Desorption to delamination:

dynamics of ~~detachment~~ in a thin film

adhesion

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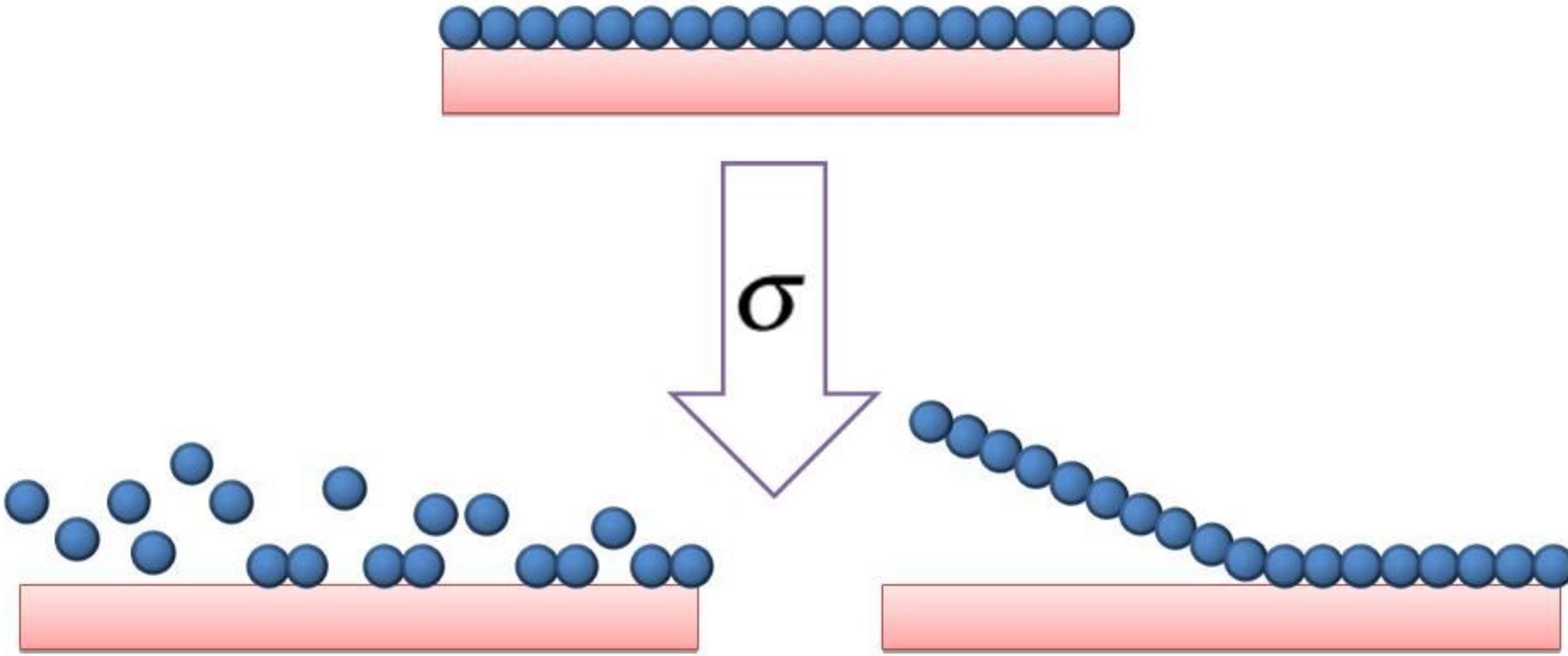


