Relevance of time-dependent particle interactions in the physical aging of colloidal suspensions

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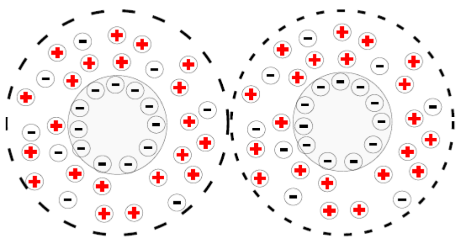
Context

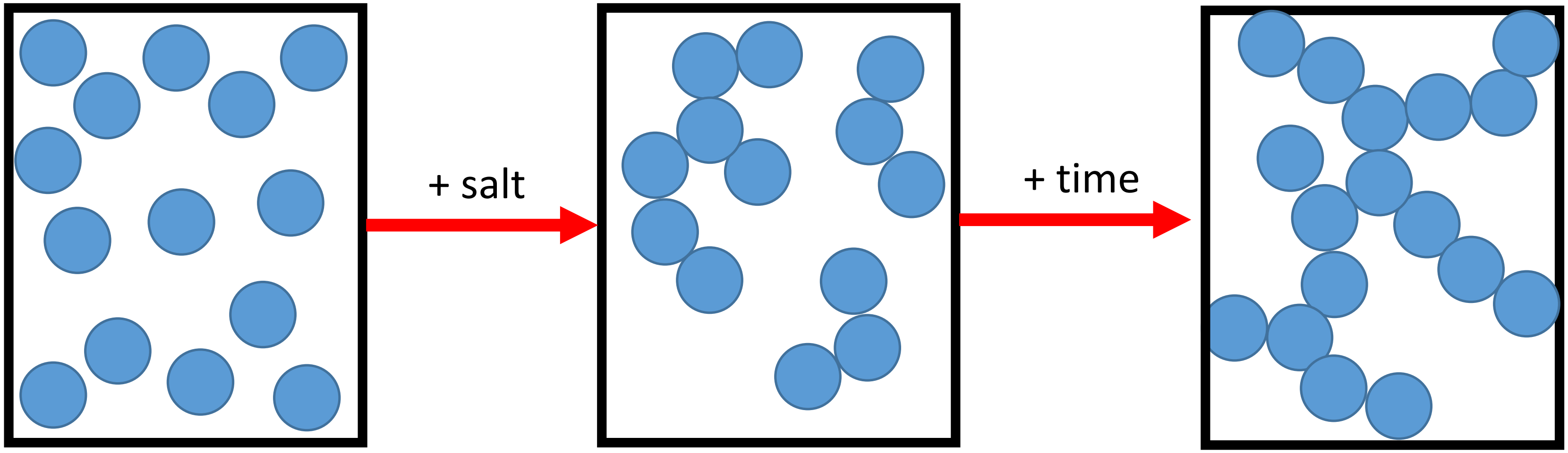
- **Rheology of colloidal suspensions:**

Colloids = thermal motion (Brownian)
+
Inter-particle interactions

DLVO potential
- Van der Waals (attraction)
- Electrostatic (repulsion)



Tuning particle interactions



Stable
Liquid like

Unstable
(flocculated)

