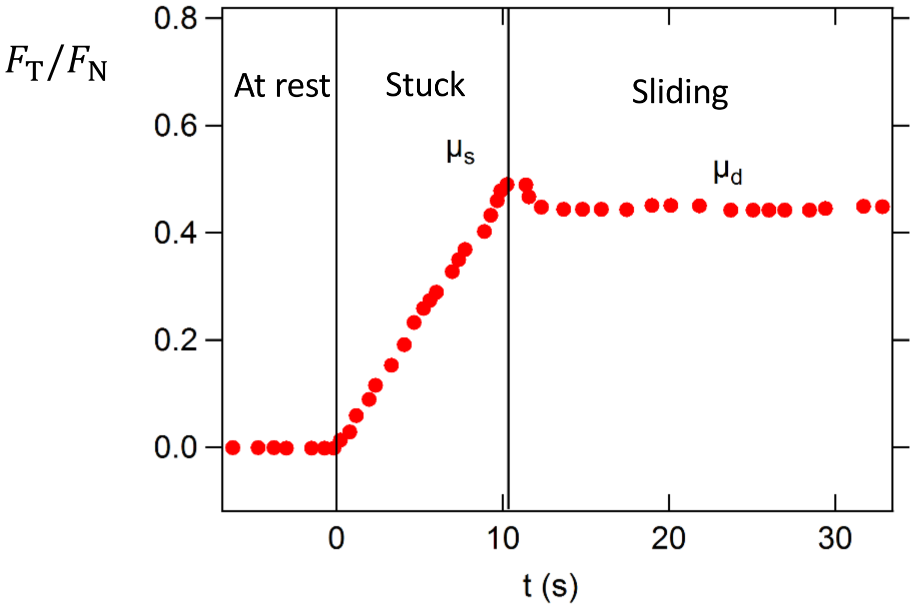
Amonton-Coulomb laws

Amonton—Coulomb empirical laws *Leonardo da Vinci (1452–1519).*

1. The friction force F_{T} is directly proportional to the applied load F_{N}
2. The friction coefficient μ is independent of the apparent area of contact, A.
3. The kinetic friction force is independent of the sliding velocity *v*.

$$F_{\mathrm{T}} = \mu F_{\mathrm{N}} \qquad \mu_s > \mu_d \qquad \mu \in [0.1, 1]$$



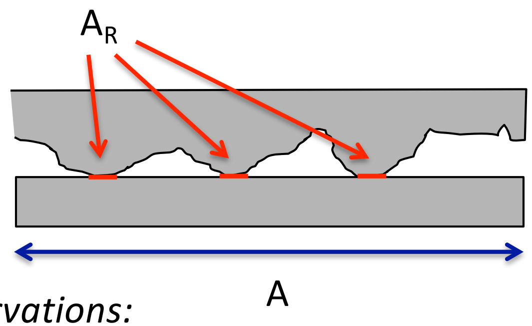


1.2 Solid Friction

Real area of contact

Bowden and Tabor (1940…): Key role of the real contact area A_R

Macroscopic interfaces are rough, and contact occurs only on top of asperities



Experimental observations:

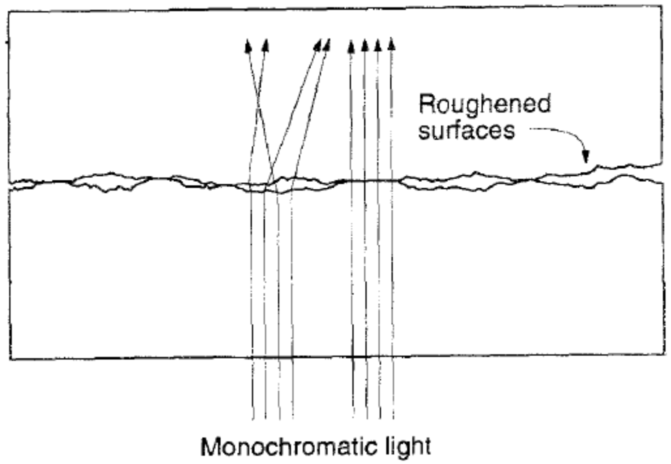
- The real contact area is much smaller than the apparent contact area.
  $A_R << A$
- The real contact area increases with the normal load.
  $A_R \sim F_N$

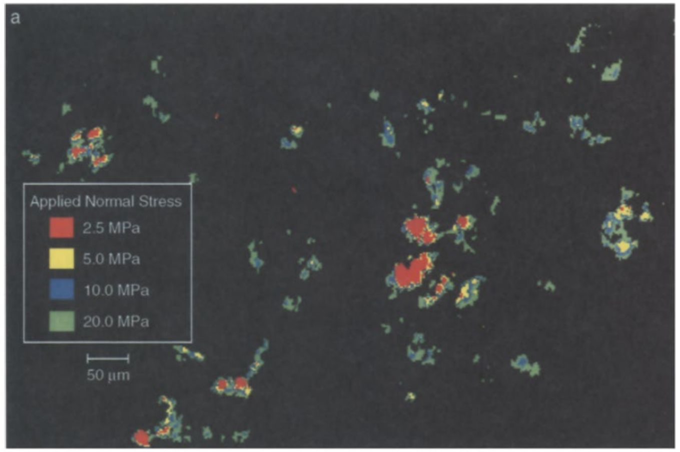
Plastic deformation of the asperities

$$F_N = \sigma_Y . A_R \qquad F_T = \tau_0 . A_R$$

$$\mu = \frac{\tau}{\sigma_Y}$$ is a material property

(See Greenwood-Williamson, Bowden-Tabor, Fuller and Tabor, Archard, Persson… for multi-asperity contact models)





Dieterich, J. H., & Kilgore, B. D. (1994). Direct observation of frictional contacts: New insights for state-dependent properties. *Pure and applied geophysics*, *143*, 283-302.

1.2 Solid Friction

Break-down of Coulomb law

Geometrical effects : breakdown of linear relationship between A_R and F_N

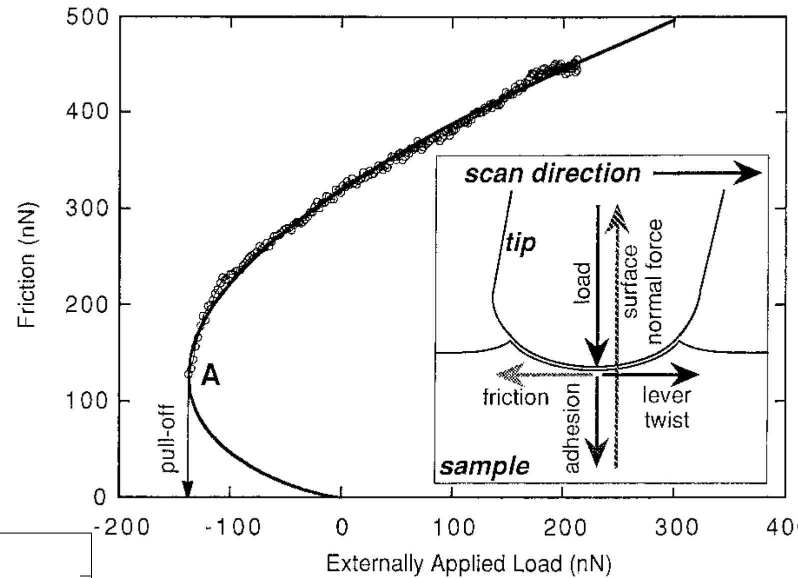
- Nanometric contacts
- Soft materials (e.g. elastomers…)
- Smooth surfaces (e.g. in surface force apparatus)

$$F_T = \tau_0 . A_R$$

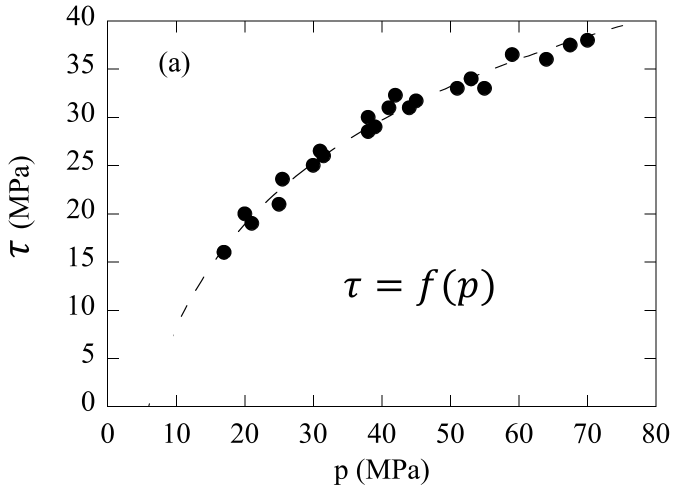
with A_R from JKR theory (elasticity + adhesion)

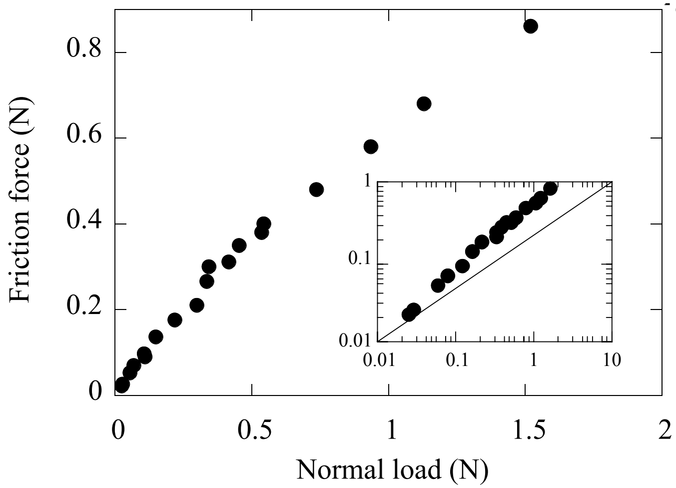
$$A_R^{3/2} = \frac{\pi^{3/2} R}{K}[L + 3\pi R\gamma + \sqrt{6\pi R\gamma L + (3\pi R\gamma)^2}]$$

(Tip of 140 nm radius)



Complex relation between shear stress and contact pressure

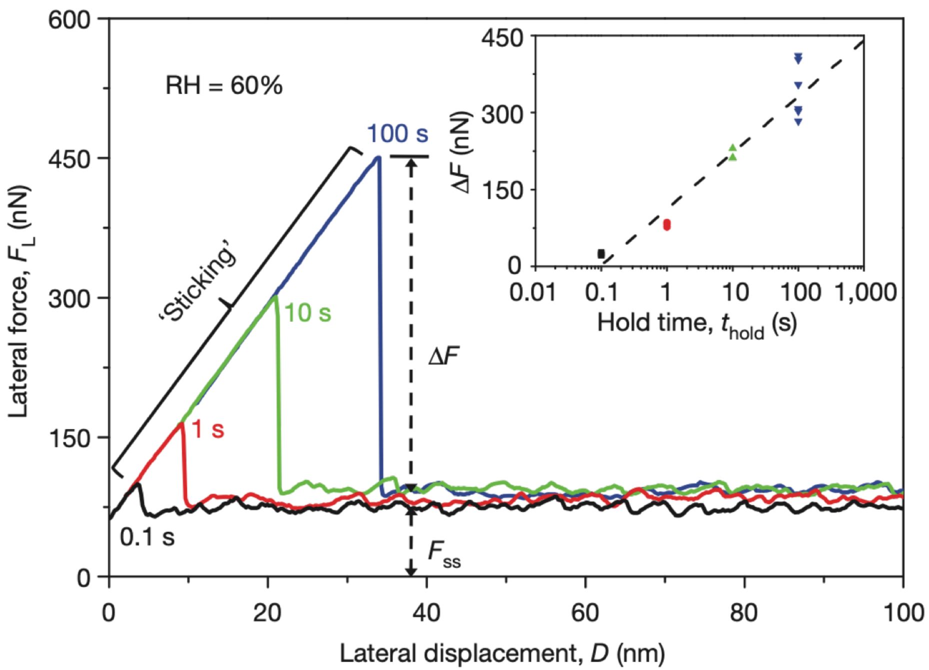




Could this breakdown happen at the colloidal/particle scale?

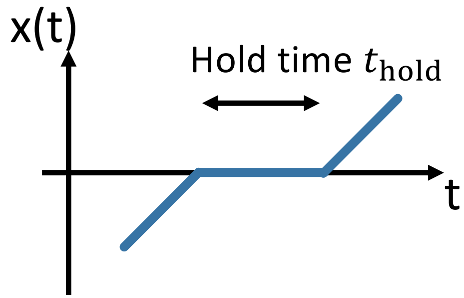
Carpick, R. W., Agrait, N., Ogletree, D. F., & Salmeron, M. (1996). Variation of the interfacial shear strength and adhesion of a nanometer-sized contact. *Langmuir*, *12*(13), 3334-3340.
Bureau, L., Baumberger, T., & Caroli, C. (2006). Non-Amontons behavior of friction in single contacts. *The European Physical Journal E*, *19*, 163-169.

1.2 Solid Friction   Aging effects



AFM Friction between SiO_2 surfaces at controlled humidity

« Slide-hold-slide » protocol



Dependence of the static friction force on the waiting time
Logarithmic ageing law : $F_S \sim \log(t_{\mathrm{hold}})$

Geometric/Plastic aging

Slow plastic creep at the contacting asperities

Chemical Aging

Interfacial chemical bonding
(e.g. hydrogen bonding, siloxane Si-O-Si bridging)

Dieterich, J. H., & Kilgore, B. D. (1994). Direct observation of frictional contacts: New insights for state-dependent properties. *Pure and applied geophysics*, *143*, 283-302.

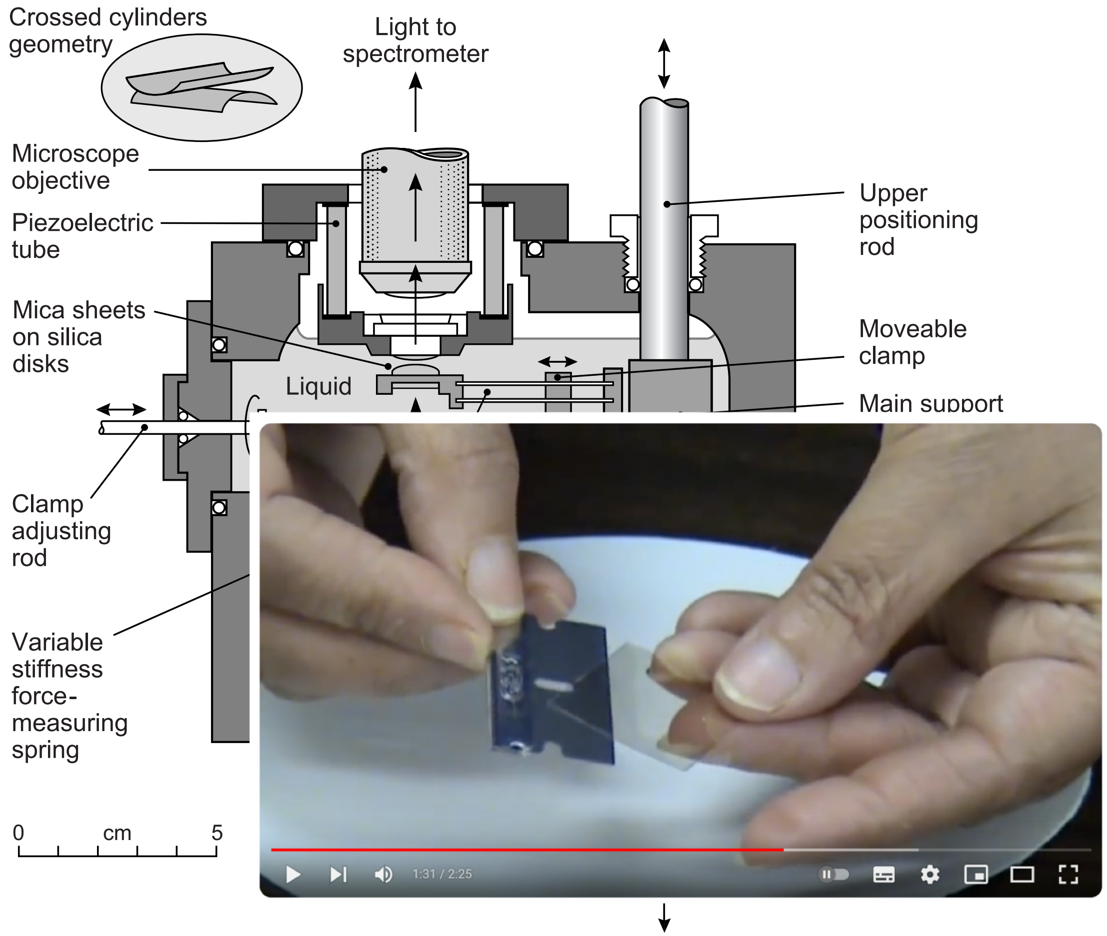
Li, Q., Tullis, T. E., Goldsby, D., & Carpick, R. W. (2011). Frictional ageing from interfacial bonding and the origins of rate and state friction. Nature, 480(7376), 233-236.