Desorption

Delamination

gas desorption from Palladium

Peeling of paints

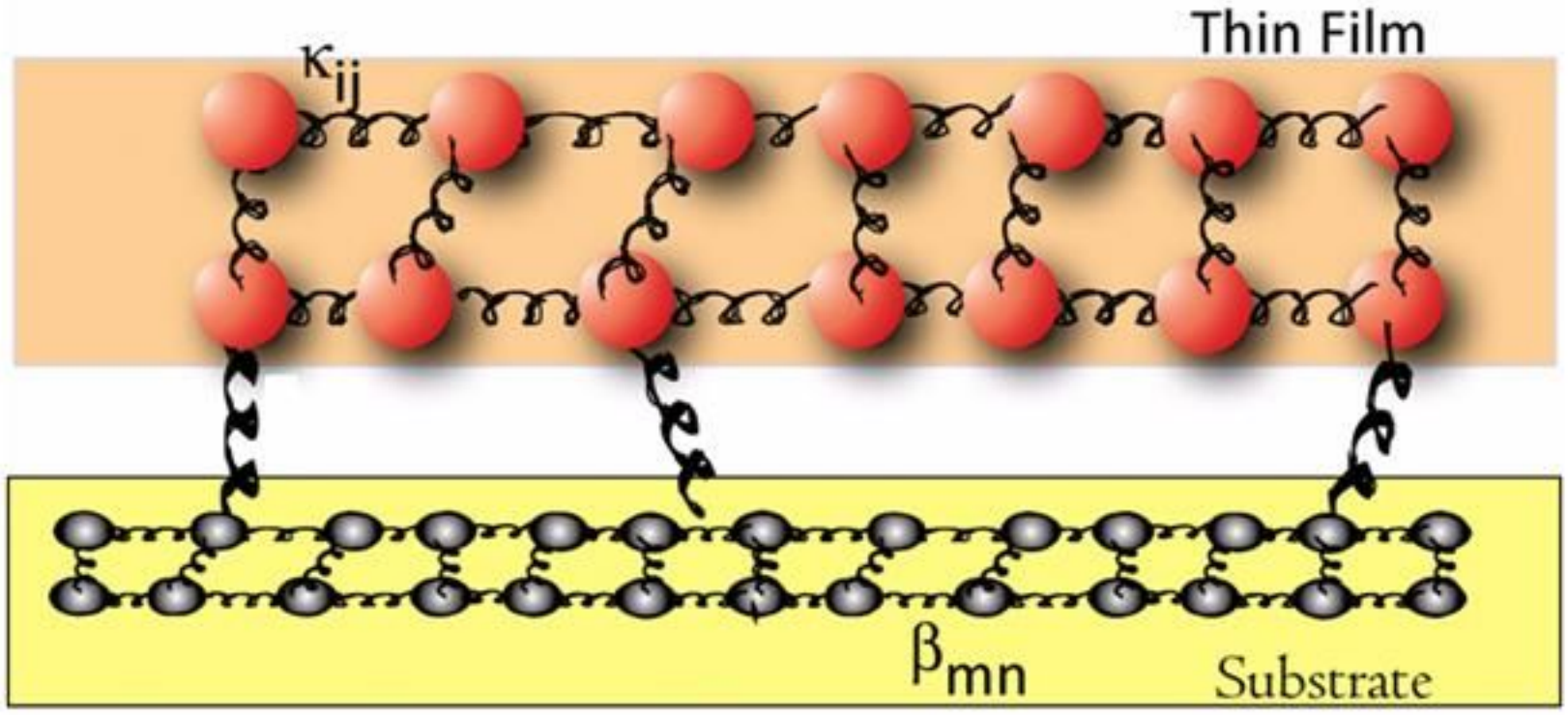
It is a complex problem !!!!!!!!!!

Can I

- **Minimal system which captures the essential complexity of the various detachment processes seen in Nature. ?**
- **Describe by using only a few system parameters?**

- **Draw up analogies and place the delamination process within a unified conceptual framework of disordered elastic media that include phenomena such as wrinkling, pinning, cracking and jamming. ?**

An observable parameter : Length scale (ξ) over which the system fails



$G(Energy/Volume)$

$f_p(Energy/Area)$

$G(Energy/Volume)$

For a critical stress value $\xi = F(G, f_p)$

If f_p is large ξ is small

If G is large ξ is large

Experimental requirements

- **Control Stress (σ)**

- **Alter rigidity (*G*) and Adhesion strength (f_p)**
  - **What is the nature of G & f_p?**

- **Observe events of failure over the entire length scale (ξ).**
- **Figure out a model system**

Plan of the talk

I will use colloids as model systems and study

- Single particle events
  - Adsorption of a single colloid to a glass plate.
  - Desorption of colloidal layer from a glass plate as single particles.