Percolated
Solid-like

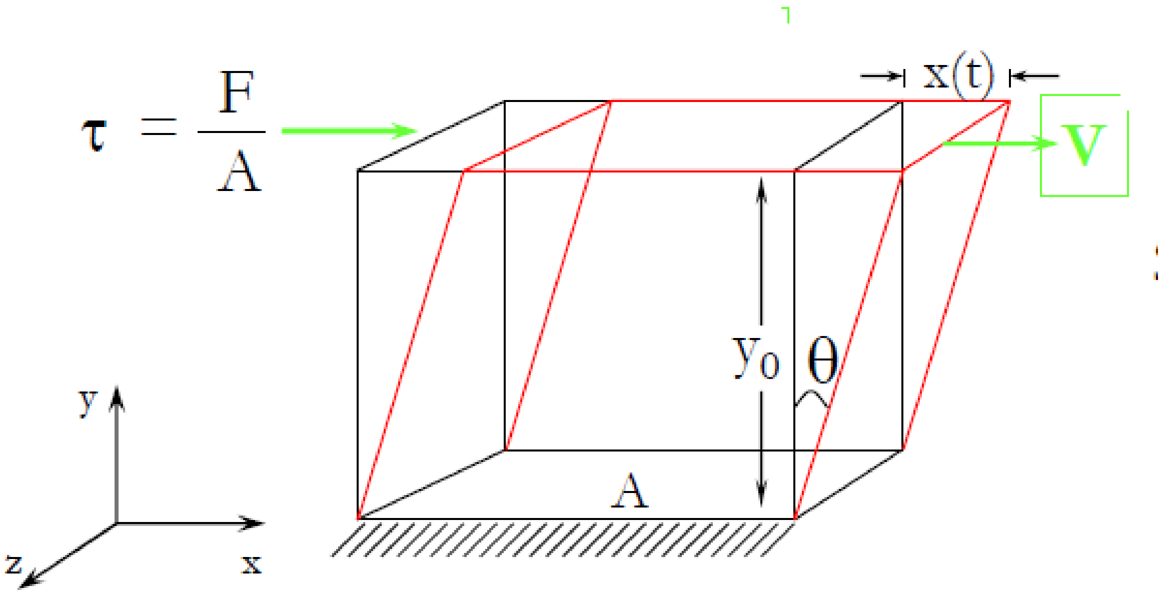
Context

- **Rheology of colloidal suspensions:**

Shear Deformation

$$\text{Strain, } \gamma = \frac{x(t)}{y_0}$$

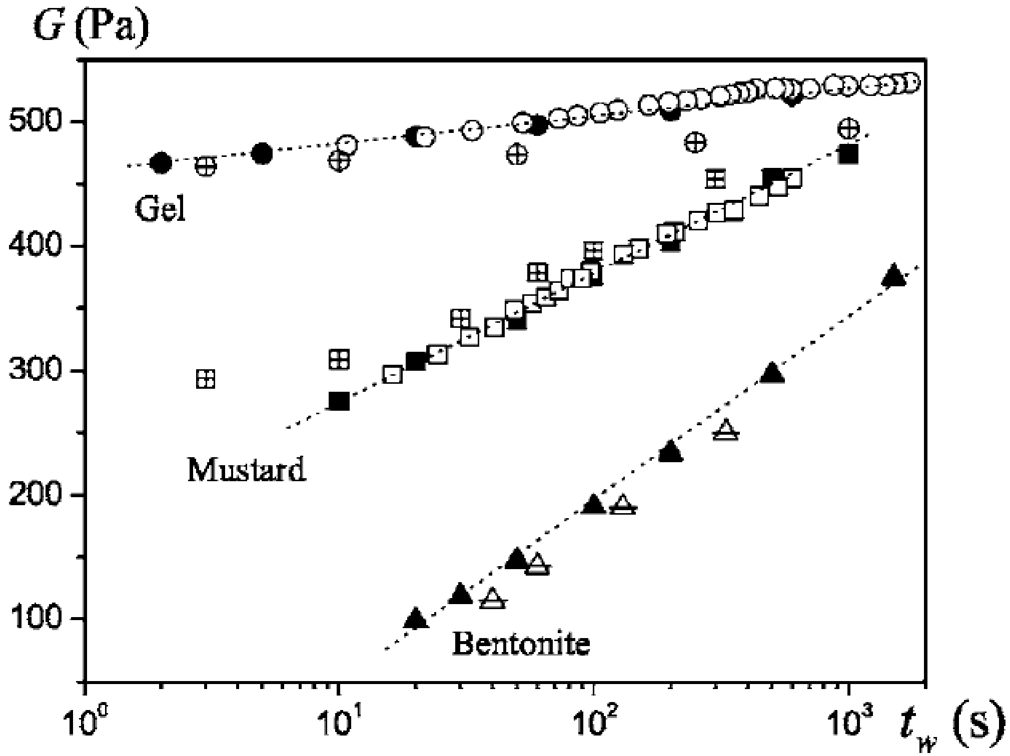
$$\tau = \frac{F}{A}$$



$$\textbf{Shear Modulus, G} = \frac{\tau}{\gamma}$$

Aging in soft glassy materials (SGMs)

- Aging: evolution of the mechanical properties with resting time
- It affects the elastic moduli of colloidal suspensions



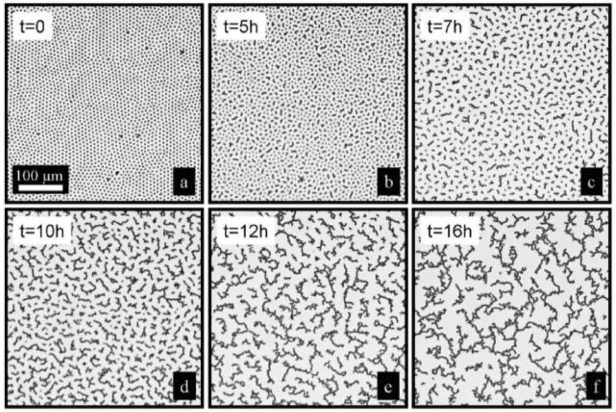
Coussot, P., Tabuteau, H., Chateau, X., Tocquer, L., & Ovarlez, G. (2006). Aging and solid or liquid behavior in pastes, 975–994.

It is crucial to understand aging in view of technological applications

Aging, open questions

Study on diluted systems:

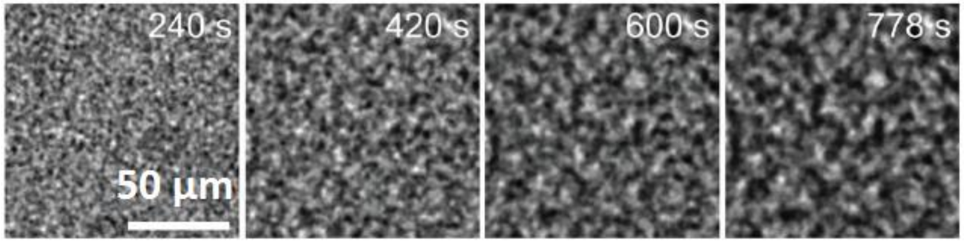
Aging ⟷ **Dynamics**



Masschaele, K., Fransaer, J., Vermant, J.,(2010) The Society of Rheology, *1437*.

Structural evolution towards equilibrium:

- Relaxation of internal stress
- "Micro-collapse"
- Thermal motion (hopping)
- Sedimentation



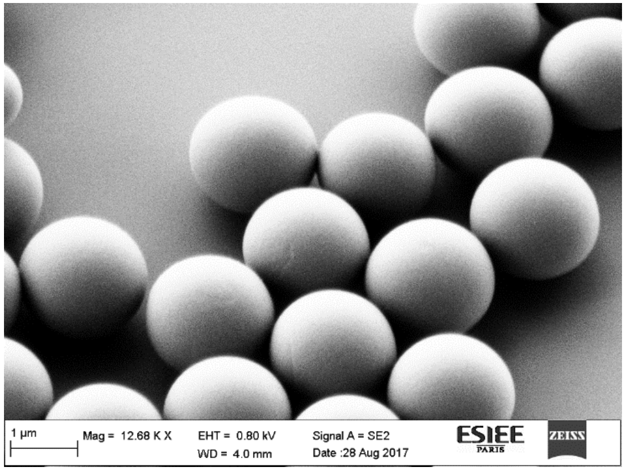
Gao, Y., Kim, J., & Helgeson, M. E. (2015) *Soft Matter.*

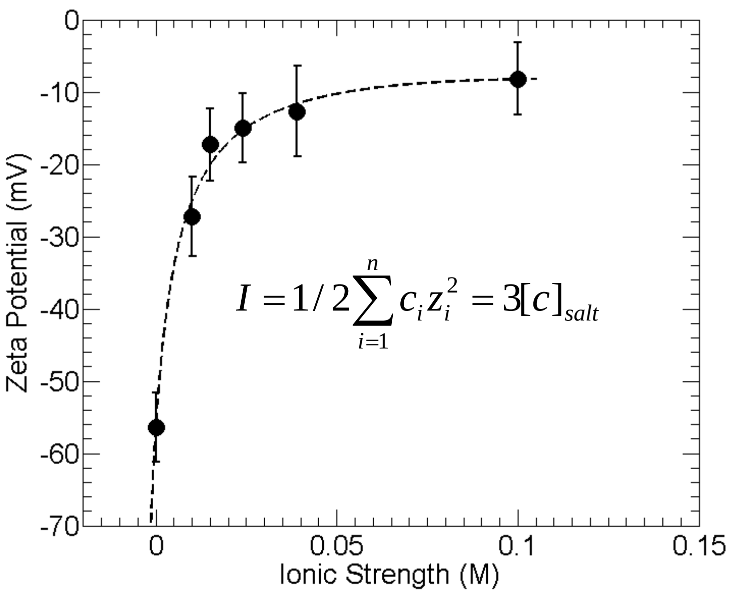
➢ Connection between structure, dynamics, and age remains unclear.

➢ No systematic study for micron-sized particles at higher volume fractions.

A "model" system

Stöber silica particles



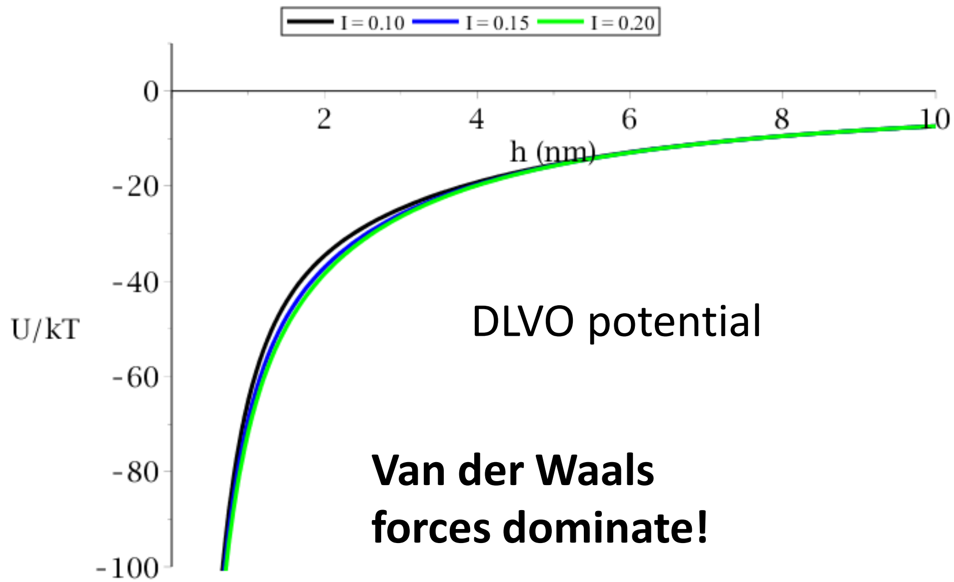


Dense aqueous suspensions with divalent salt

Parameters:

- Size d = 0,7-2 µm
- Volume fraction ϕ = 0.3 - 0.4
- Aging time t = 0 – 20 minutes
- Ionic strength $[CaCl_2]$ = 0,10-0,20 M

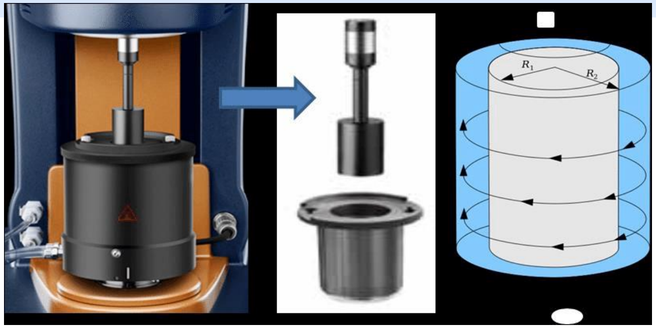
Rapid flocculation: no electrostatic barrier



Mechanical aging

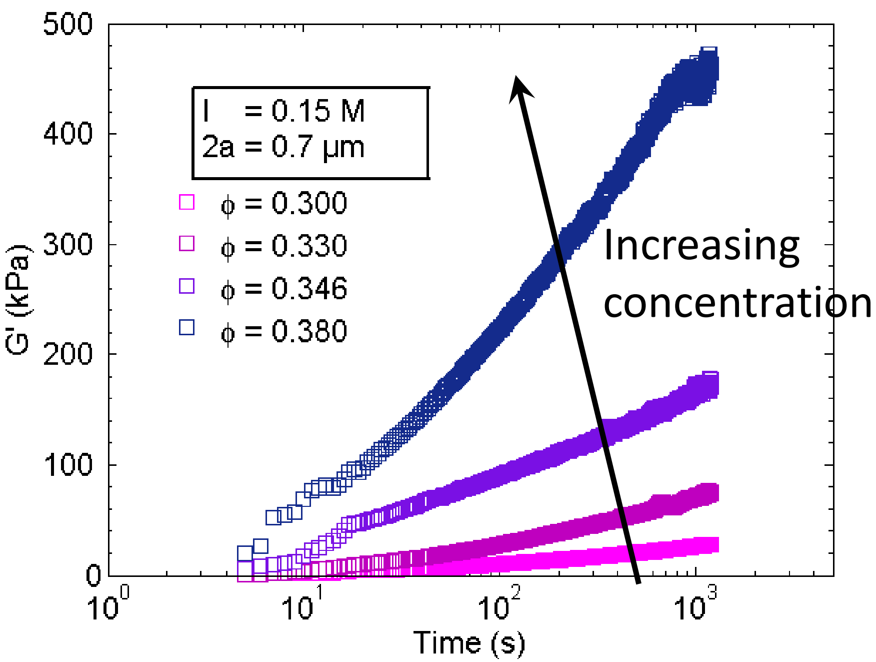
The system is rejuvenated by preshearing at 200 s^{-1}