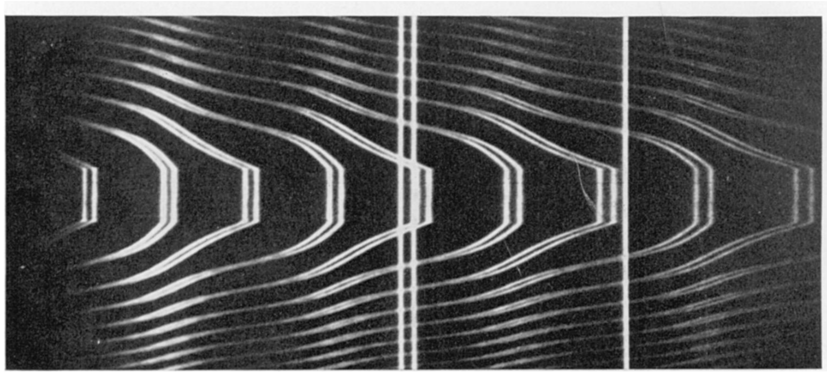
1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. **Measuring interaction forces at the nanoscale**
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Shear Thickening
    2. Contact Aging
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

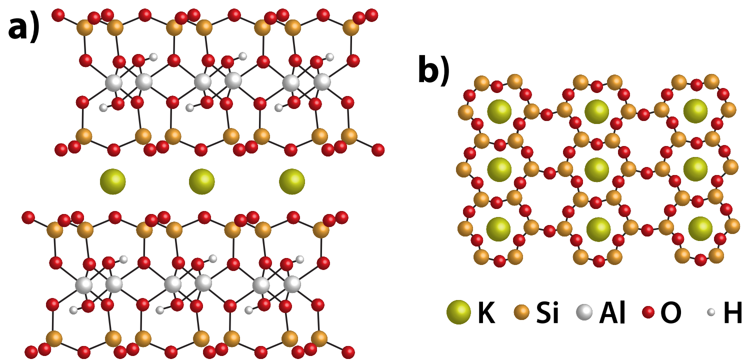
1.3 Measuring Forces

Surface Force Apparatus

F = K. Δ X



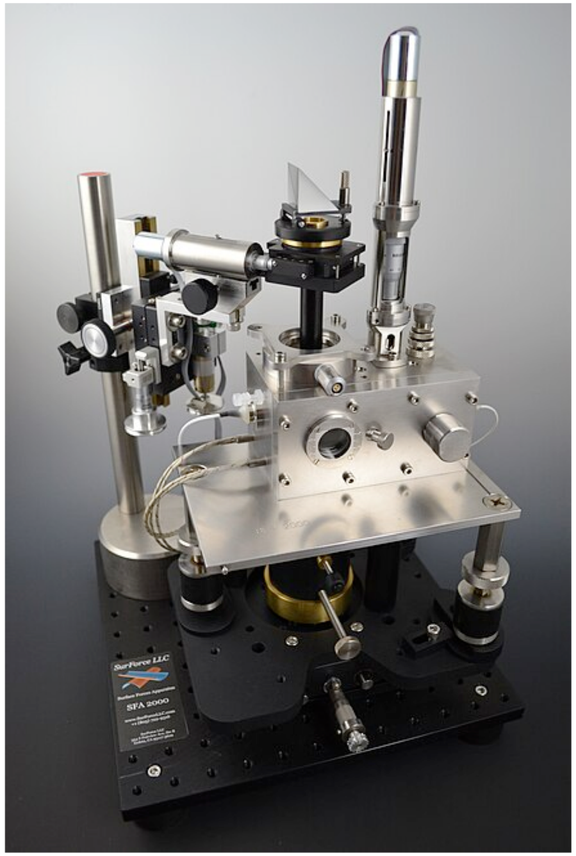




Tabor, D., & Winterton, R. S. (1969). The direct measurement of normal and retarded van der Waals forces. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, *312*(1511), 435-450.

1.3 Measuring Forces

Surface Force Apparatus



Resolution in displacement ≈ 0.1 nm

Stiffness K ~ 10^3 $N.m^{-1}$

Force sensitivity : 100 nN

Large surfaces R ≈ 1-10 mm

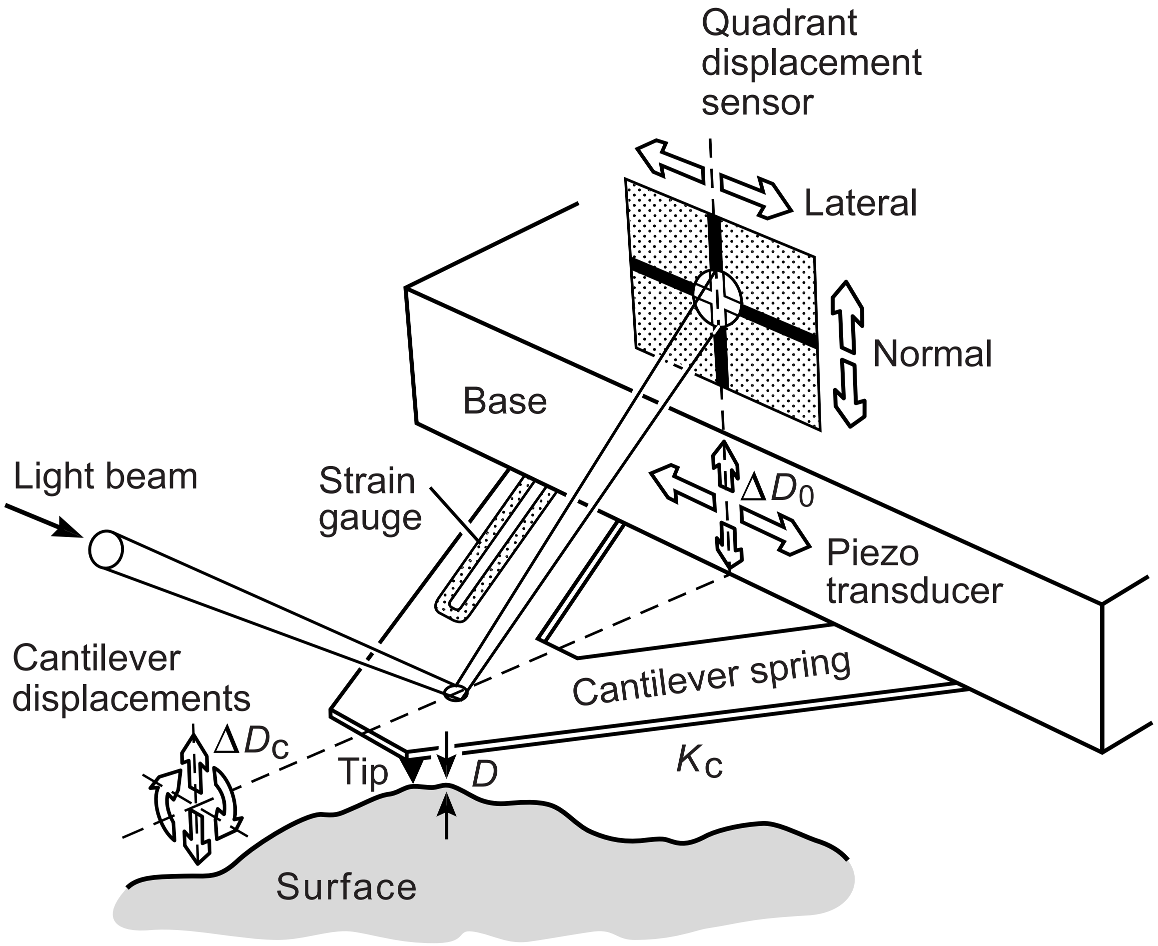
Quantity to compare for
surface forces : F/R ~ 10 μ $J.m^{-2}$

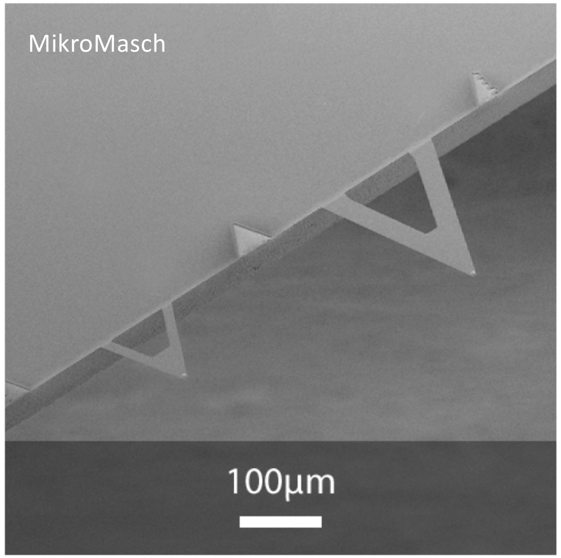
+ Ultra-high sensitivity
+ Direct visualization of the shape of the contact through interferences
+ Knowledge of the “absolute zero” corresponding to contact

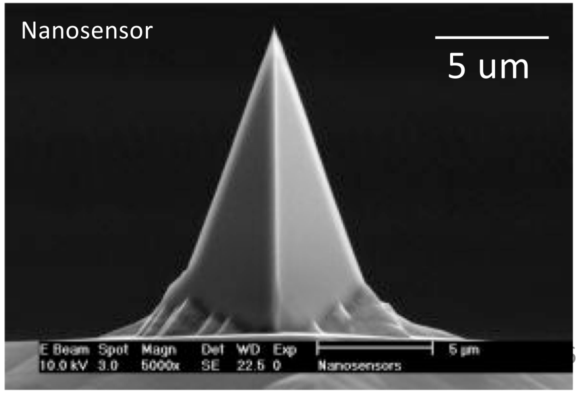
- **Limitation to mica/mica contacts**
- **VERY difficult experiments**

1.3 Measuring Forces

Atomic Force Microscope

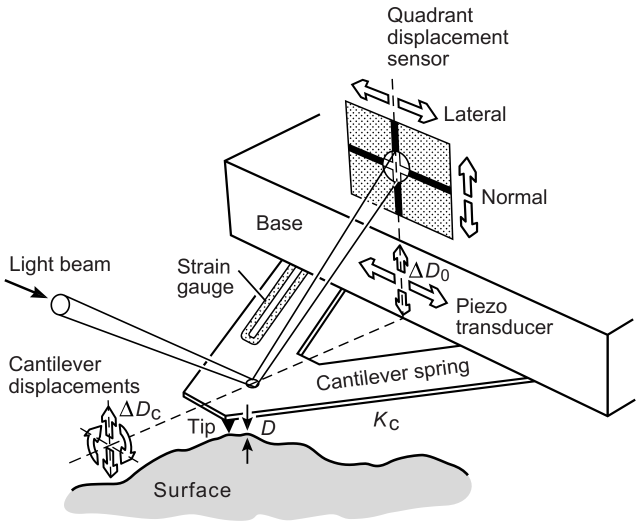






1.3 Measuring Forces

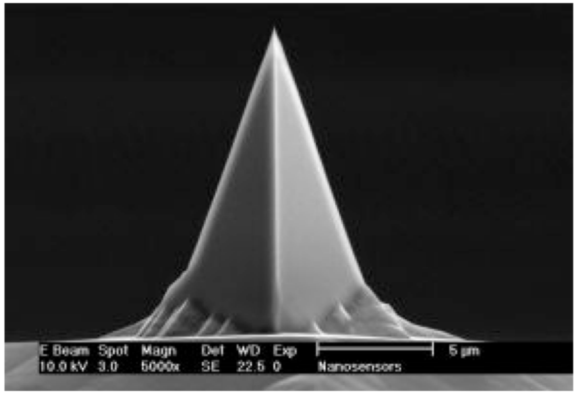
Atomic Force Microscope



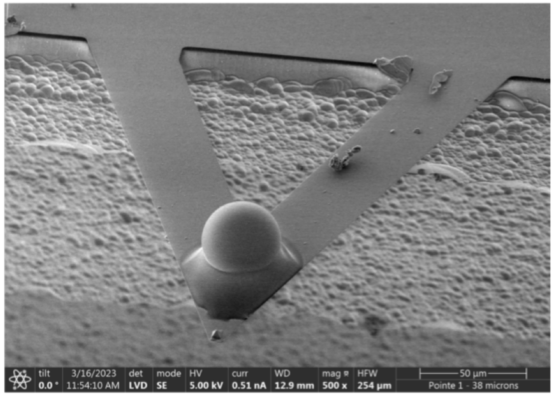
Resolution in displacement **~** 0.1 nm

Stiffness K **~** 10^{-2} – 10 $N.m^{-1}$

Force sensitivity ~ 10 pN



Sharp tips



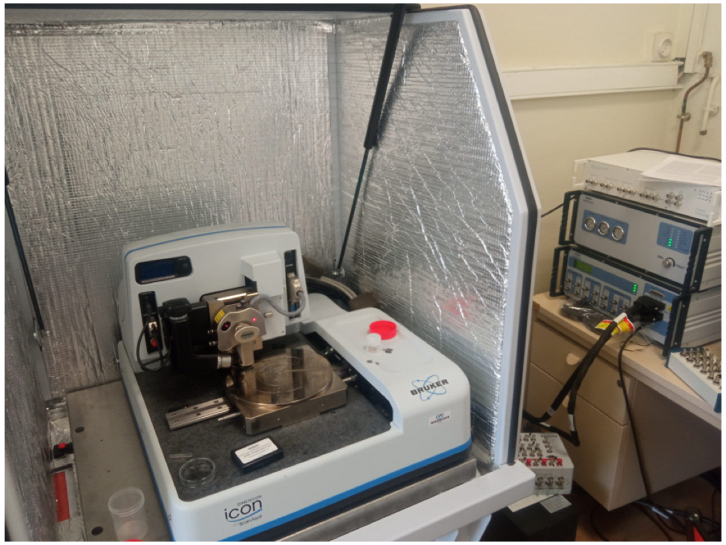
Colloidal tips

+ Tunability in terms of force range
+ Versatility in terms of materials
+ Easier than SFA due to small contact radius (but still not "easy")

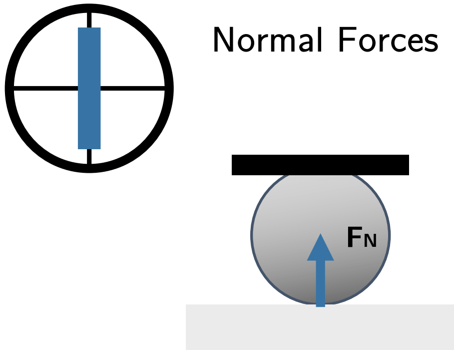
- **No knowledge of the absolute contact**