- Many particle events
  - Desorption of colloidal layer from a glass plate as chunks of particles (achieved by altering rigidity).

Rheological Characterization of the spring

$$\mathrm{stress}(\sigma) \propto \mathrm{strain}(\gamma)$$

$$\sigma(\omega) = G(\omega)\gamma(\omega)$$

$$G(\omega) = G'(\omega) + \imath G''(\omega)$$

G' : Elasticity

Ideal Newtonian Liquid (viscosity η)

$$G'(\omega) = 0$$
$$G''(\omega) = \omega\eta$$

G'' : viscosity

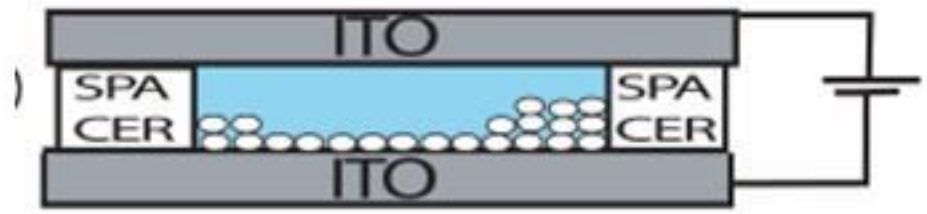
Ideal Solid (rigidity G_0)

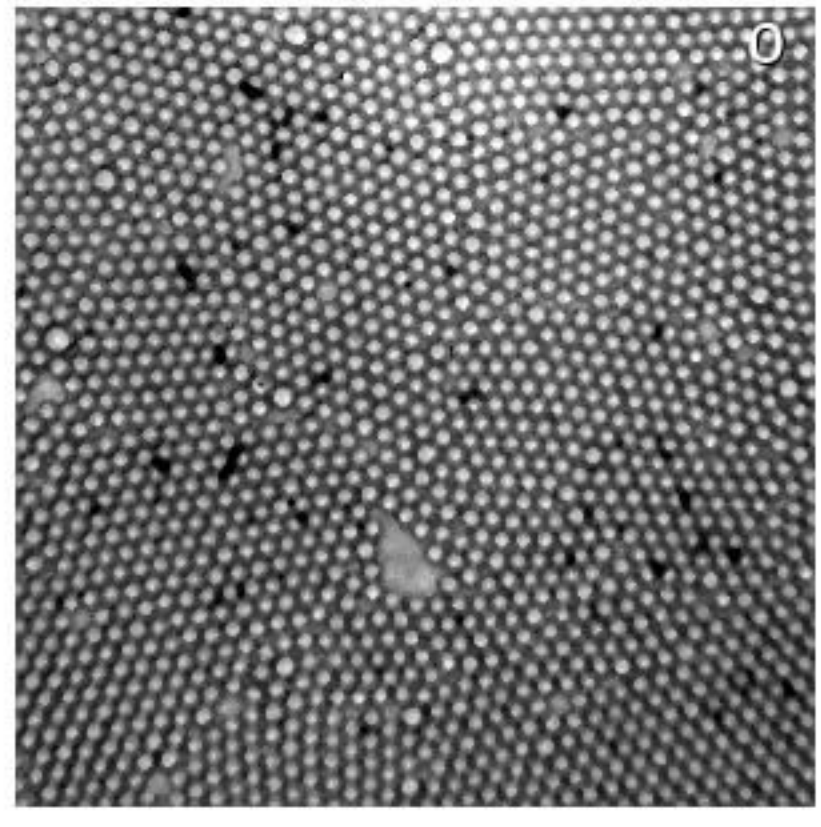
$$G'(\omega) = G_0$$
$$G''(\omega) = 0$$