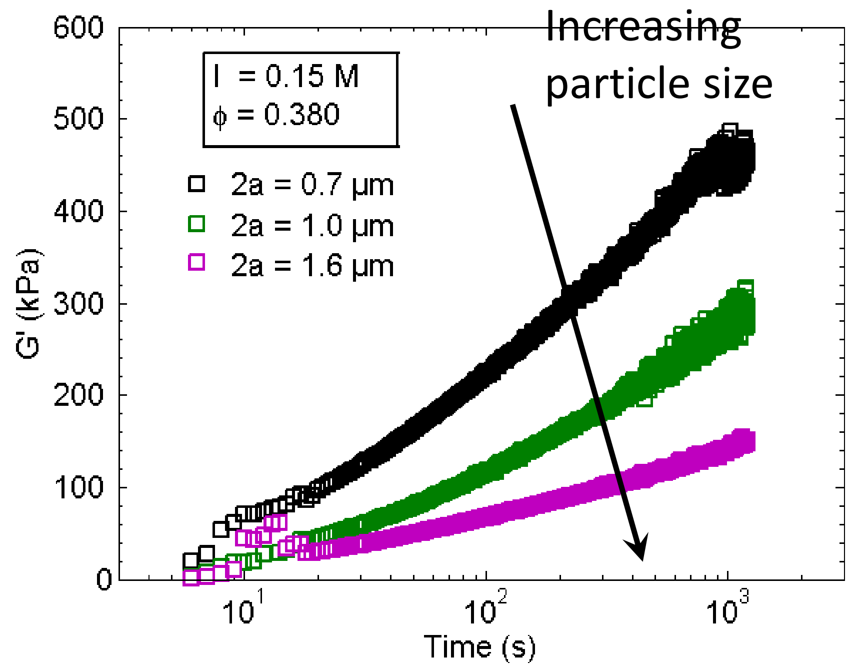
Initial reproducible state



$\gamma = 0{,}01\%$
f = 1 Hz

Couette geometry

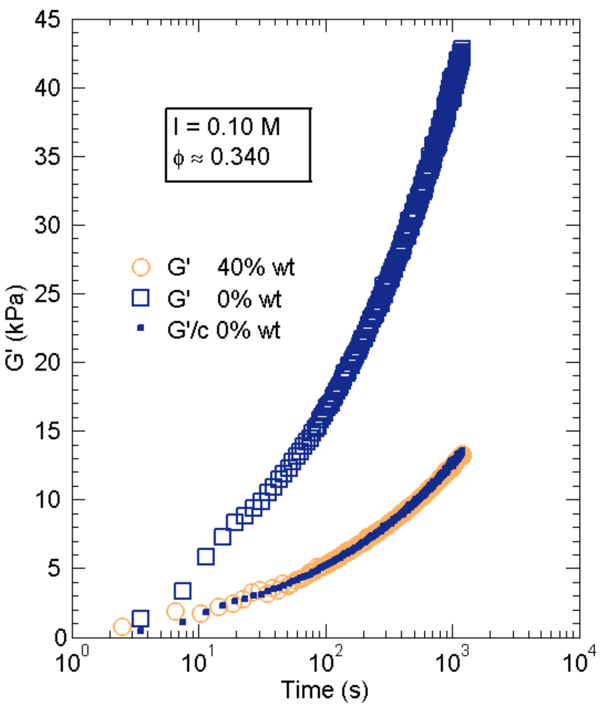


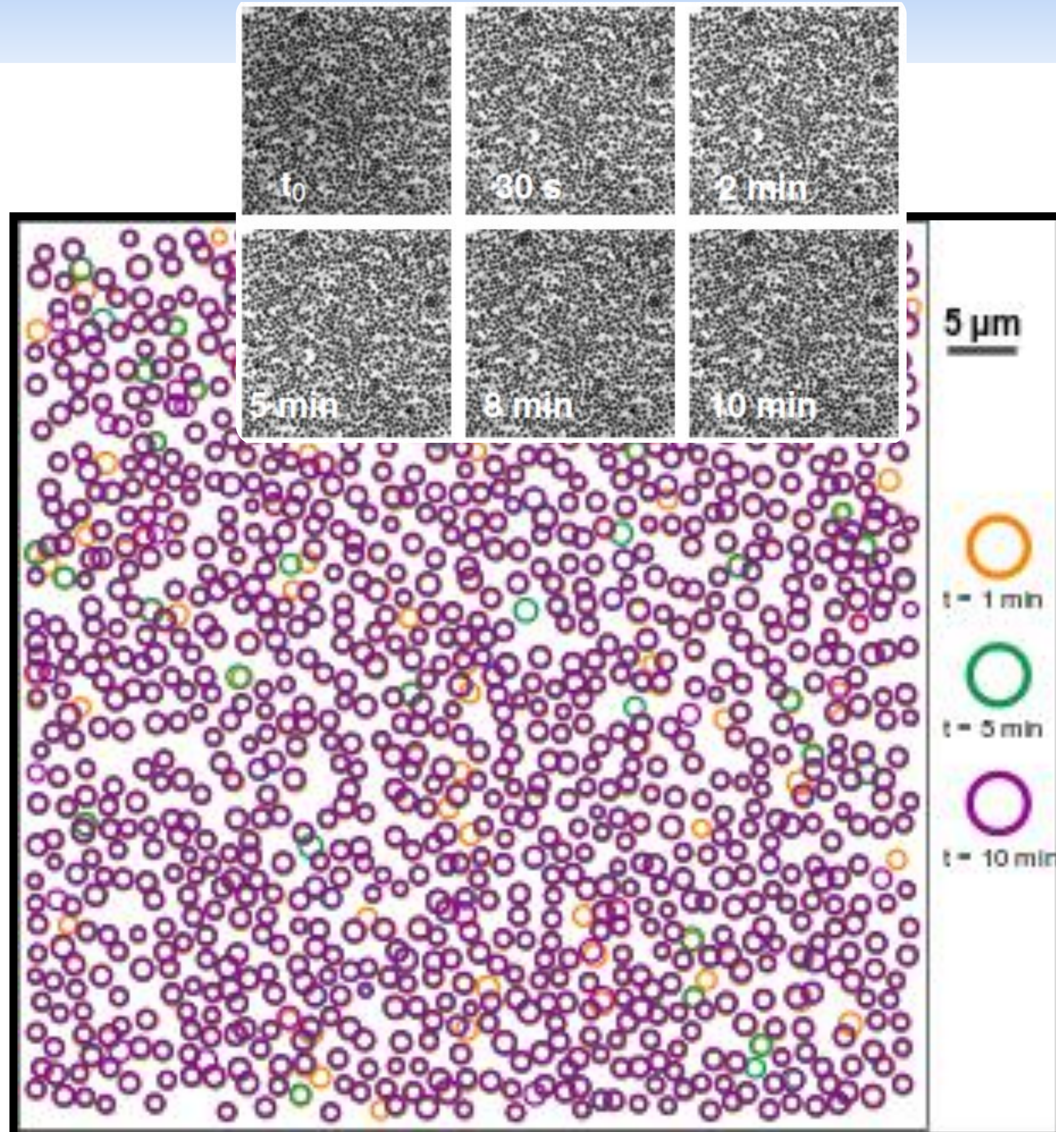


Dynamics

- **Confocal Microscopy**

ϕ = 0.39
I = 0.15 M
d = 1,6 μm
60/40% wt water/glycerol

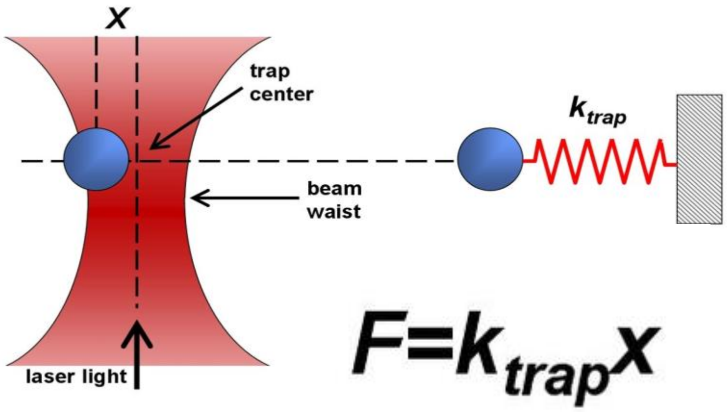




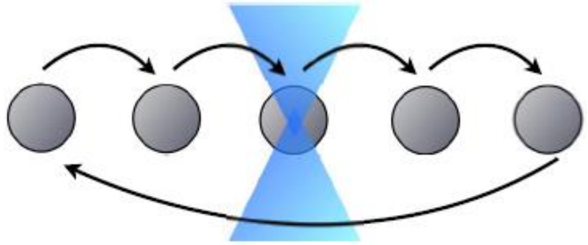
Sample reconstruction based on computed particle centers and radii (centroid algorithm)

Optical traps (OT)