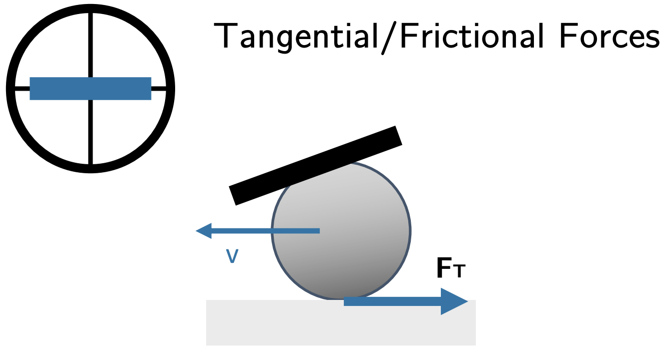
1.3 Measuring Forces

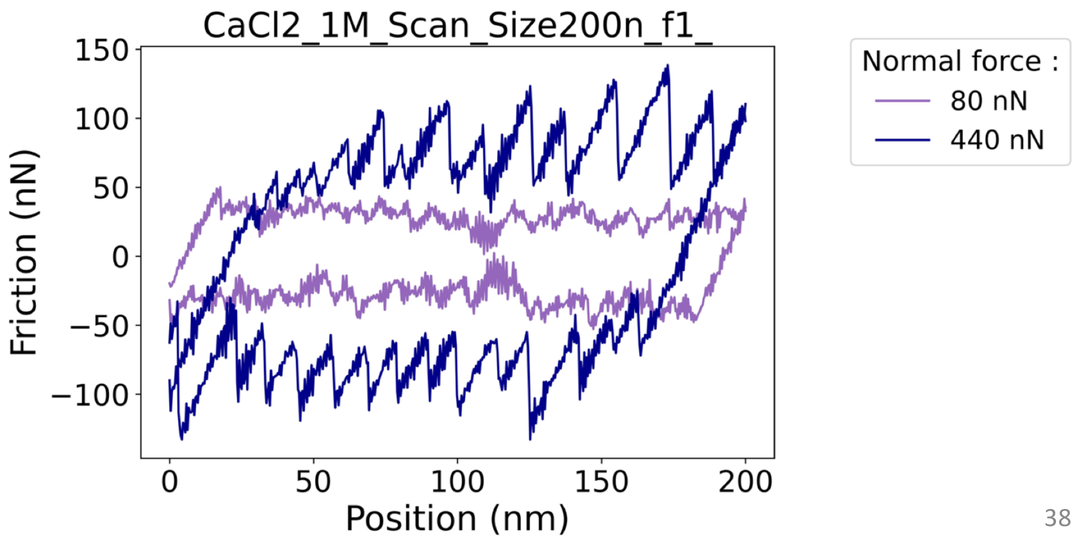
Atomic Force Microscope - Friction



Bruker Nanoscope V

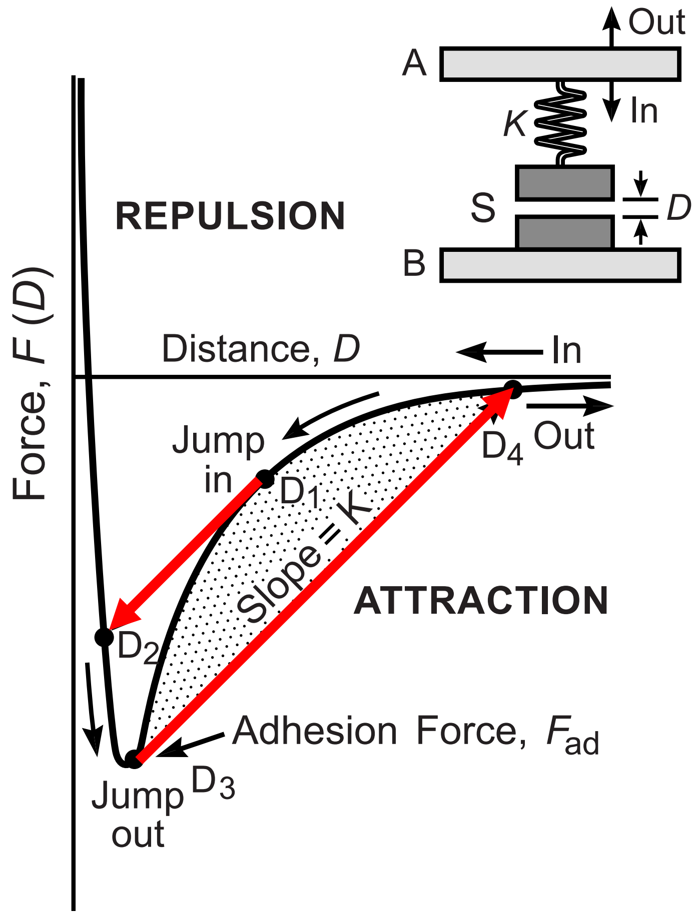






1.3 Measuring Forces Jump to contact instability

Intrinsic limitations for the force resolution : "Jump to contact" instability



When $\left|\frac{dF}{dz}\right| > k_{\text{spring}}$

Intrinsic to all force measurements relying on a deflecting spring (SFA, AFM…)

Practical challenges :

Thermal Drift

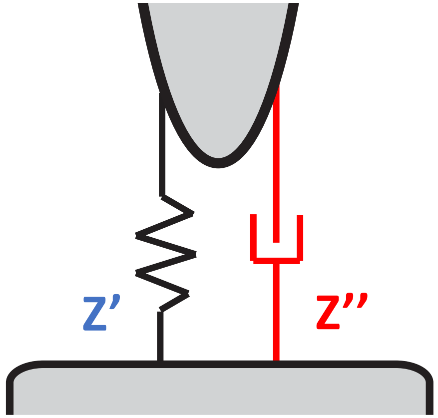
Vibrations/stability

Calibration

Surface and system preparation

1.3 Measuring Forces

Dynamic force measurements



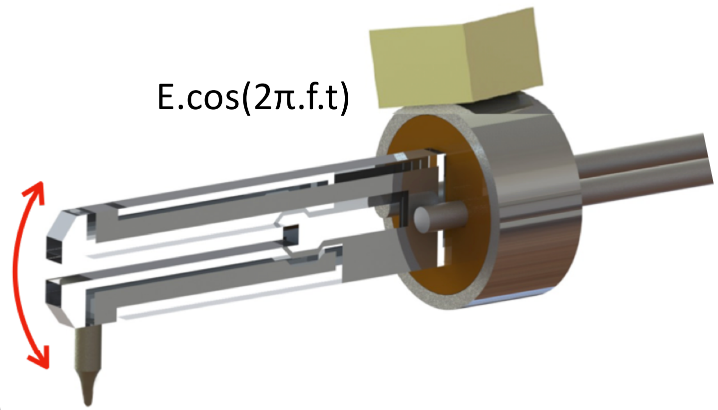
Complex mechanical impedance : $\boldsymbol{Z^*} = \boldsymbol{F^*(\omega)/a_0} = Z' + i.Z''$ **[N/m]**

"in phase" elastic forces | *"out of phase" dissipative forces*

Disentangle dissipative and conservative interactions

Tuning Fork based AFM

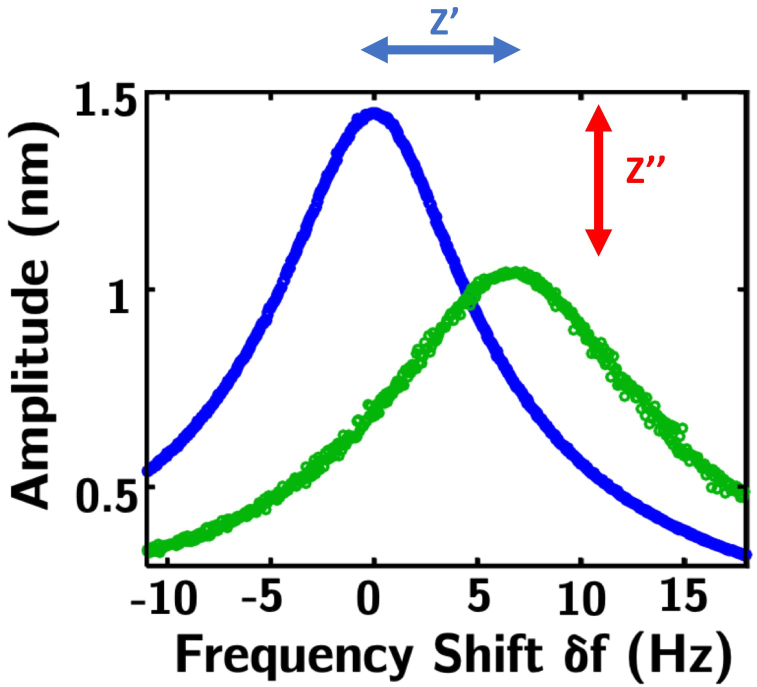
$a.\cos(2\pi.\mathrm{f}.t + \varphi)$



$$m\ddot{x} + F_{\mathrm{D}} + \left(k_0 - \frac{\partial F}{\partial x}\right)x = F_{\mathrm{ext}}\, e^{i\omega t}$$

Dissipation | Stiffness | Piezoelectric forcing

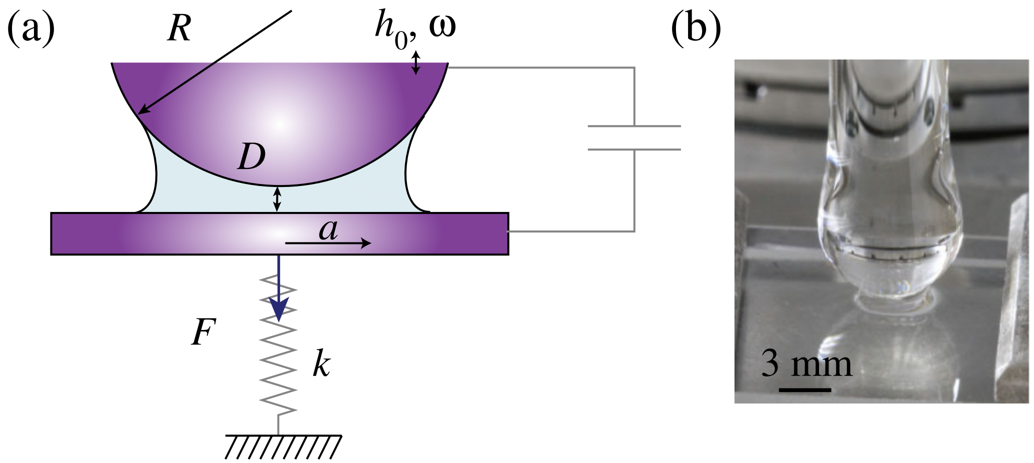
Stiffness $k_0 = 10^4$ N.m^{-1}
Quality factor $Q = 10^4$
Dynamic stiffness k_0/Q



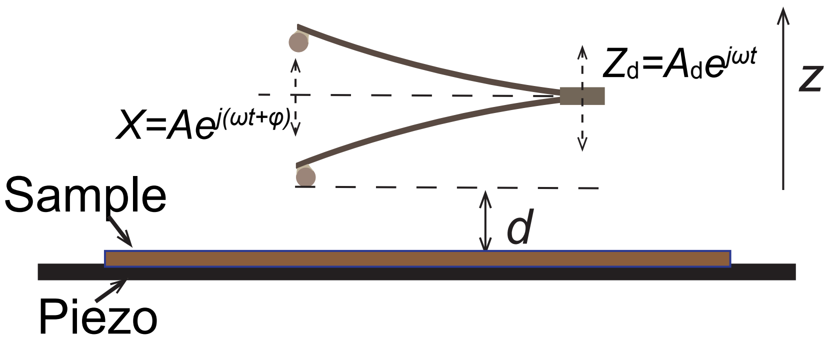
1.3 Measuring Forces

Dynamic force measurements

Dynamic SFA/AFM



Villey, R., Martinot, E., Cottin-Bizonne, C., Phaner-Goutorbe, M., Léger, L., Restagno, F., & Charlaix, E. (2013). Effect of surface elasticity on the rheology of nanometric liquids. *Physical review letters*, *111*(21), 215701.



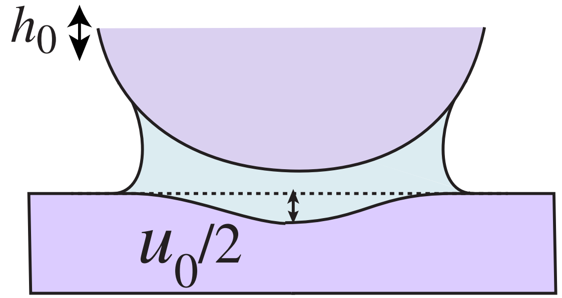
Zhang, Z. (2020). *Nano-rheology at soft interfaces probed by atomic force microscope* (Doctoral dissertation, Université de Bordeaux).

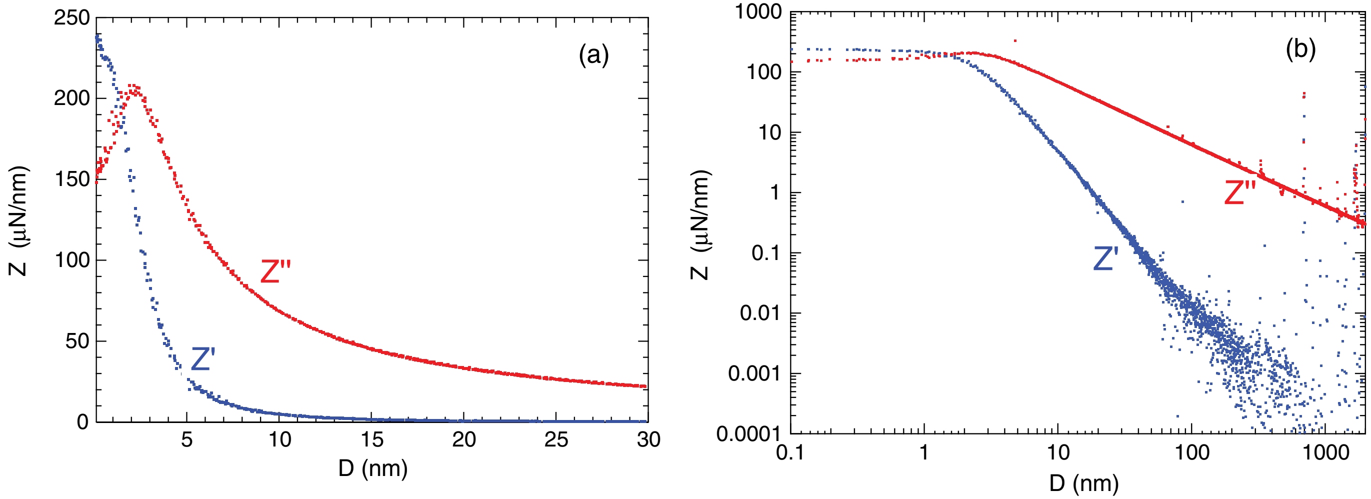
1.3 Measuring Forces

Dynamic force measurements

An example : Elasto-hydrodynamic interactions

$$\boldsymbol{Z^*} = \boldsymbol{F^*(\omega)/a_0} = \boldsymbol{Z' + i.Z''}\ \textbf{[N/m]}$$