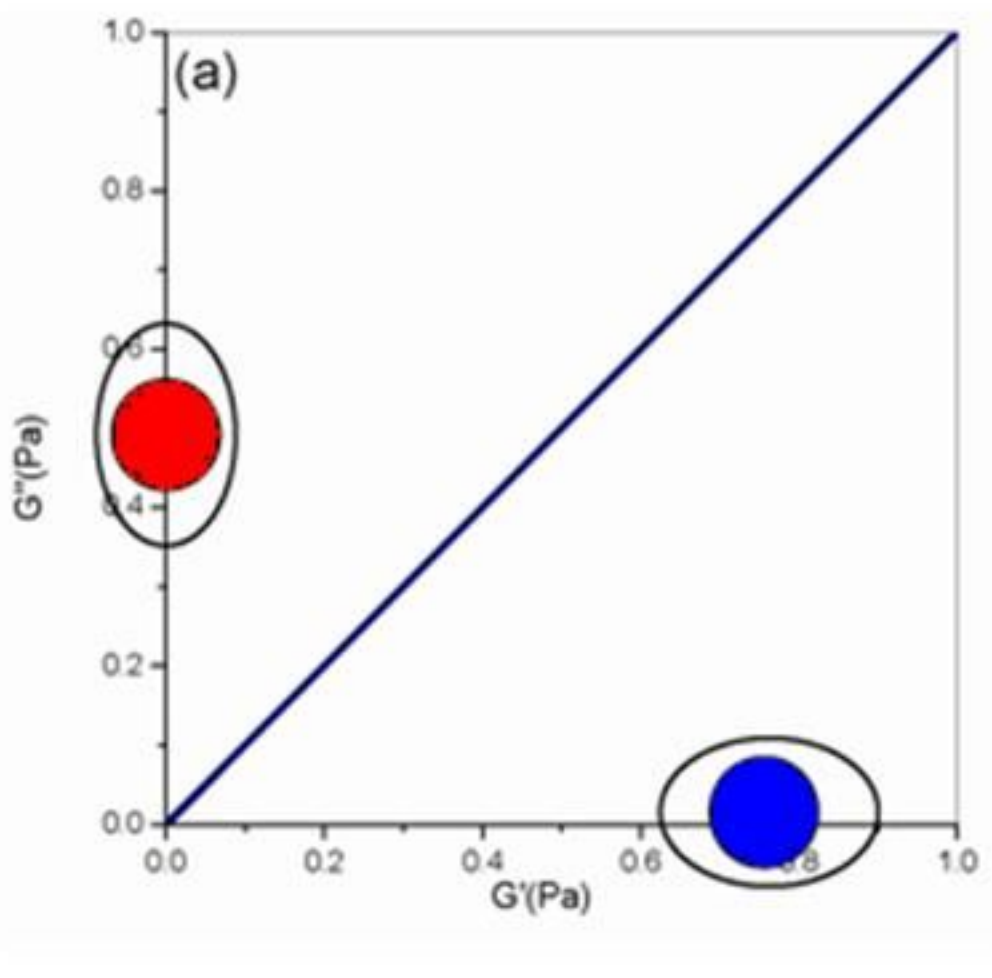
Adsorption of a single colloid to a glass plate.

Desorption of colloidal layer from a glass plate as single particles.

$$D = \frac{\text{Thermal Energy}}{\text{Frictional Coeff.}} = \frac{K_B T}{\xi}$$