Manipulation of multiple particles with Laser Tweezers

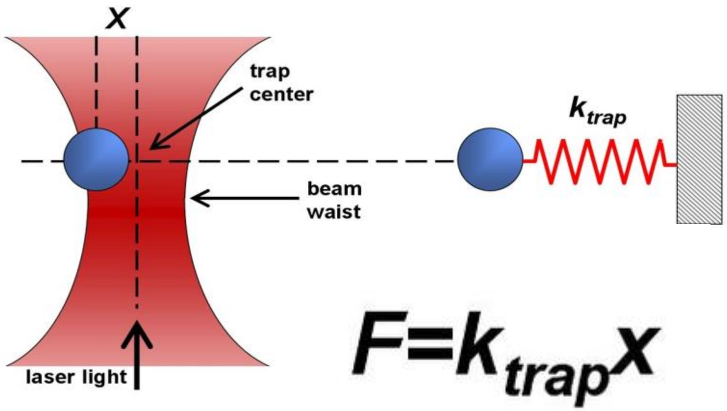


Time –shared optical trap

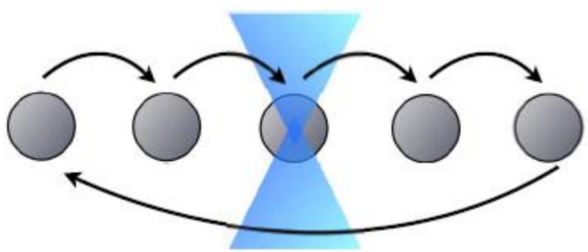


Micro-mechanics with OT

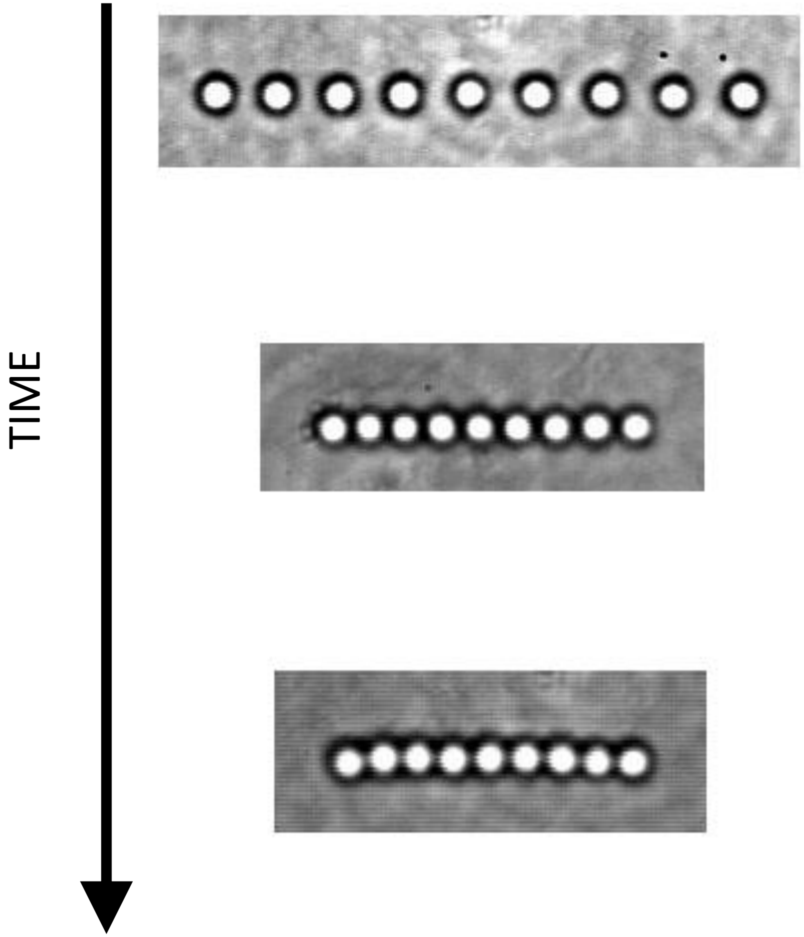
Manipulation of multiple particles with Laser Tweezers



Time –shared optical trap

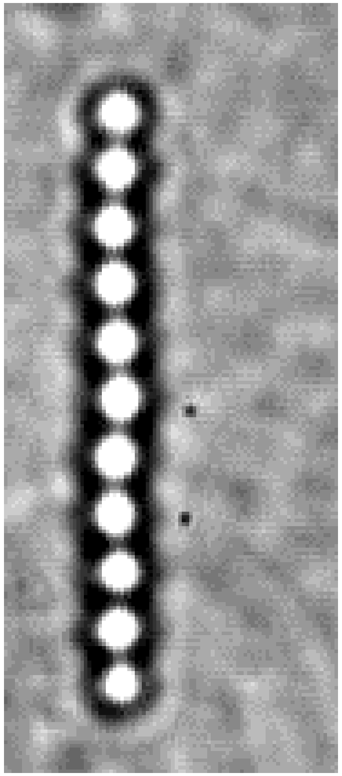


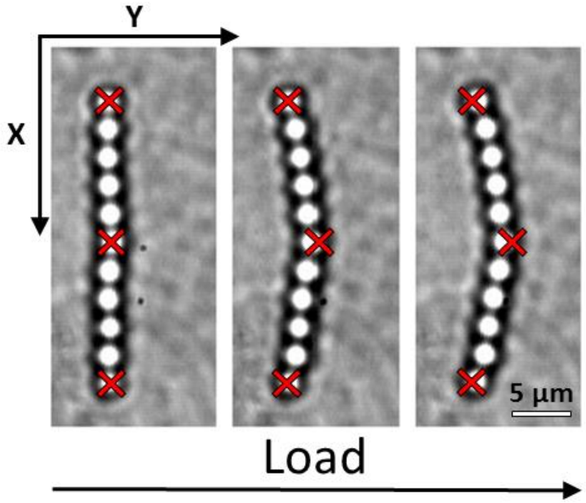
We formed linear aggregates composed by 11 and 13 particles