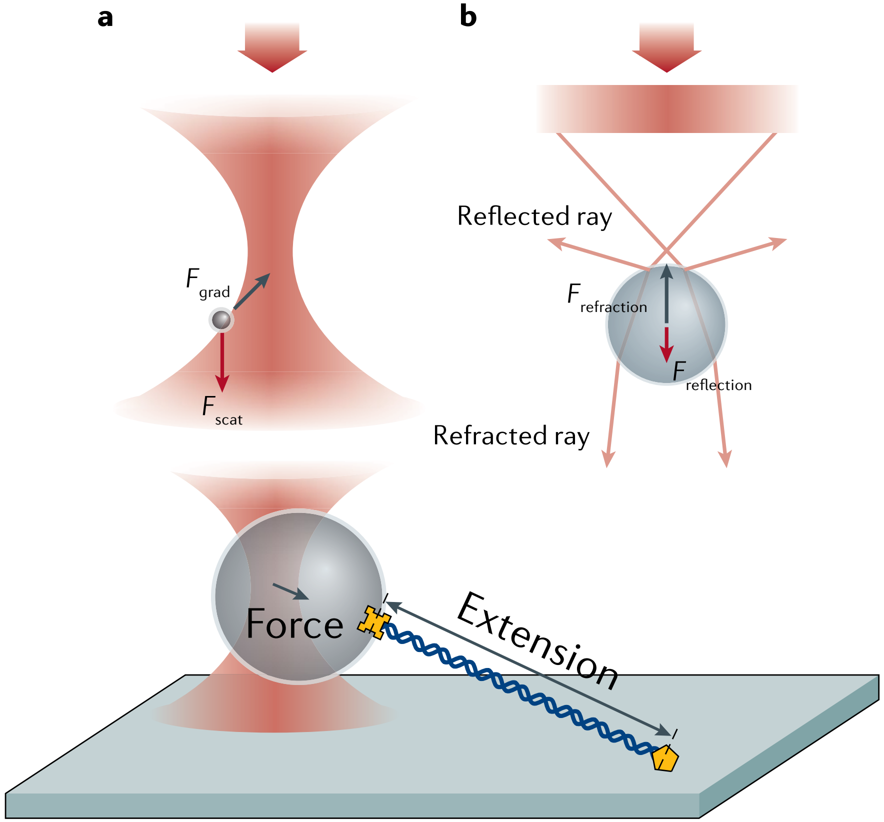
$$Z^*(\omega, D) = iZ'' = i\frac{6\pi\eta_0\omega R^2}{D}$$

$$D_c = 8R\left(\frac{\omega\eta_0}{E^*}\right)^{2/3},$$

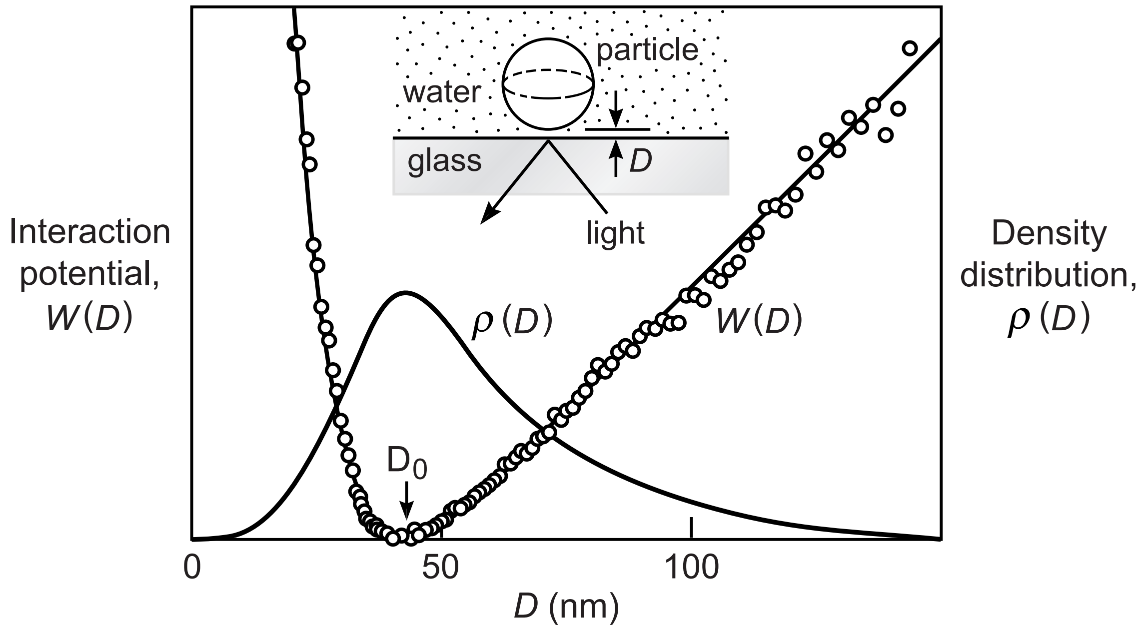
Villey, Richard, et al. "Effect of surface elasticity on the rheology of nanometric liquids." Physical review letters 111.21 (2013): 215701.

1.3 Measuring Forces Other approaches

Optical Tweezer



TIRFM



Bustamante, C. J., Chemla, Y. R., Liu, S., & Wang, M. D. (2021). Optical tweezers in single-molecule biophysics. *Nature Reviews Methods Primers*, *1*(1), 25.

1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Contact Aging
    2. Shear Thickening
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

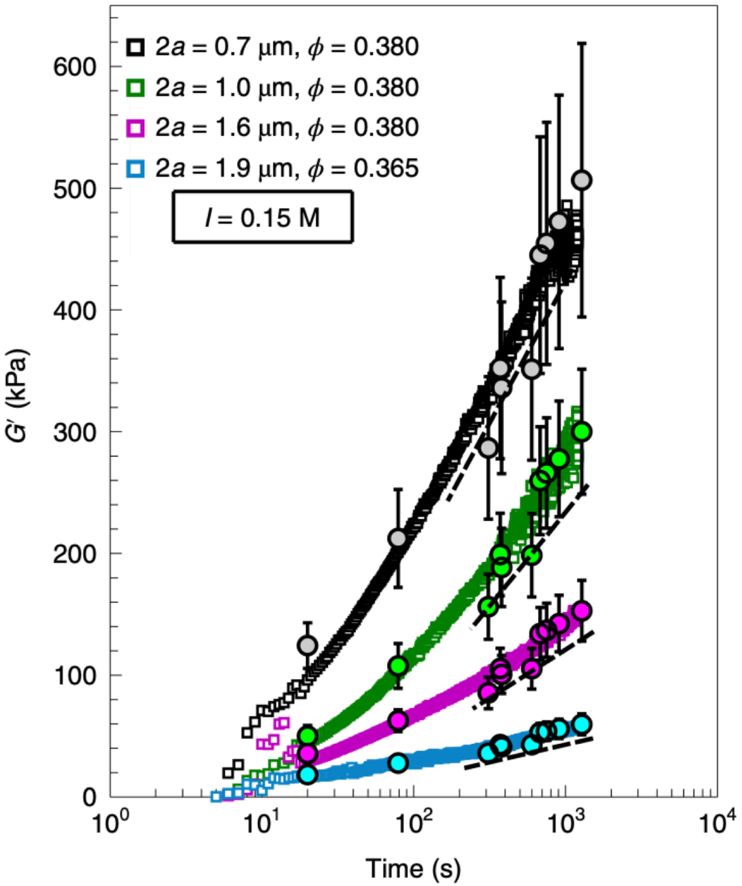
1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. **Contact Aging**
    2. Shear Thickening
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

2.1 Contact Ageing

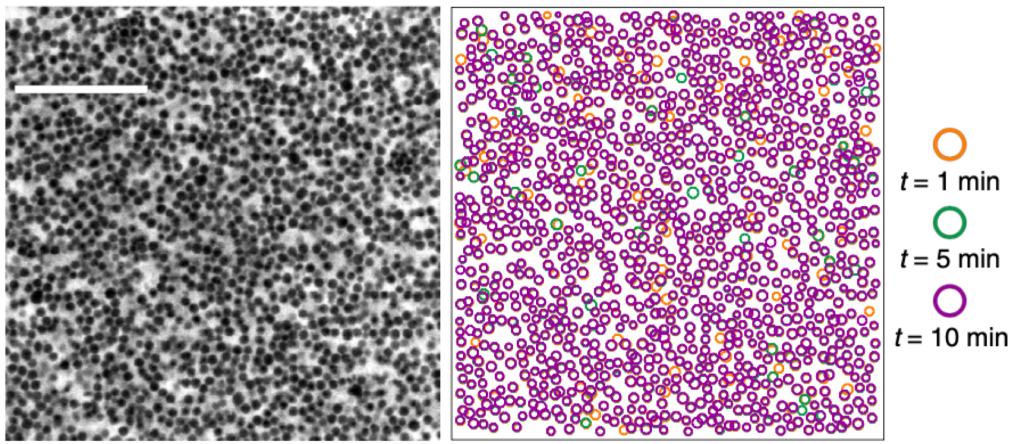
Macroscopic aging

« Attractive » Silica and PMMA suspensions at high salt concentrations

Slow temporal evolution of the macroscopic elastic modulus



Macroscopic aging occurs without structural rearrangements

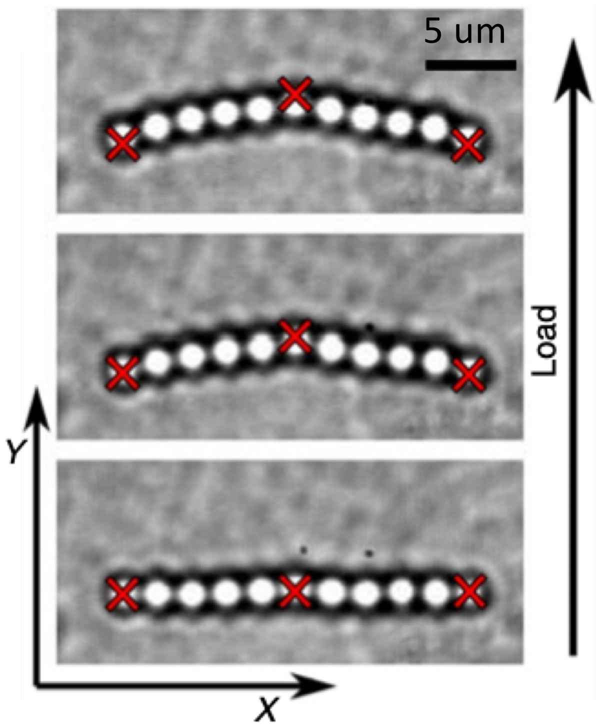


Bonacci, F., Chateau, X., Furst, E. M., Fusier, J., Goyon, J., & Lemaître, A. (2020). Contact and macroscopic ageing in colloidal suspensions. *Nature Materials*, *19*(7), 775-780.

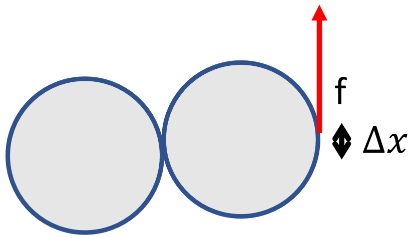
2.1 Contact Ageing

Microscopic contact evolution

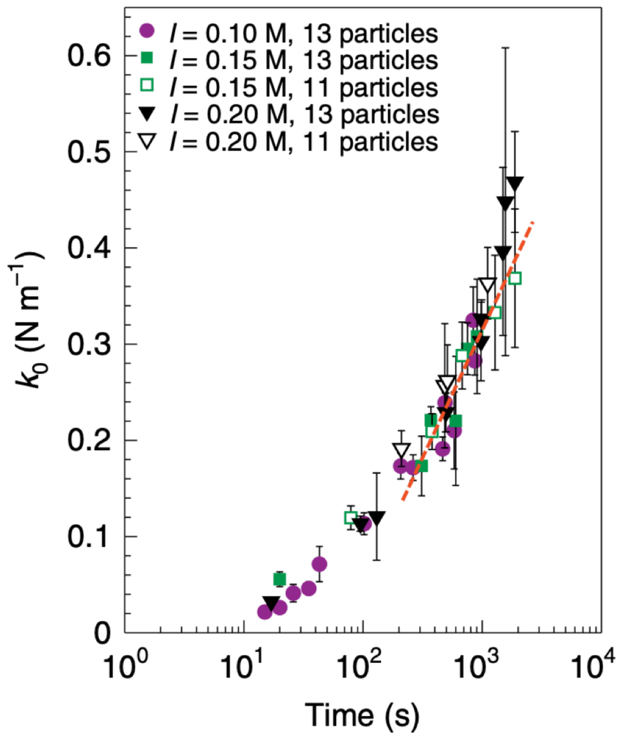
Does microscopic contact stiffness evolve with time?



Three-point bending test using optical tweezers



→ Estimation of a "contact stiffness" k_0 [N.m^{-1}]



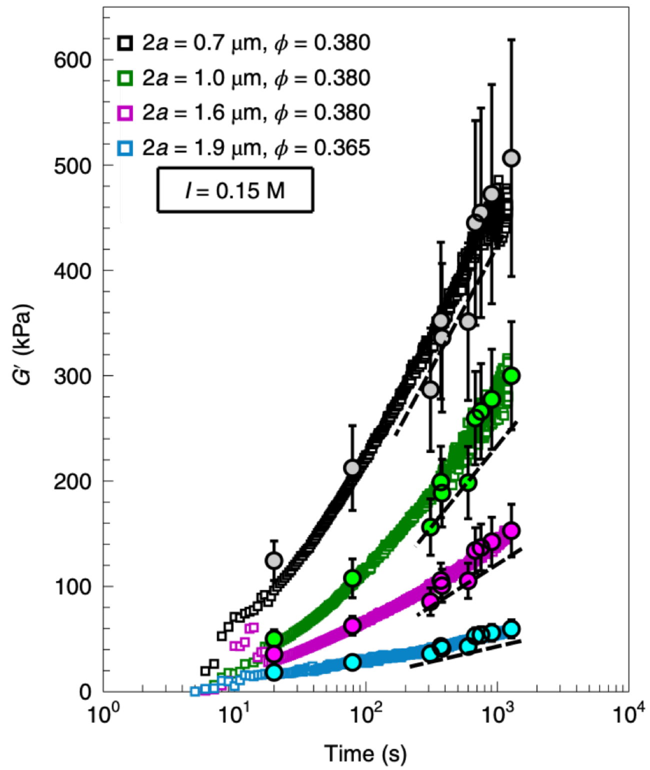
k_0 increases with time

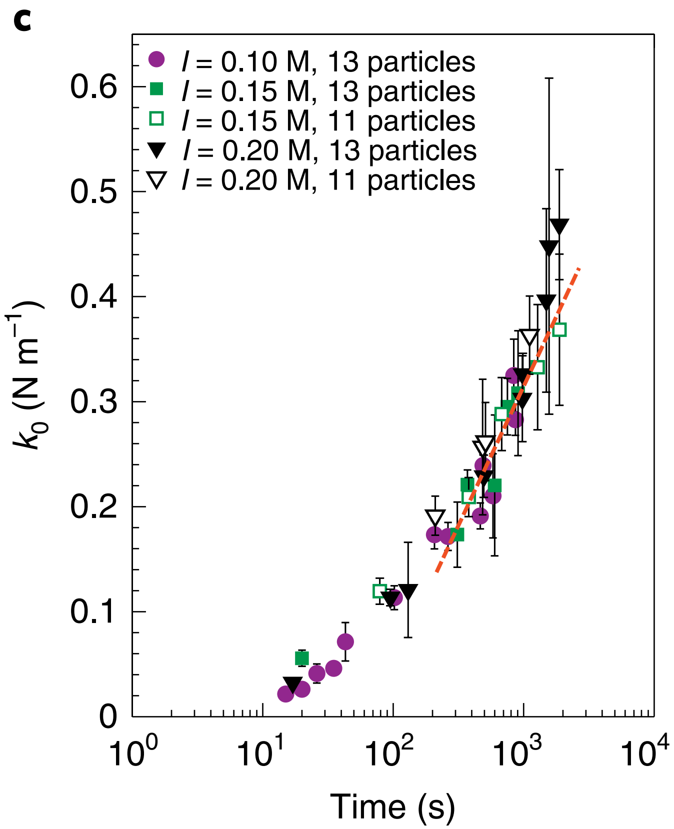
$$k_0 \sim \log(t)^{4/3}$$

Bonacci, F., Chateau, X., Furst, E. M., Fusier, J., Goyon, J., & Lemaître, A. (2020). Contact and macroscopic ageing in colloidal suspensions. *Nature Materials*, *19*(7), 775-780.