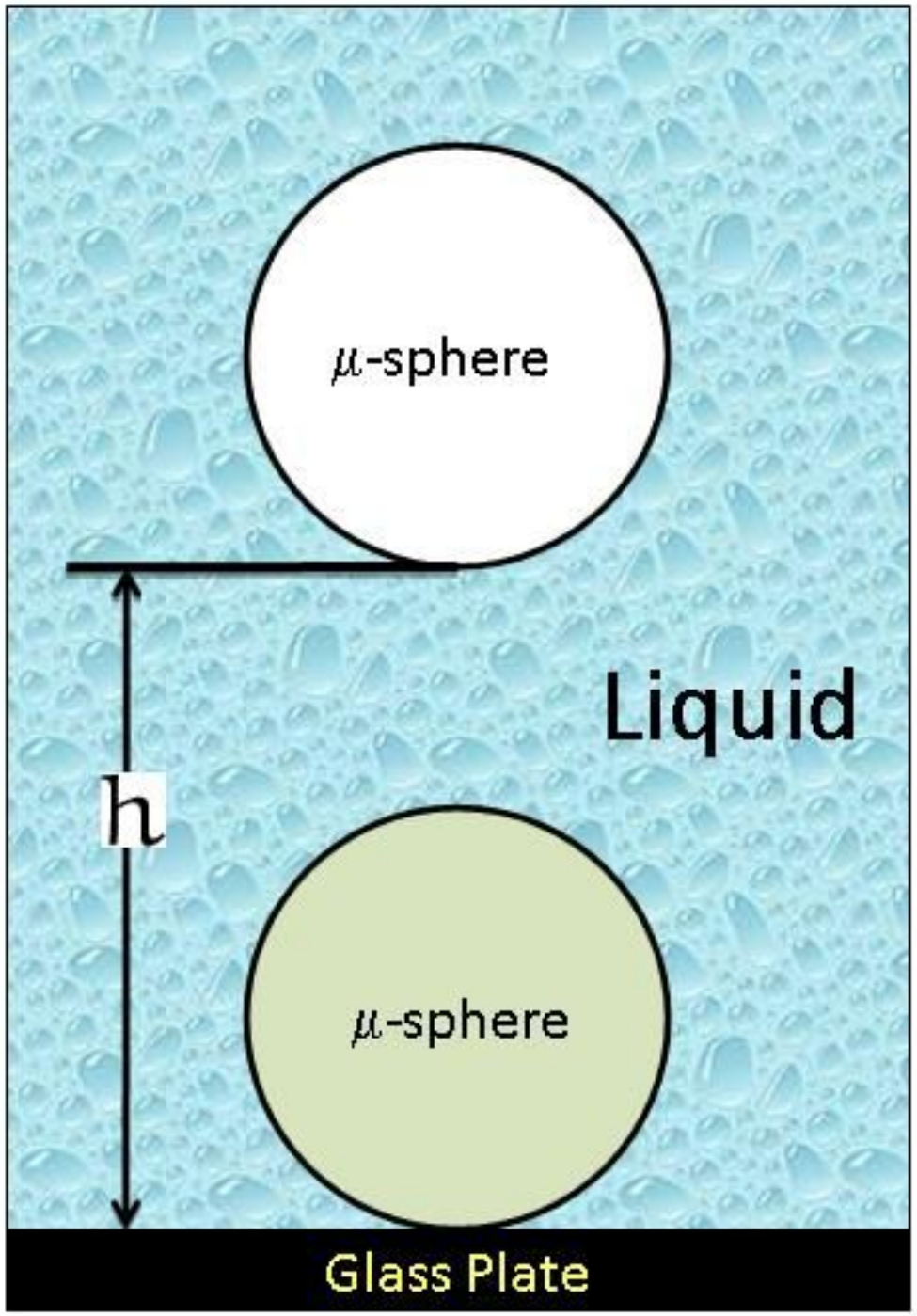
Sticking of a colloidal particle onto a substrate