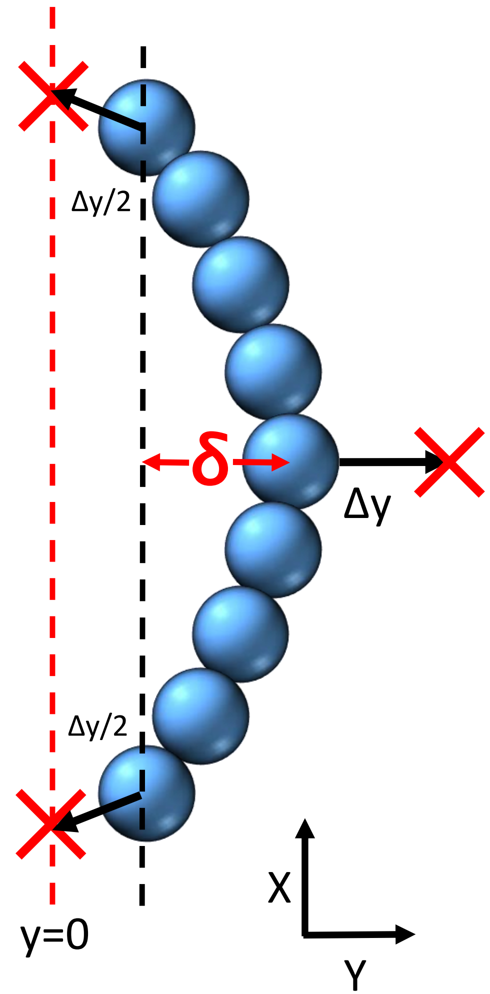
Three-point bending tests

Three-point bending tests with Laser Tweezers



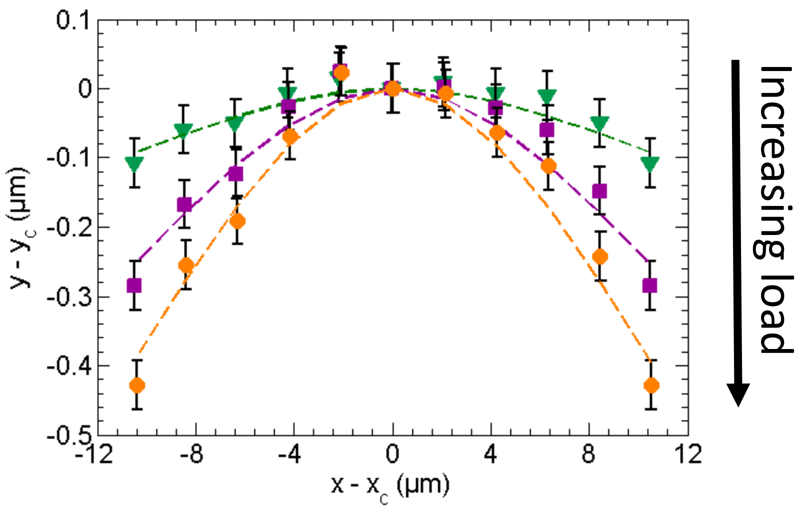


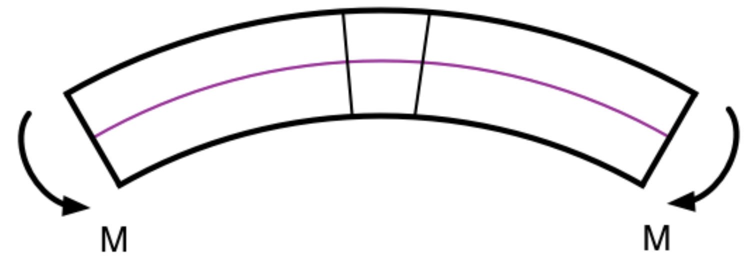
$$k_b = \frac{F_{bend}}{\delta}$$



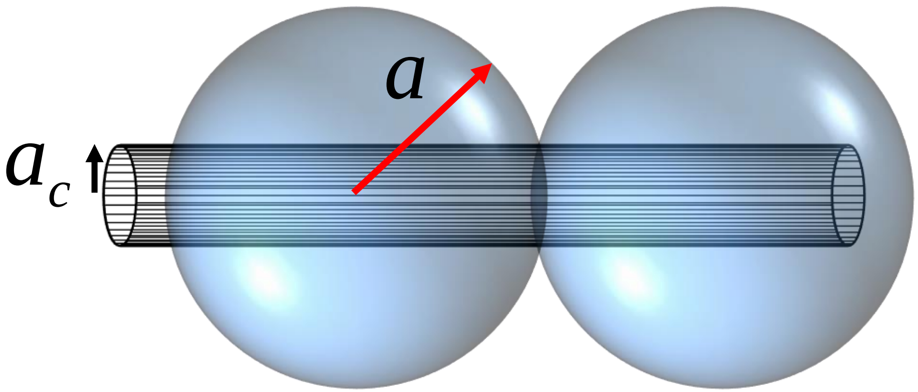
Rolling friction between particles

Particles form **irreversible roll resisting contacts**, not accounted by DLVO theory





$$a_c^{DMT} = \left(\frac{3\pi a^2 W}{8E^*} \right)^{1/3}$$



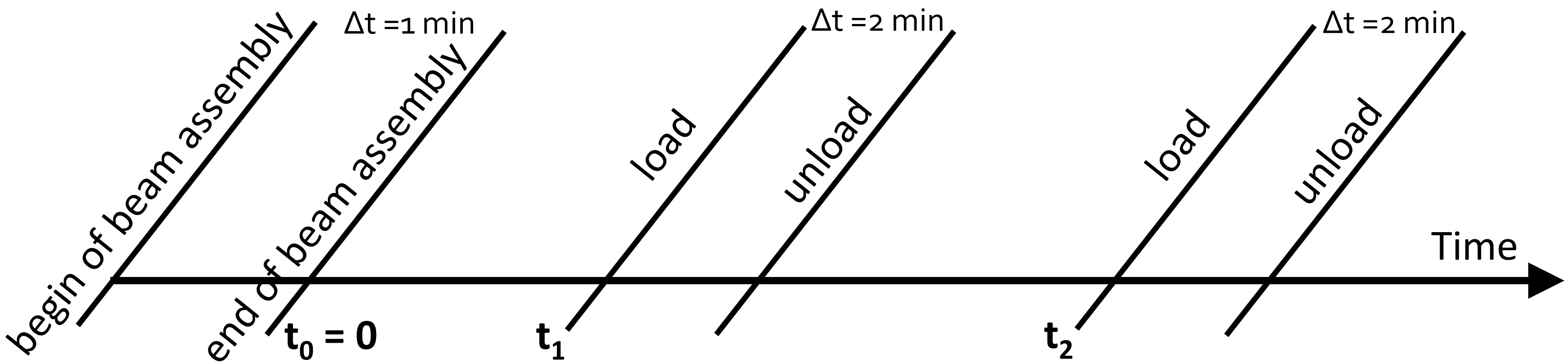
W = interaction energy

E* = Silica reduced bulk modulus

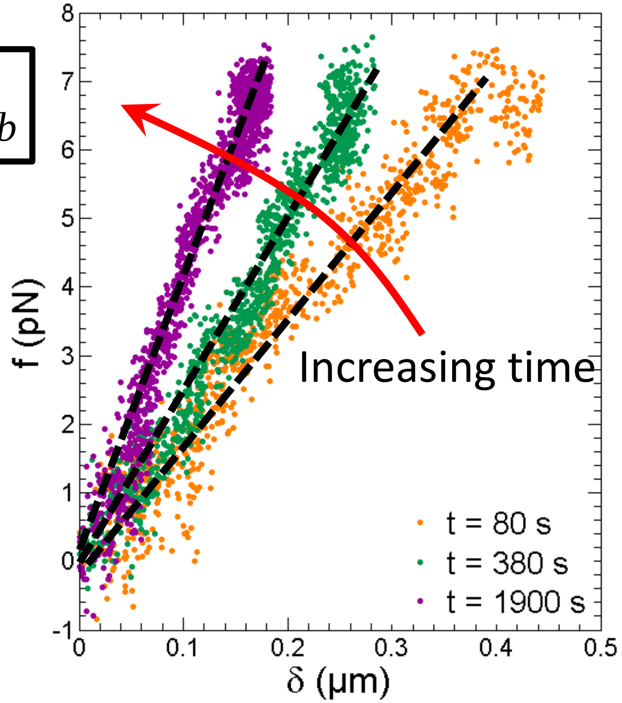
$$k_0 = \frac{(3\pi)^{7/3} E}{4a^{1/3}} \left(\frac{W}{E^*} \right)^{4/3}$$