2.1 Contact Ageing

Macroscopic suspension aging stems from microscopic contact stiffening





structure

microscopic contact stiffness

$$G'(t) = \frac{S}{a} \times k_0(t)$$

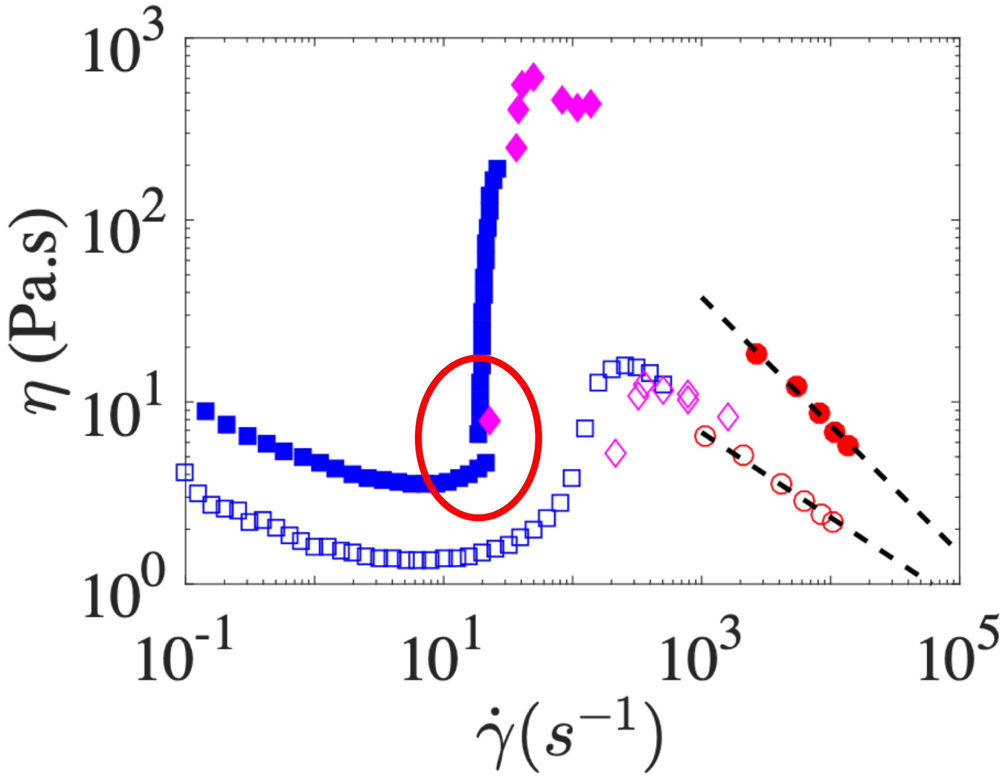
Particle radius

Bonacci, F., Chateau, X., Furst, E. M., Fusier, J., Goyon, J., & Lemaître, A. (2020).
Contact and macroscopic ageing in colloidal suspensions. *Nature Materials*, *19*(7), 775-780.

1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Contact Aging
    2. **Shear Thickening and the frictional transition**
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

2.2 Shear Thickening

Macroscopic characterization

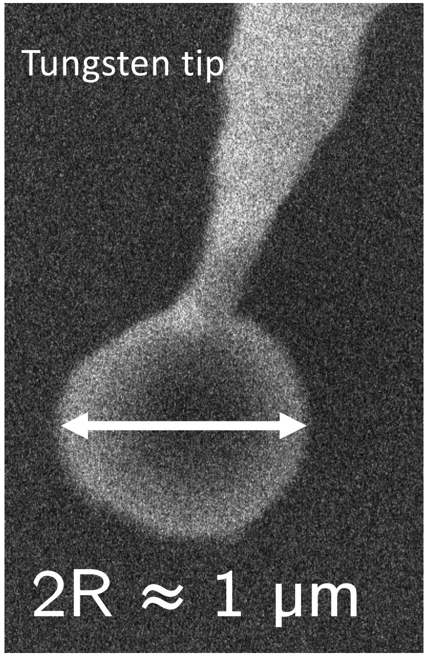


(PVC particles in plasticizer)

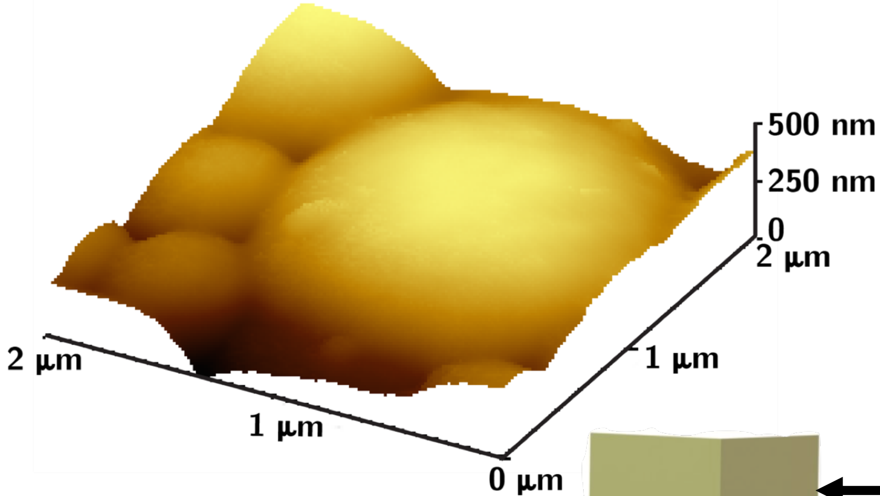
Comtet, J., Chatté, G., Nigues, A., Bocquet, L., Siria, A., & Colin, A. (2017). Pairwise frictional profile between particles determines discontinuous shear thickening transition in non-colloidal suspensions. *Nature communications*, *8*(1), 15633.

2.2 Shear Thickening

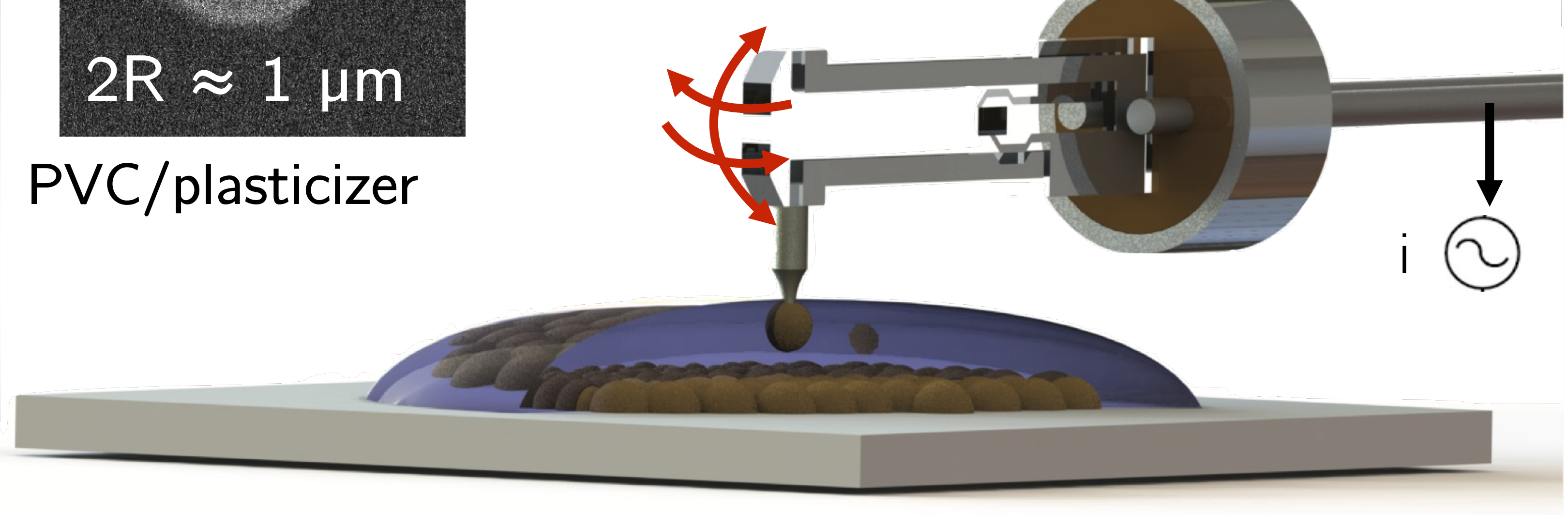
Probing microscopic interactions



PVC/plasticizer

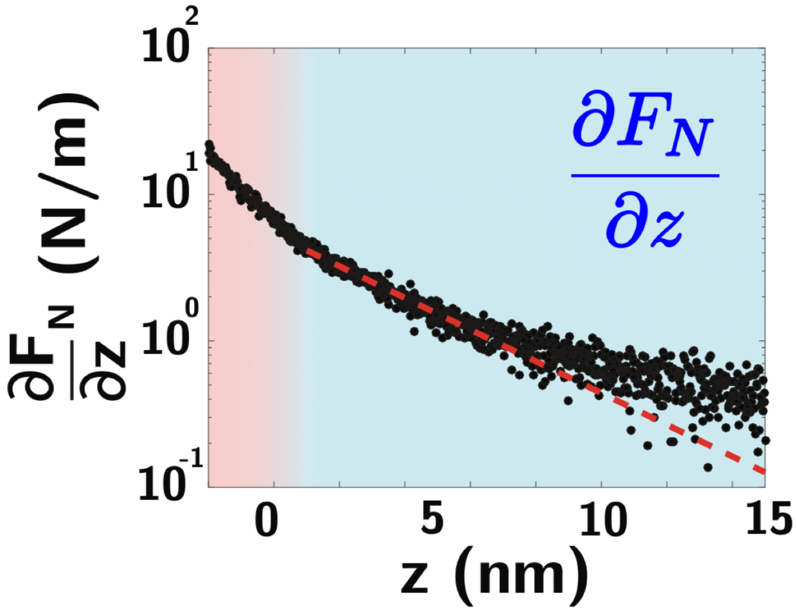


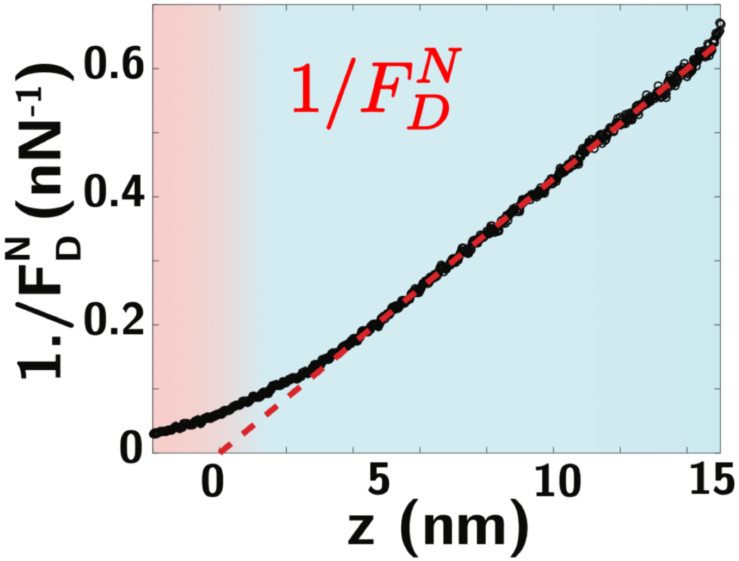
- Normal Interactions
- Frictional Interactions



2.2 Shear Thickening

Normal force profile

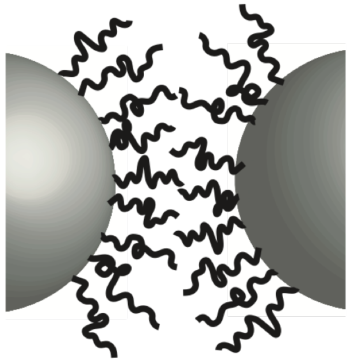




$$\frac{\partial F_N}{\partial z} \approx \exp(-z/\lambda)$$

$$\lambda \approx 4\ \mathrm{nm}$$

Entropic repulsion



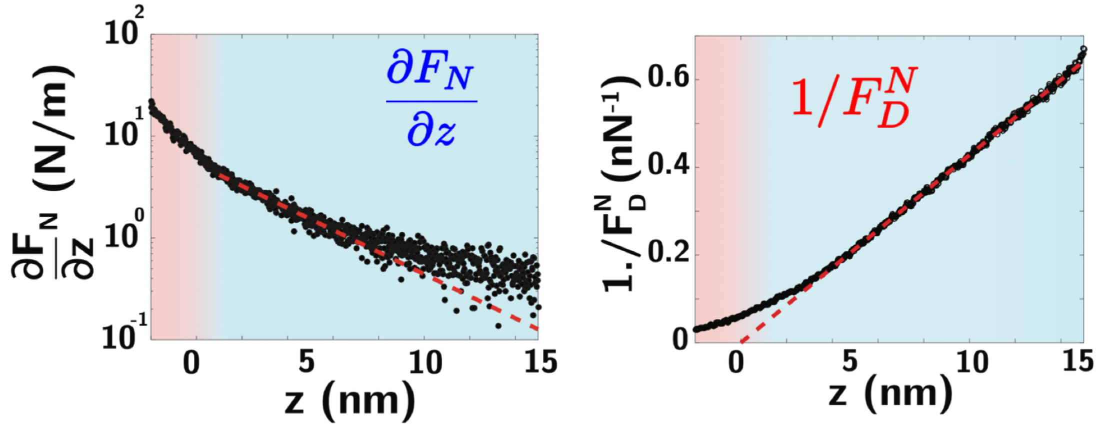
$$F_D^N \approx \frac{\eta R^2 v}{z}$$

Stockes lubrification

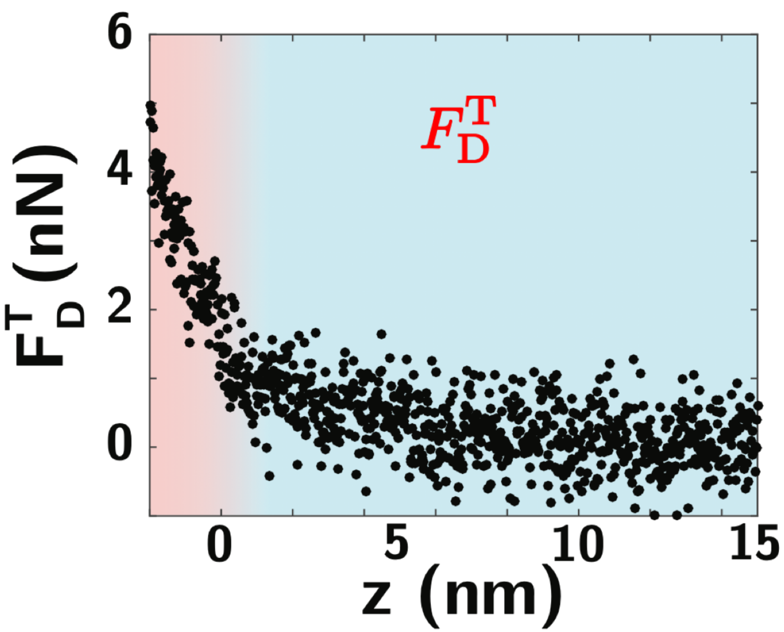
2.2 Shear Thickening

Tangential frictional profile

Normal Force Profile

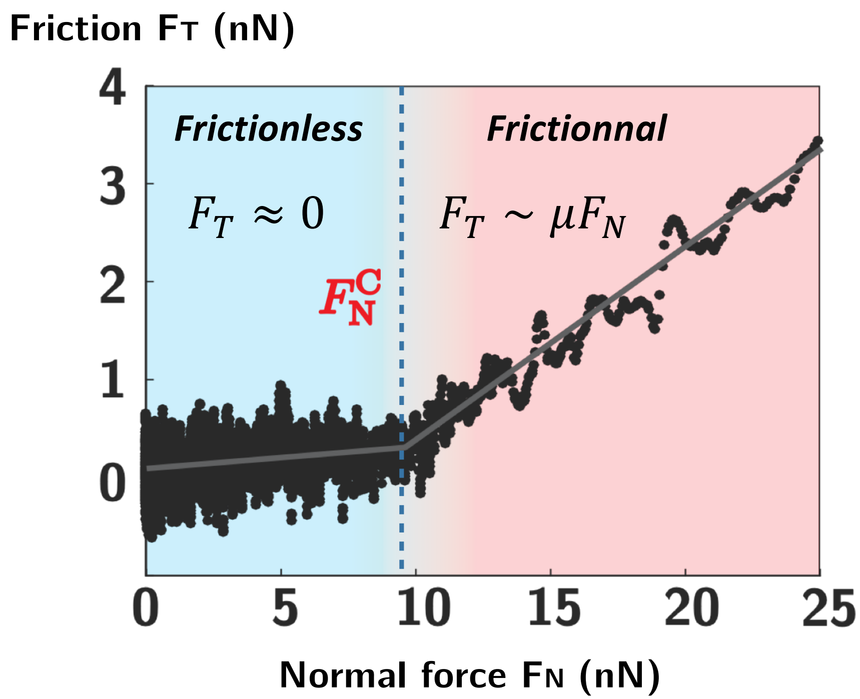


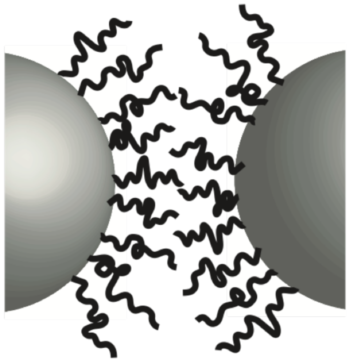
Tangential Frictional Profile



2.2 Shear Thickening

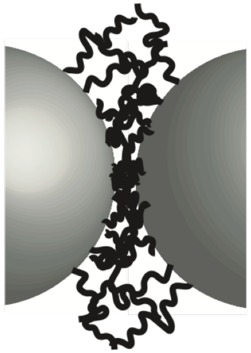
Threshold in the frictional behavior





$F_N < F_N^C$

Low Friction
(*hydrodynamics*)
μ ≈ 0



$F_N > F_N^C$

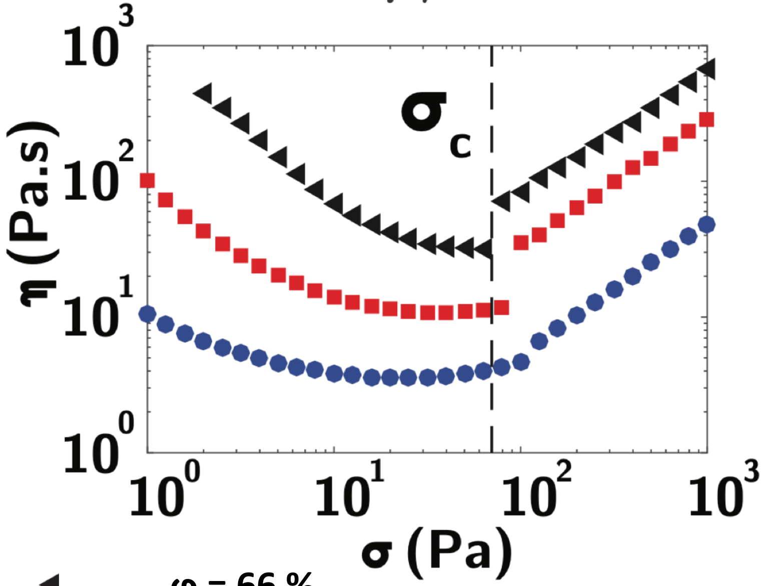
High Friction
(*solide-like*)
μ ≈ 0.45

2.2 Shear Thickening

Relationship with the shear-thickening transition

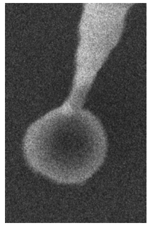
Macroscale hydrodynamic stress

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



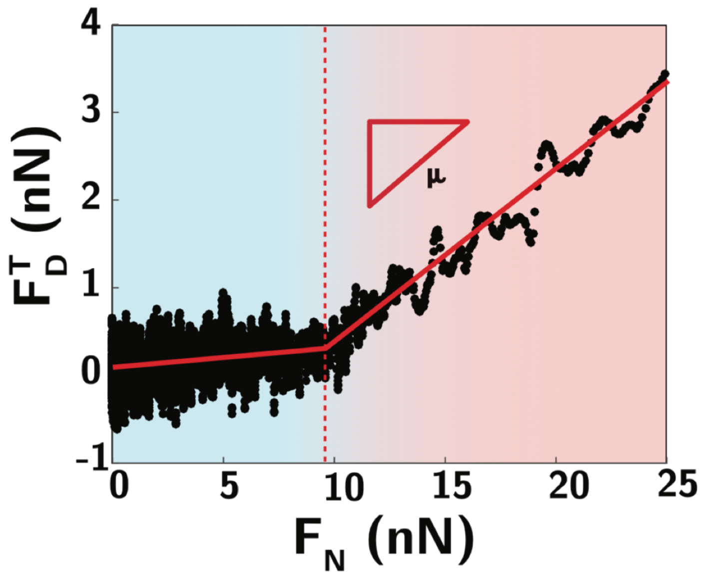
◀ φ = 66 %
■ φ = 64 % φc = 69 %
● φ = 60 %

M. Cates, J. Morris, M. Wyart, M. Denn

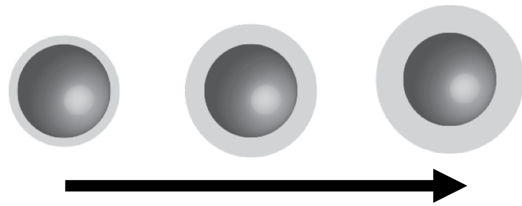


Nanoscale critical force

$$P_C = \frac{F_N^C}{\pi R^2}$$



$$P \sim \sigma$$

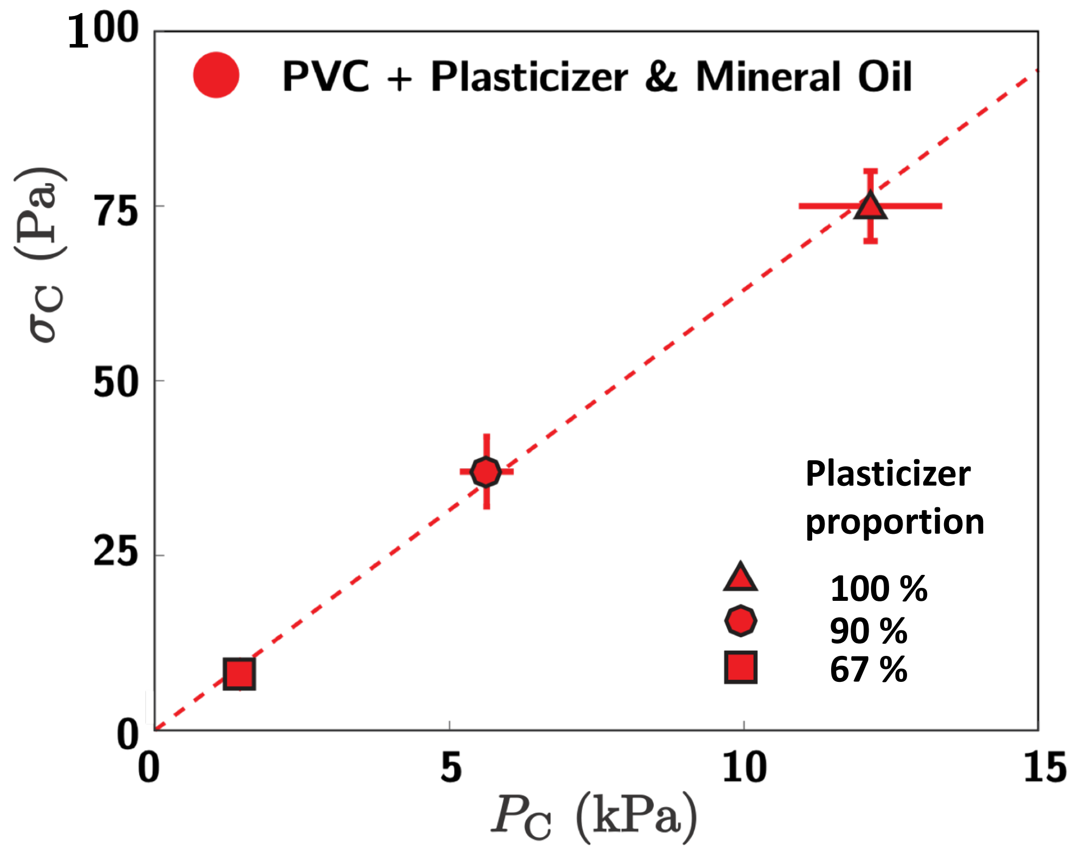


increasing plasticizer concentration

2.2 Shear Thickening

From micro to macro

Critical *Macroscale* Shear Stress



Critical *Nanoscale* Pressure

$$\sigma_C \approx \alpha \cdot P_C$$

$$\alpha_{PVC} = 0.006$$
$$\alpha_{th} = 0.05$$

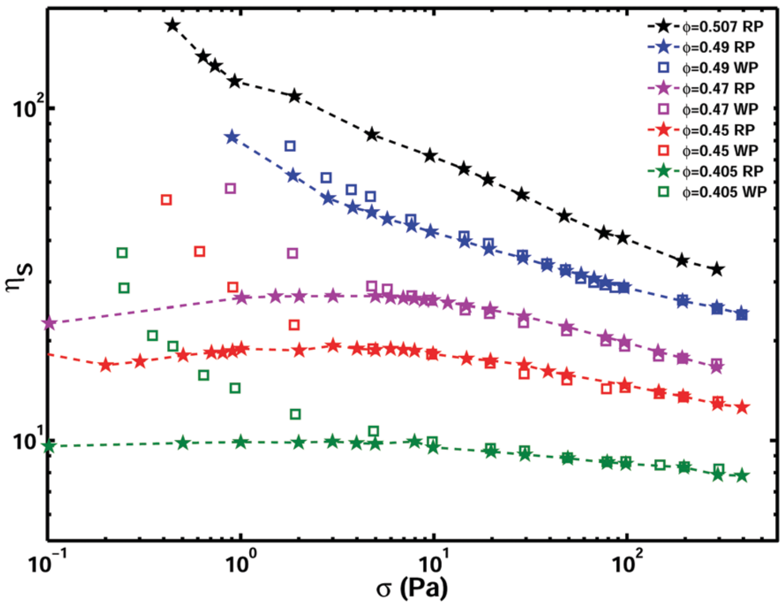
Mari et al., JoR 2014

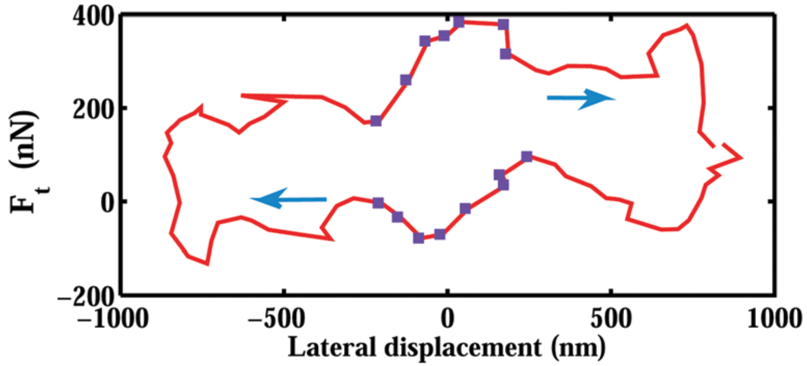
Discontinuous Shear Thickening involves stress-induced transition from lubricated to frictional contacts between particles

1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Shear Thickening
    2. Contact Aging
    3. **Shear Thinning**
    4. Roughness and Friction
3. **Opening and conclusions**

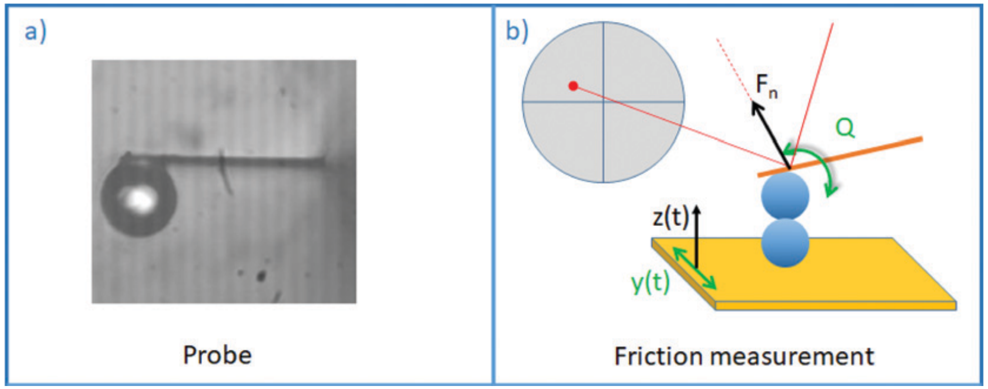
2.3 Shear Thinning

Polystyrene particles in water showing shear thinning rheology





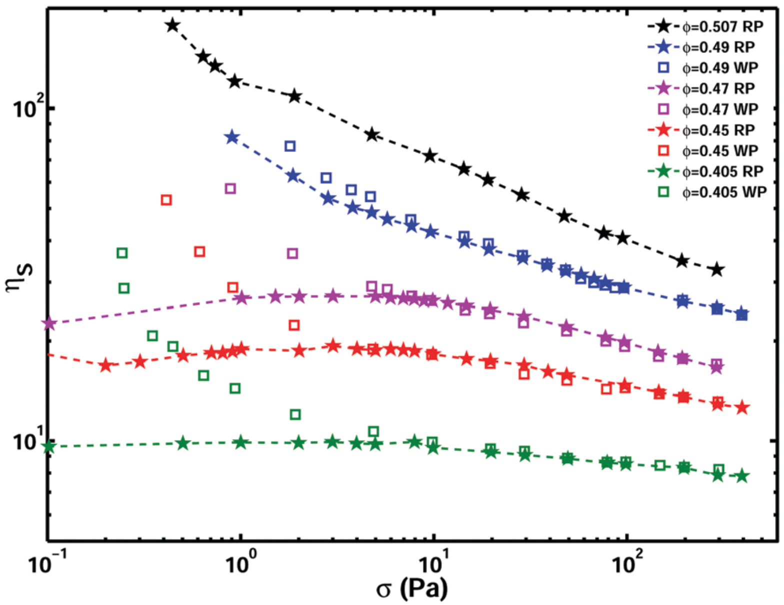
AFM measurements

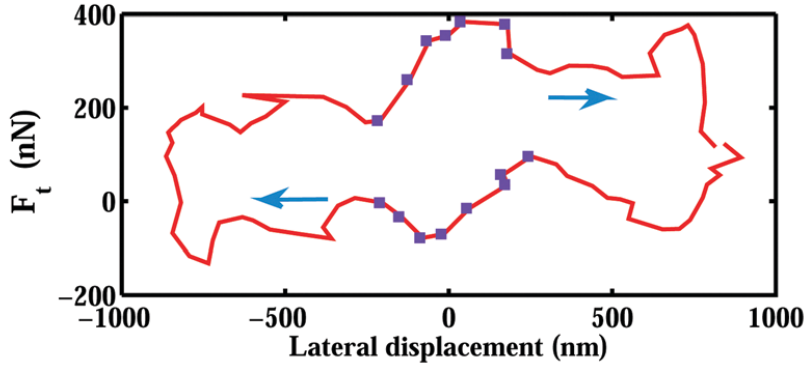


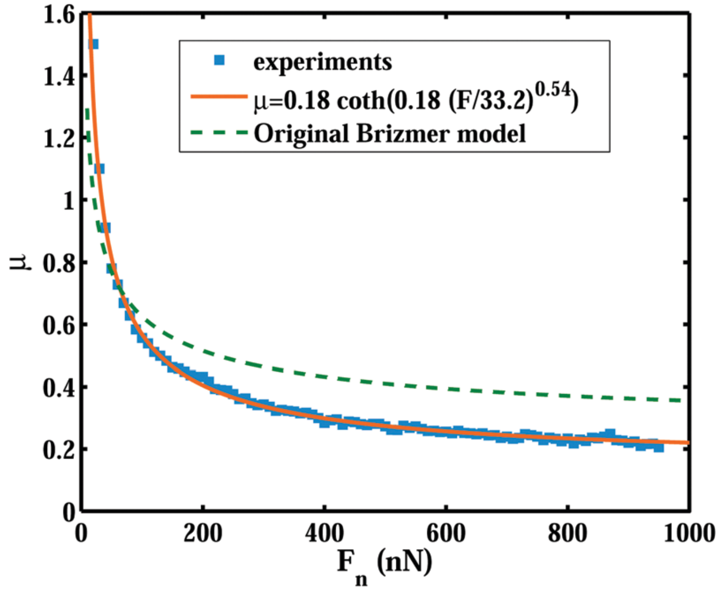
Arshad, M., Maali, A., Claudet, C., Lobry, L., Peters, F., & Lemaire, E. (2021). An experimental study on the role of inter-particle friction in the shear-thinning behavior of non-Brownian suspensions. *Soft Matter*, *17*(25), 6088-6097.