E = Silica Young's modulus

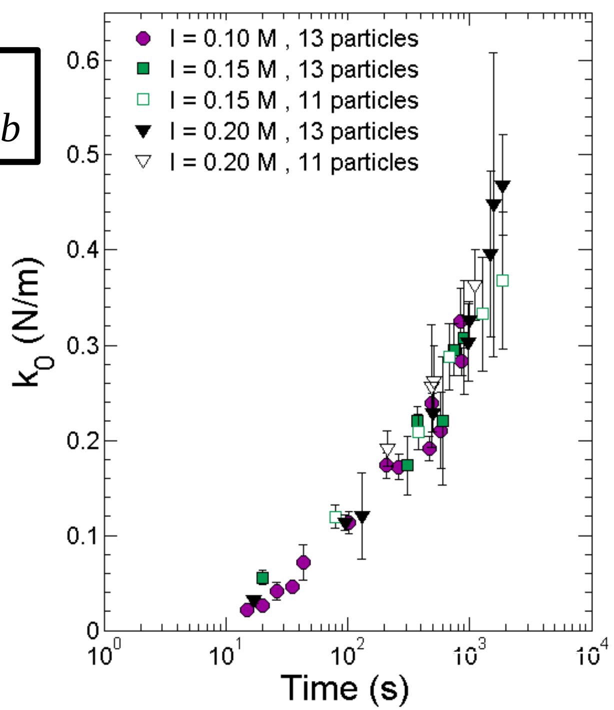
Contact aging



k_b



$k_0 \propto N \cdot k_b$



Contact and mechanical aging

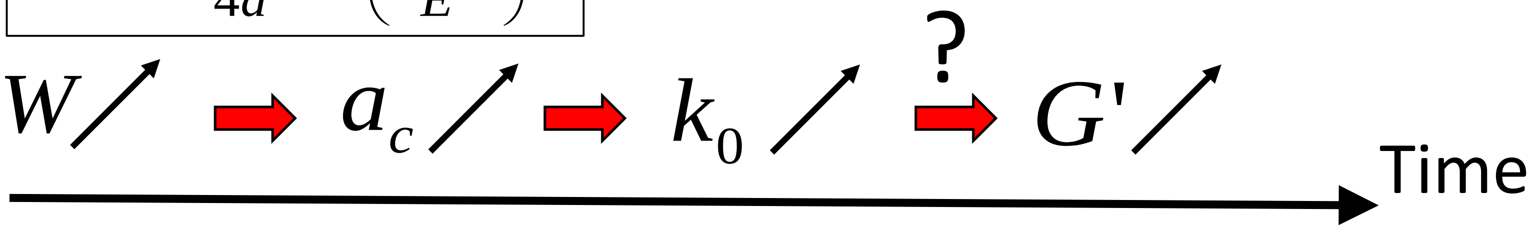
$$k_0(t) = \frac{(3\pi)^{7/3} E}{4a^{1/3}} \left(\frac{W(t)}{E^*} \right)^{4/3}$$

$$W \nearrow \;\Rightarrow\; a_c \nearrow \;\Rightarrow\; k_0 \nearrow \;\overset{?}{\Rightarrow}\; G' \nearrow$$

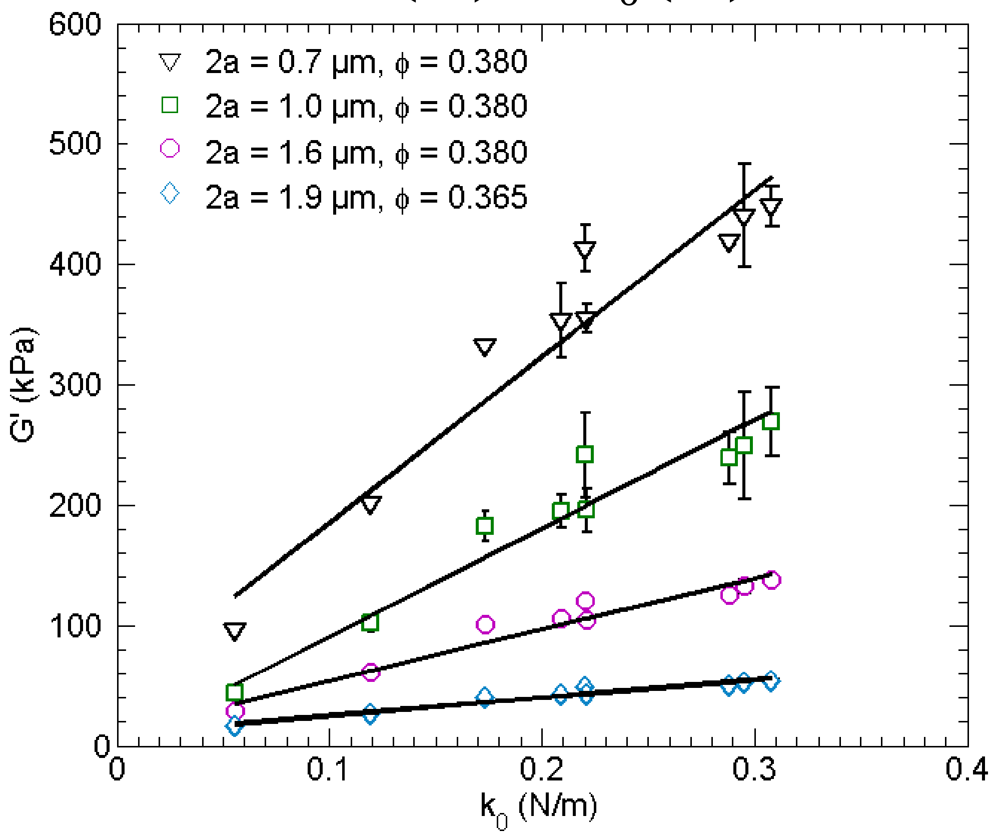
Time

Contact and mechanical aging

$$k_0(t) = \frac{(3\pi)^{7/3} E}{4a^{1/3}} \left(\frac{W(t)}{E^*} \right)^{4/3}$$



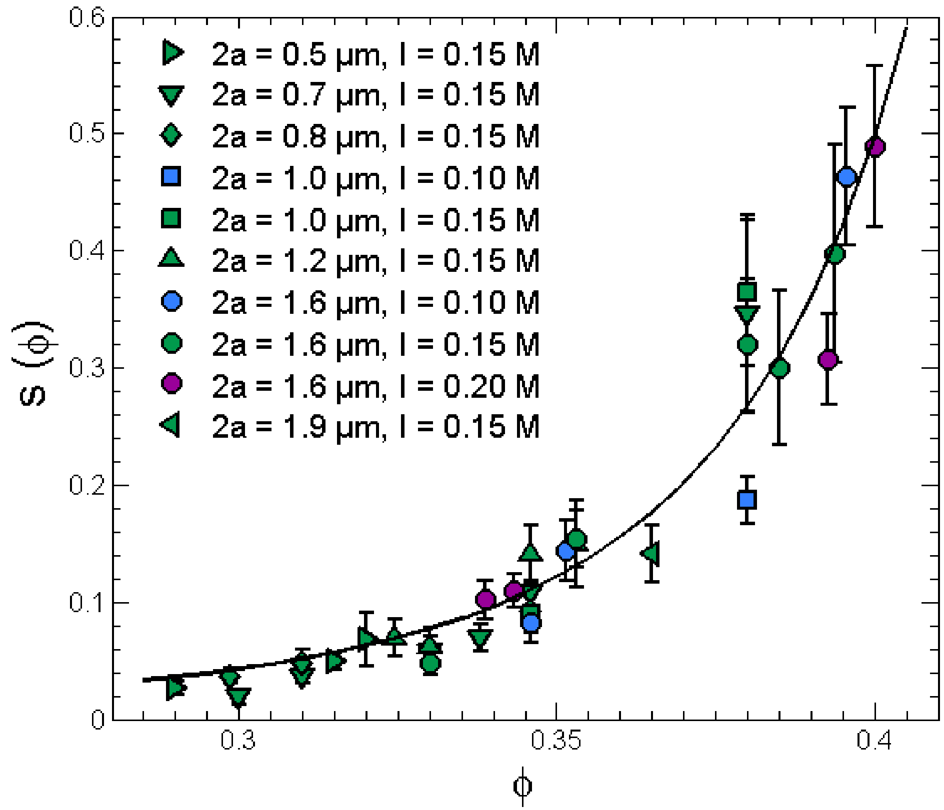
$$G'(t^*) \propto k_0(t^*)$$



A simple model

$$G' = \left(\frac{S(\phi)}{a} \right) \cdot k_0(a,t)$$

$$k_0(t) = \frac{(3\pi)^{7/3} E}{4a^{1/3}} \left(\frac{W(t)}{E^*} \right)^{4/3}$$