2.3 Shear Thinning

Polystyrene particles in water showing shear thinning rheology



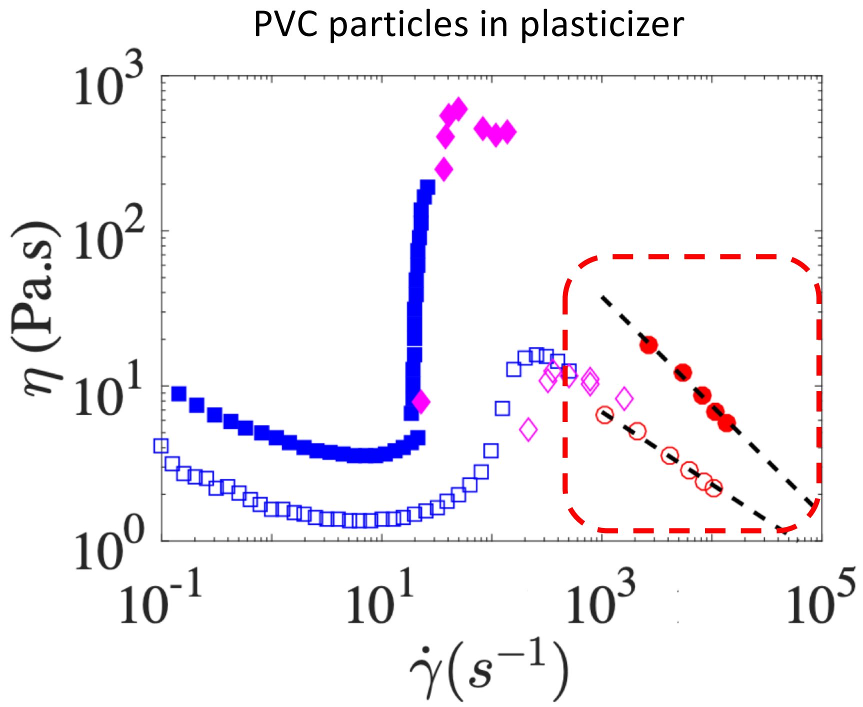


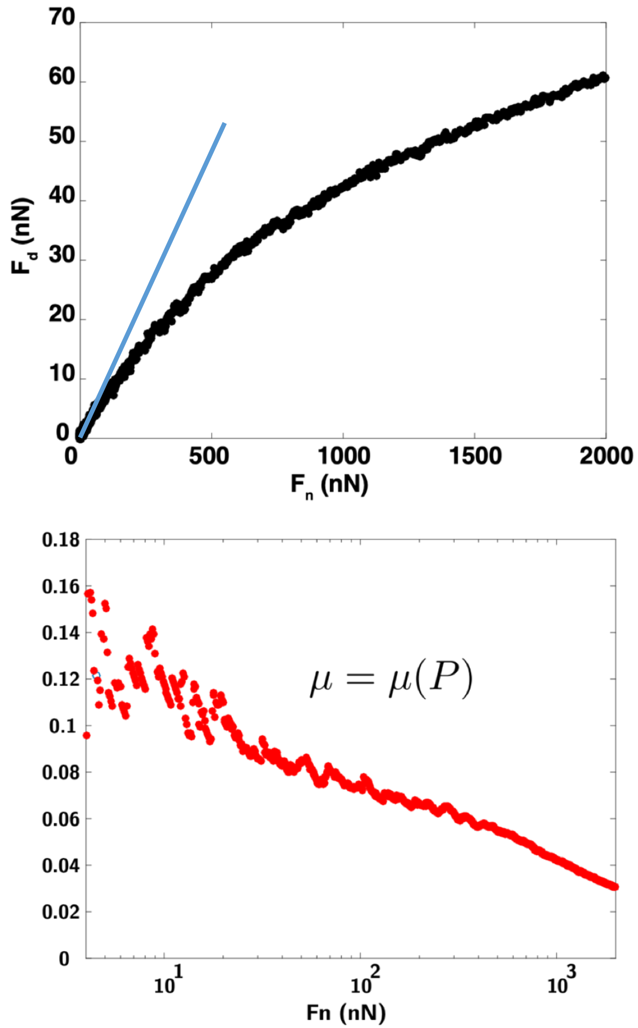


Decrease of the friction coefficient with load

Arshad, M., Maali, A., Claudet, C., Lobry, L., Peters, F., & Lemaire, E. (2021). An experimental study on the role of inter-particle friction in the shear-thinning behavior of non-Brownian suspensions. *Soft Matter*, *17*(25), 6088-6097.

2.3 Shear Thinning





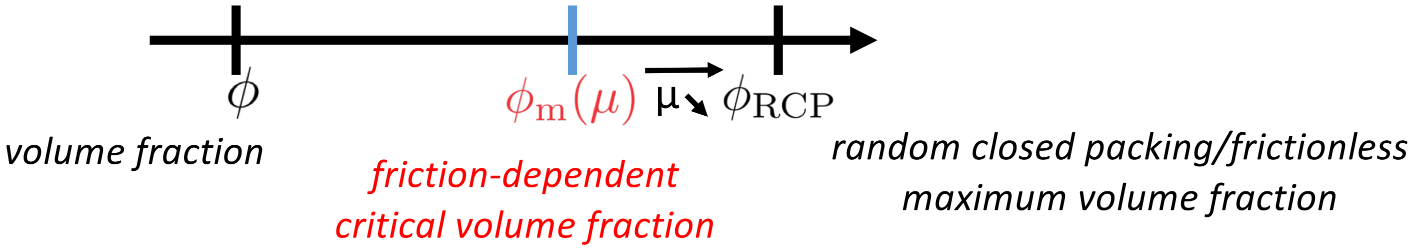
Decrease of the friction coefficient with load

Chatté, G., Comtet, J., Nigues, A., Bocquet, L., Siria, A., Ducouret, G., ... & Colin, A. (2018). Shear thinning in non-Brownian suspensions. *Soft matter*, *14*(6), 879-893.

2.3 Shear Thinning

$$\frac{\eta}{\eta_s} = \left(\frac{1}{1-\phi/\phi_m(\mu)}\right)^n$$

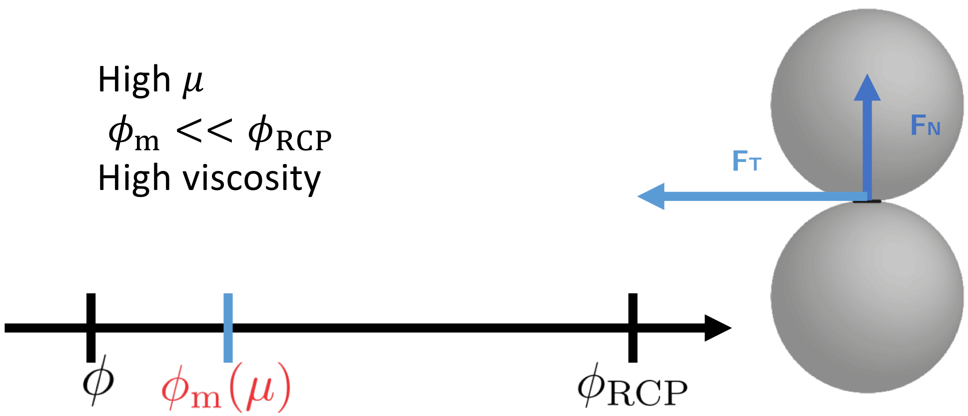
Interpretation



$\phi_m(\mu)$ increases when μ decreases

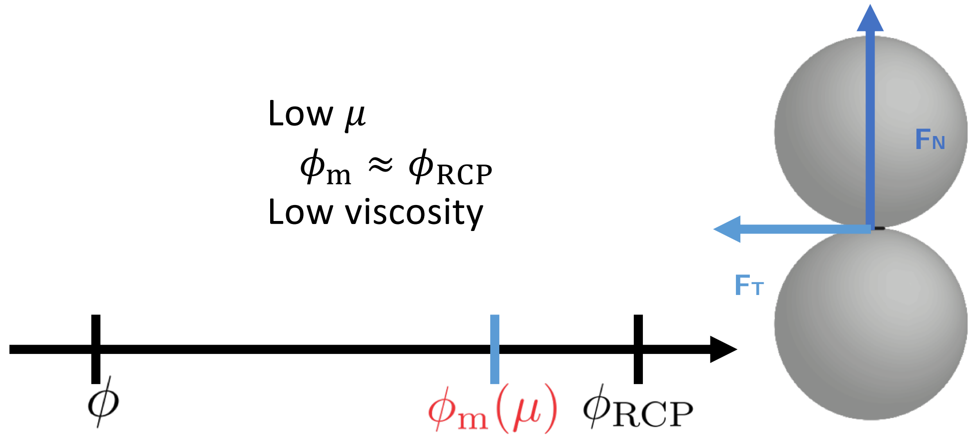
Intermediate pressure/shear rate

High μ
$\phi_m << \phi_{RCP}$
High viscosity



Large pressure/shear rate

Low μ
$\phi_m \approx \phi_{RCP}$
Low viscosity



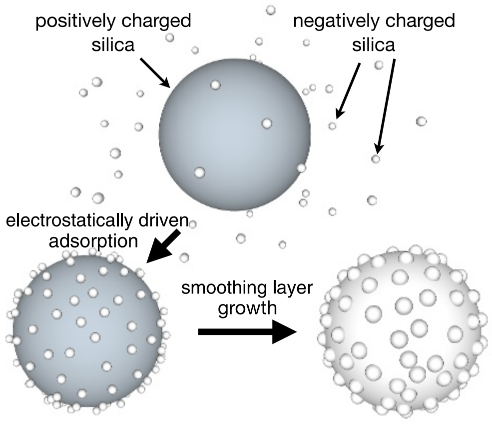
General Outline

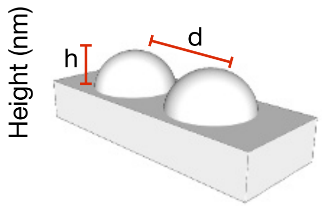
1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Shear Thickening
    2. Contact Aging
    3. Shear Thinning
    4. **Roughness and Friction**
3. **Opening and conclusions**

2.4 Roughness and Friction

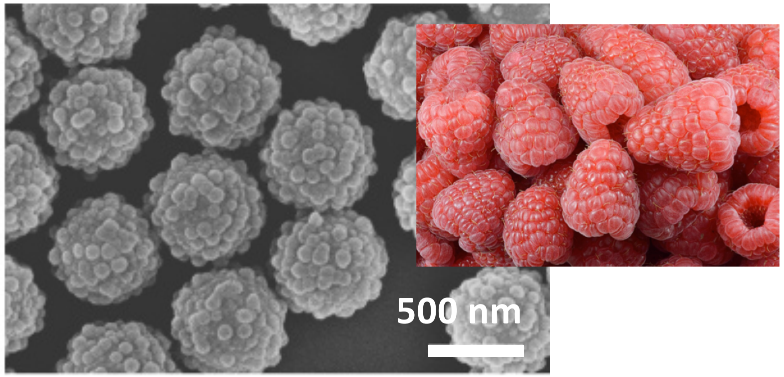
Controlling colloidal roughness

Controlling colloidal roughness

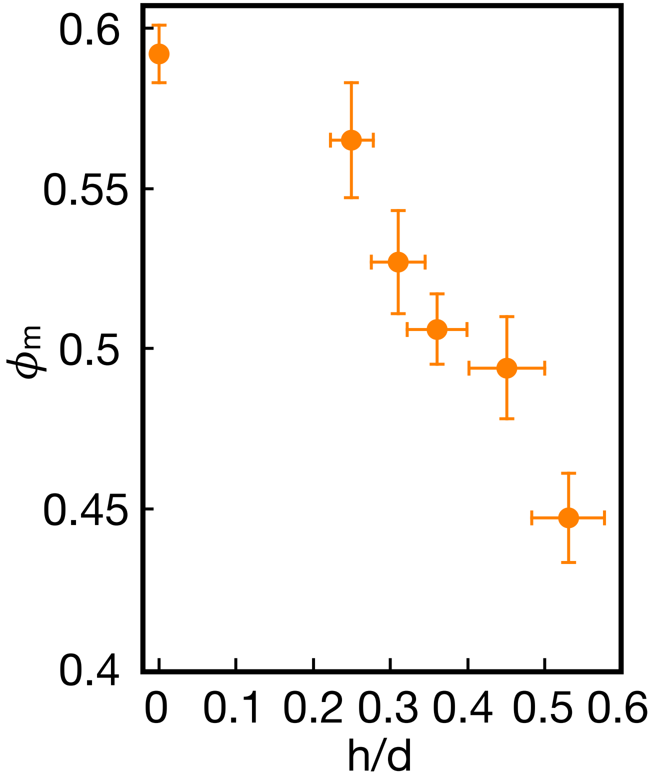




raspberry-like colloids



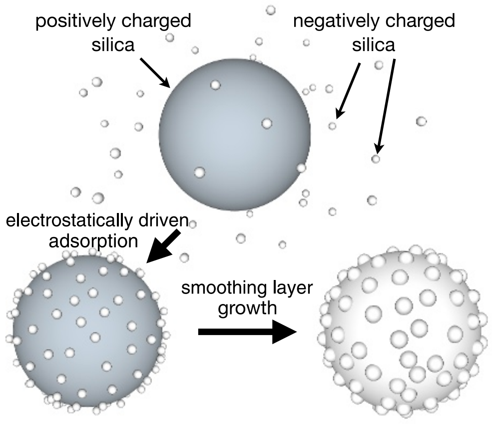
Roughness affects the maximum packing fraction

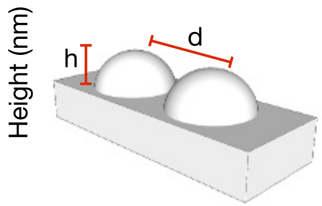


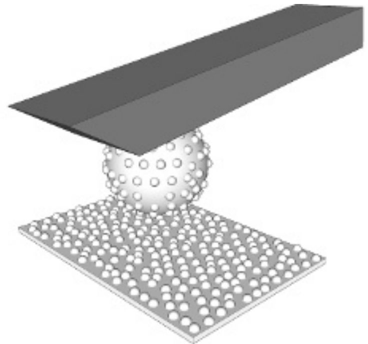
Hsu, C. P., Ramakrishna, S. N., Zanini, M., Spencer, N. D., & Isa, L. (2018). Roughness-dependent tribology effects on discontinuous shear thickening. *Proceedings of the National Academy of Sciences*, *115*(20), 5117-5122.

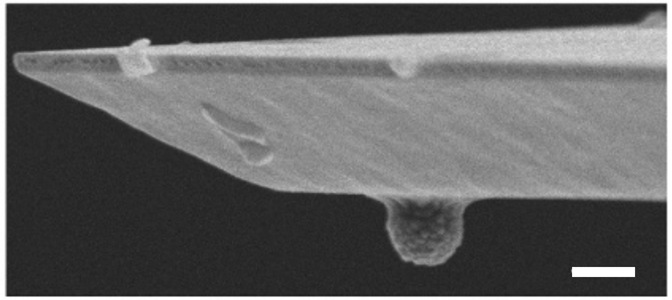
2.4 Roughness and Friction

Controlling colloidal roughness

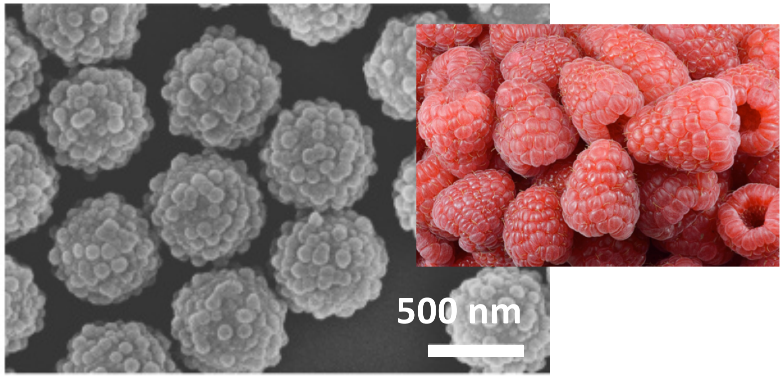




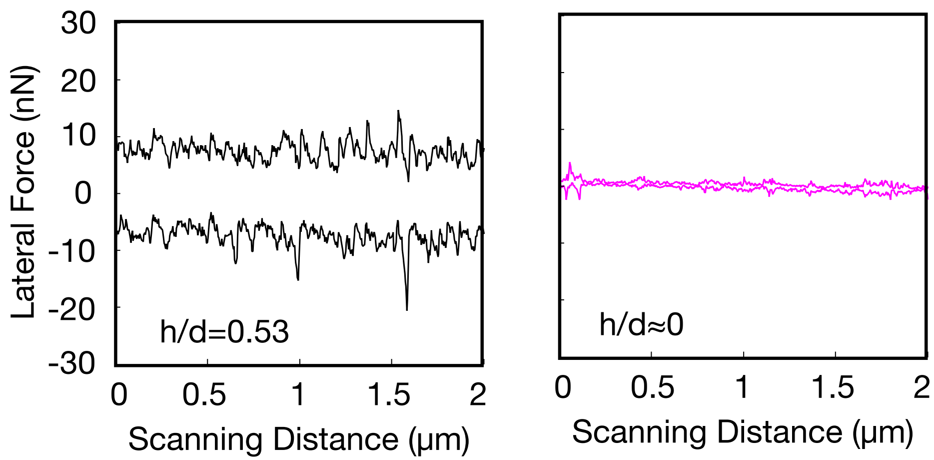




raspberry-like colloids



Roughness affects friction

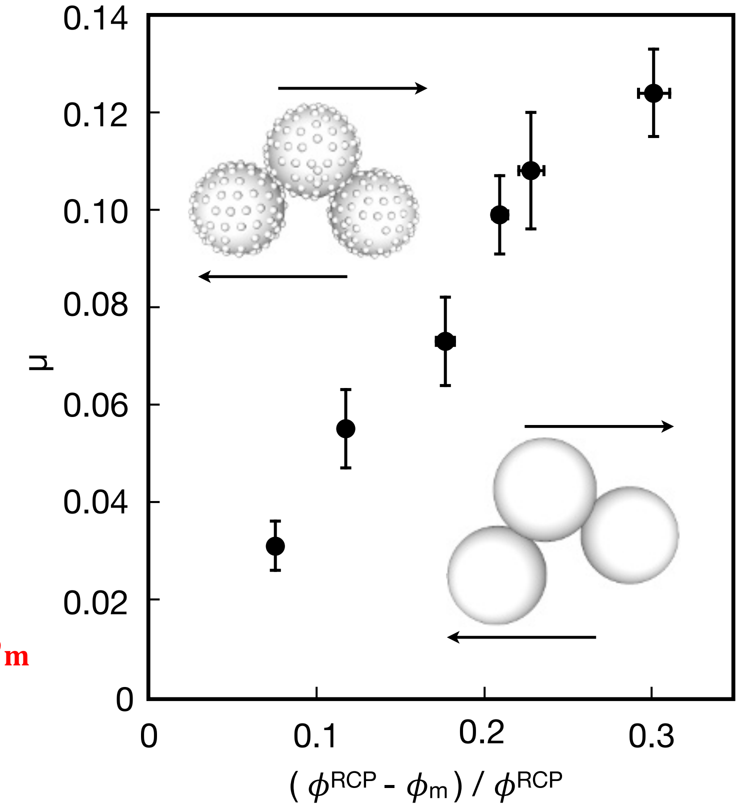


Hsu, C. P., Ramakrishna, S. N., Zanini, M., Spencer, N. D., & Isa, L. (2018). Roughness-dependent tribology effects on discontinuous shear thickening. *Proceedings of the National Academy of Sciences*, *115*(20), 5117-5122.

2.4 Roughness and Friction

Correlating friction coefficient μ and the critical volume fraction ϕ_m

High friction/Low ϕ_m

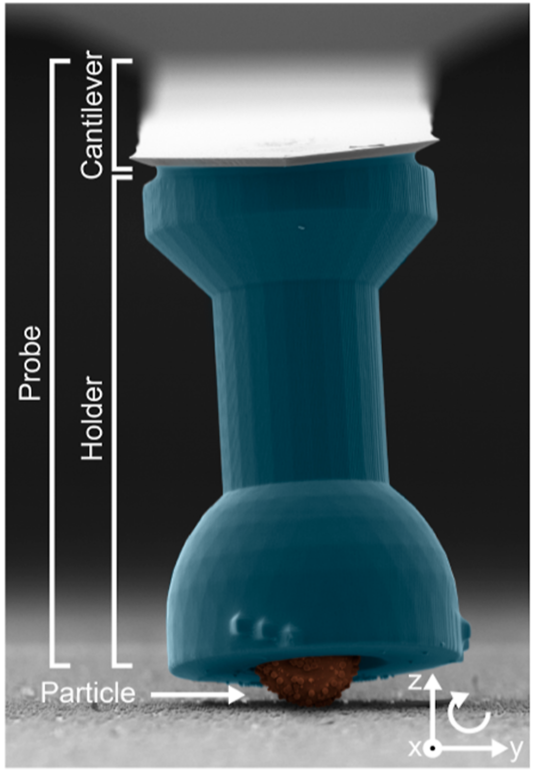


Low friction/high ϕ_m

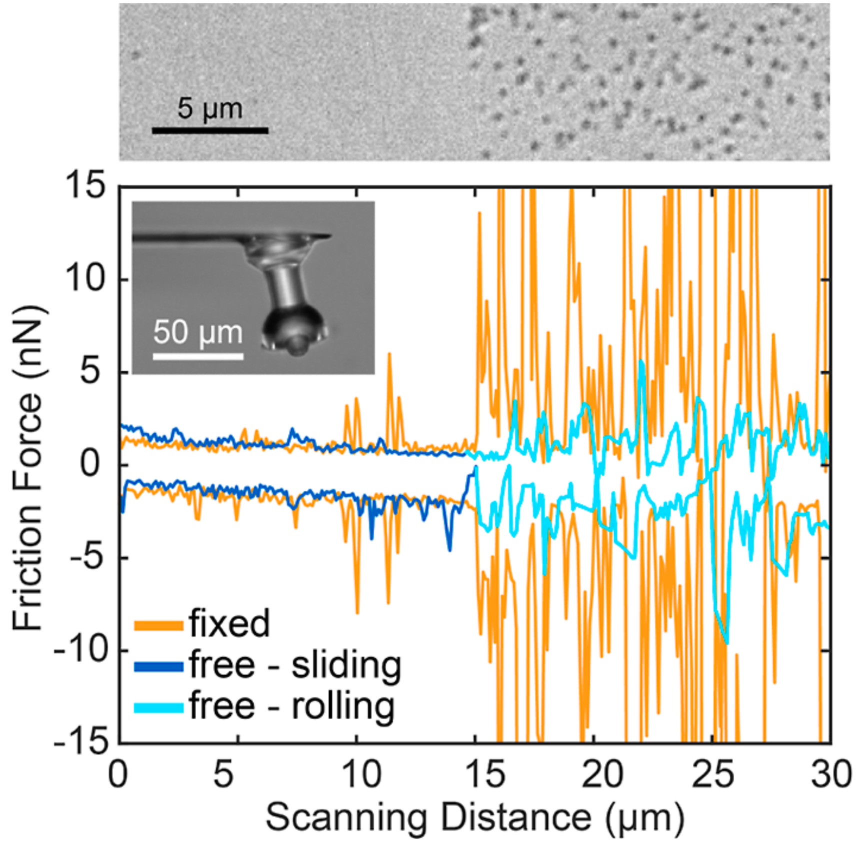
Hsu, C. P., Ramakrishna, S. N., Zanini, M., Spencer, N. D., & Isa, L. (2018). Roughness-dependent tribology effects on discontinuous shear thickening. *Proceedings of the National Academy of Sciences*, *115*(20), 5117-5122.

1. **Surface forces and friction – General Concepts**
    1. Surface Forces
    2. Friction
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Shear Thickening
    2. Contact Aging
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

3. Opening – Rolling Friction



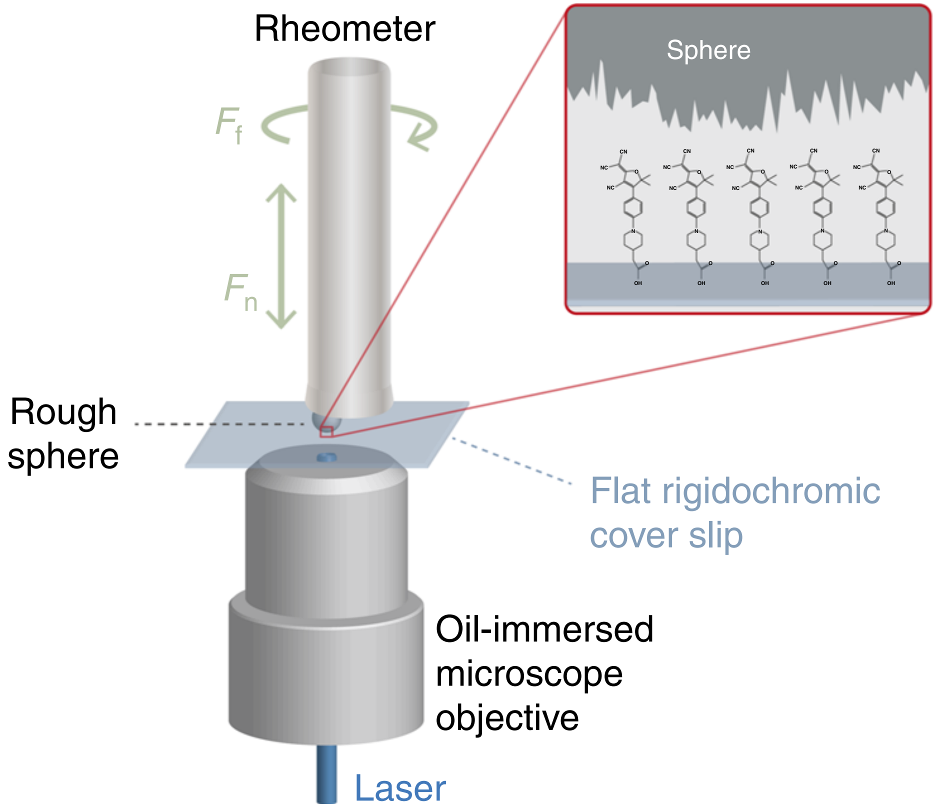
Particle free to rotate

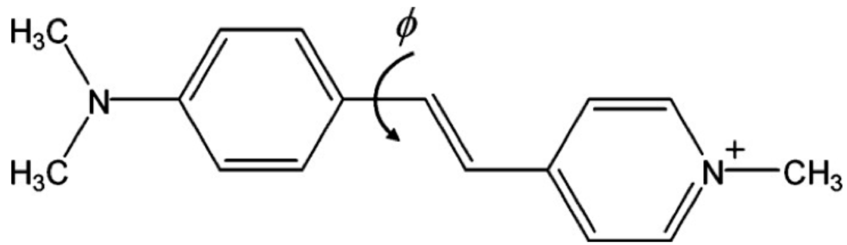


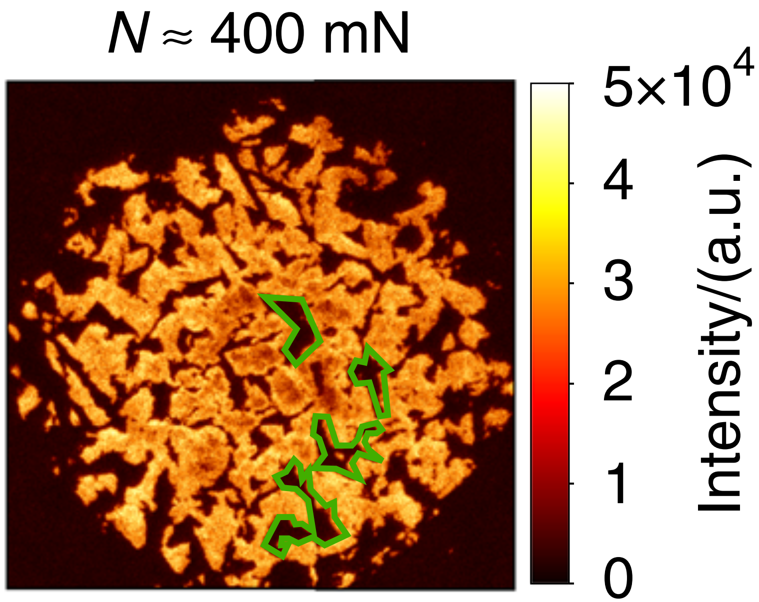
Scherrer, S., Ramakrishna, S. N., Niggel, V., Spencer, N. D., & Isa, L. (2024). **Measuring Rolling Friction at the Nanoscale.** *Langmuir*, *40*(13), 6750-6760.

3. Opening – Watching contacts?

« Rigidochromic molecule »　　Confinement/contact sensor







Weber, B., Suhina, T., Junge, T., Pastewka, L., Brouwer, A. M., & Bonn, D. (2018). Molecular probes reveal deviations from Amontons' law in multi-asperity frictional contacts. *Nature communications*, *9*(1), 888.

Conclusion

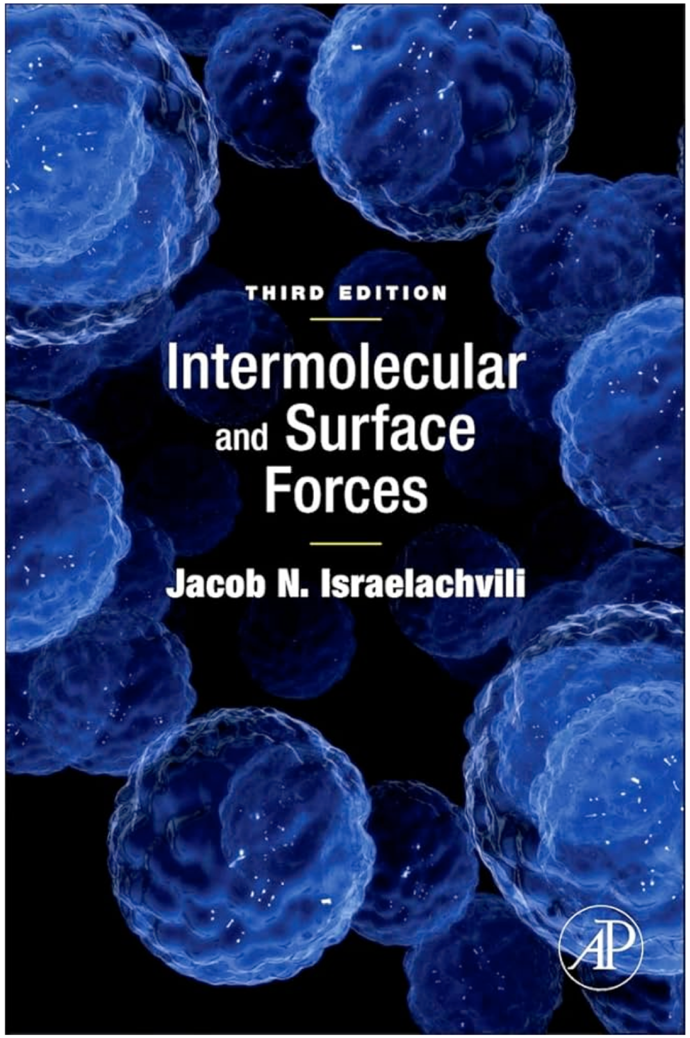
1. **Surface forces and friction – General Concepts**
    1. Surface forces
    2. Frictional forces
    3. Measuring interaction forces at the nanoscale
2. **Microscale measurements in suspensions and relations with macroscopic rheology**
    1. Shear Thickening
    2. Contact Aging
    3. Shear Thinning
    4. Roughness and Friction
3. **Opening and conclusions**

Bibliography

Israelachvili, J. N. (2011). Intermolecular and surface forces. Academic press.

Persson, B. N. (2013). *Sliding friction: physical principles and applications*. Springer Science & Business Media.

Baumberger, T., & Caroli, C. (2006). Solid friction from stick–slip down to pinning and aging. *Advances in Physics*, *55*(3-4), 279-348.



Acknowledgments to Nicolas Sanson (SIMM, ESPCI)