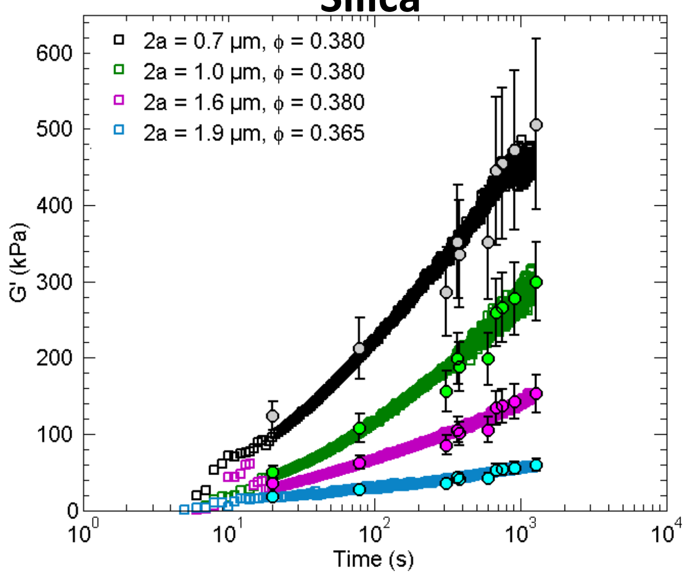


$$G' \propto \left(\frac{W}{a} \right)^{4/3}$$

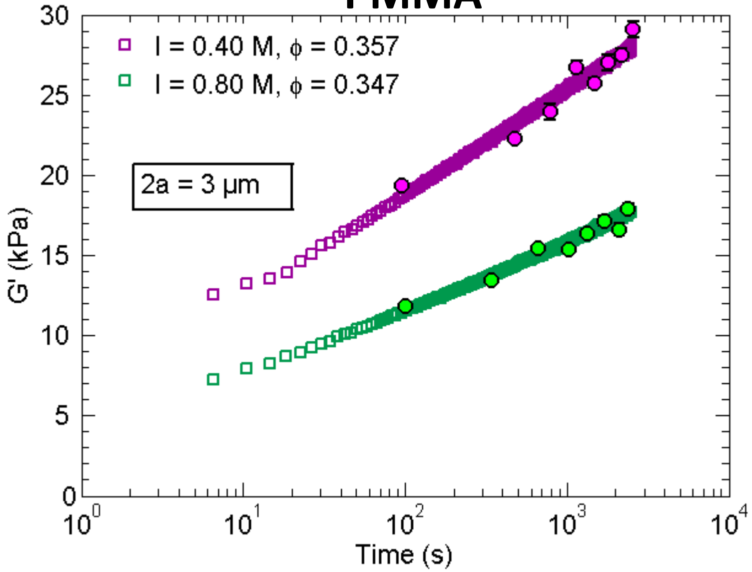
Conclusions

- **Contact aging drives mechanical aging in dense colloidal suspensions where strong vdW forces are operative**
- **The formation of solid-solid contacts is a stabilizing factor (against sedimentation) for un-density-matched, micron-sized particles.**
- **Solid-solid contacts, although irreversible under thermal activation, are broken by mechanical forcing (shearing = rejuvenation).**
- **Same results for a PMMA suspensions in $CaCl_2$.**

Silica



PMMA



LABEX MMCD

IFSTTAR

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Thank you for the attention.

Navier

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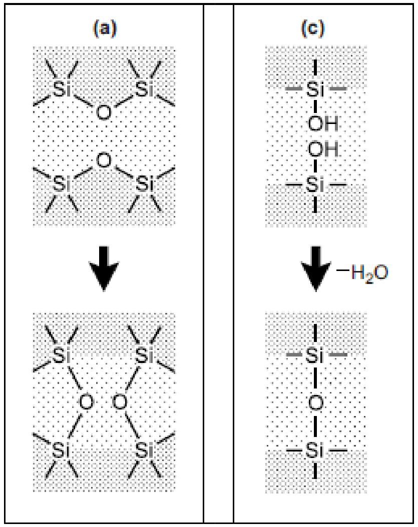
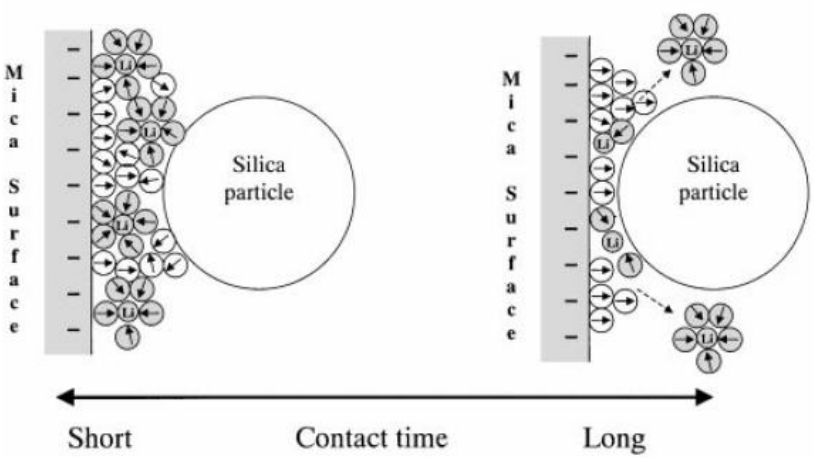
Contact aging

- Cold sintering of silica surfaces ?



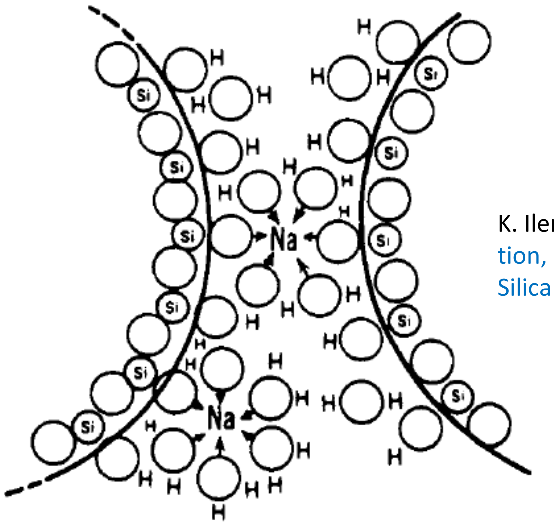
J. N. Israelachvili, in Intermolecular and Surface Forces (Third Edition), edited by J. N. Israelachvili (Academic Press, San Diego, 2011) third edition ed.

- Hydration of the adsorbed cations ?



Vakarelski, I. U., Ishimura, K., & Higashitani, K. (2000). Adhesion between Silica Particle and Mica Surfaces in Water and Electrolyte Solutions, *118*, 111–118.

- Formation of ion bridges?



K. Iler, The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica (John Wiley and Sons Inc, 1979) p. 896.