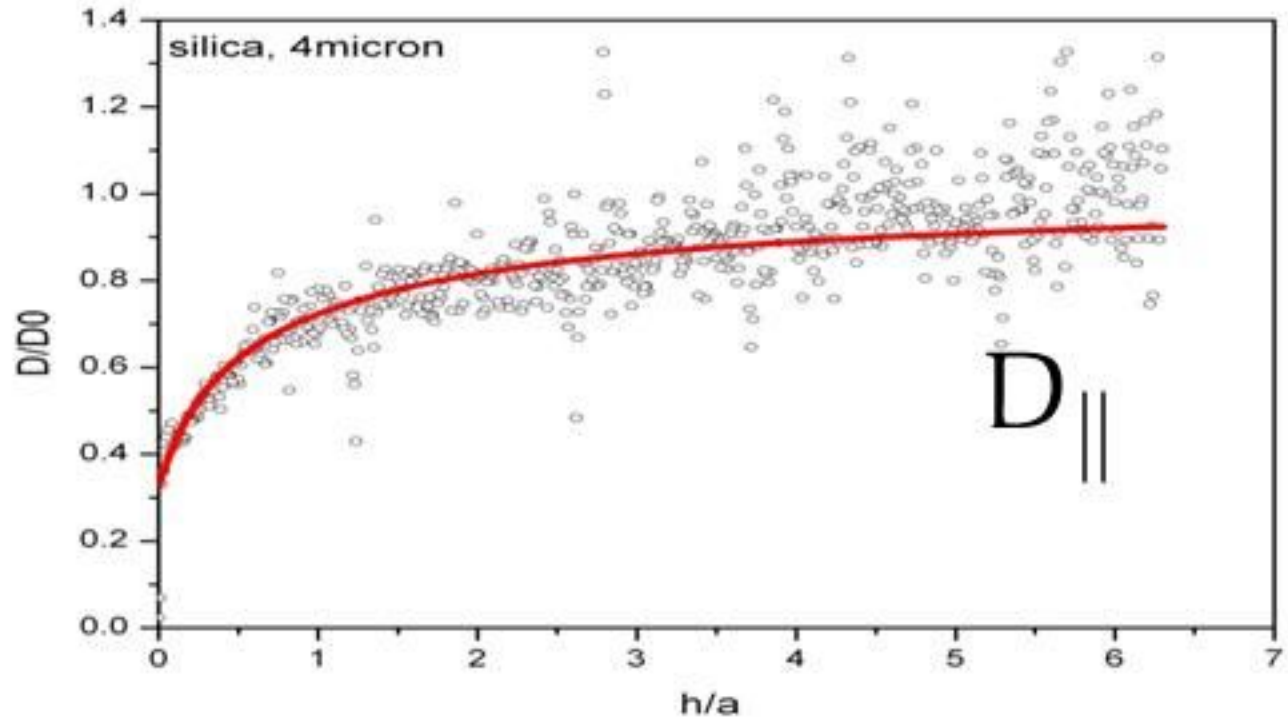
- What does it mean to be stuck?

- **How does one study the dynamics of sticking?**

- **Differences in sticking between rigid and soft particle**

Sticking Transition ==Liquid to solid transition





Away from the Plate $D_\perp = D_\parallel = D_0$

In absence of sticking on the Plate (h=o)

$D_\perp \to 0$ $D_\parallel \to D_0/3$

In presence of sticking on the Plate

$D_\parallel \to 0$

Stokes-Einstein equation

Einstein showed that the diffusion coefficient of a particle undergoing Brownian motion is

$$D = \frac{\text{Thermal Energy}}{\text{Frictional Coeff.}} = \frac{K_B T}{\xi}$$

For Spherical particles

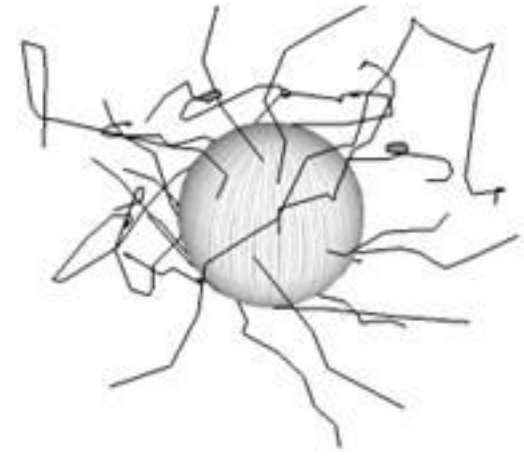
$$\xi = 6\pi\eta a \qquad \text{Stokes Result} \qquad D = \frac{K_B T}{6\pi\eta a}$$

$$D \to 0 \Rightarrow \xi \to \infty$$

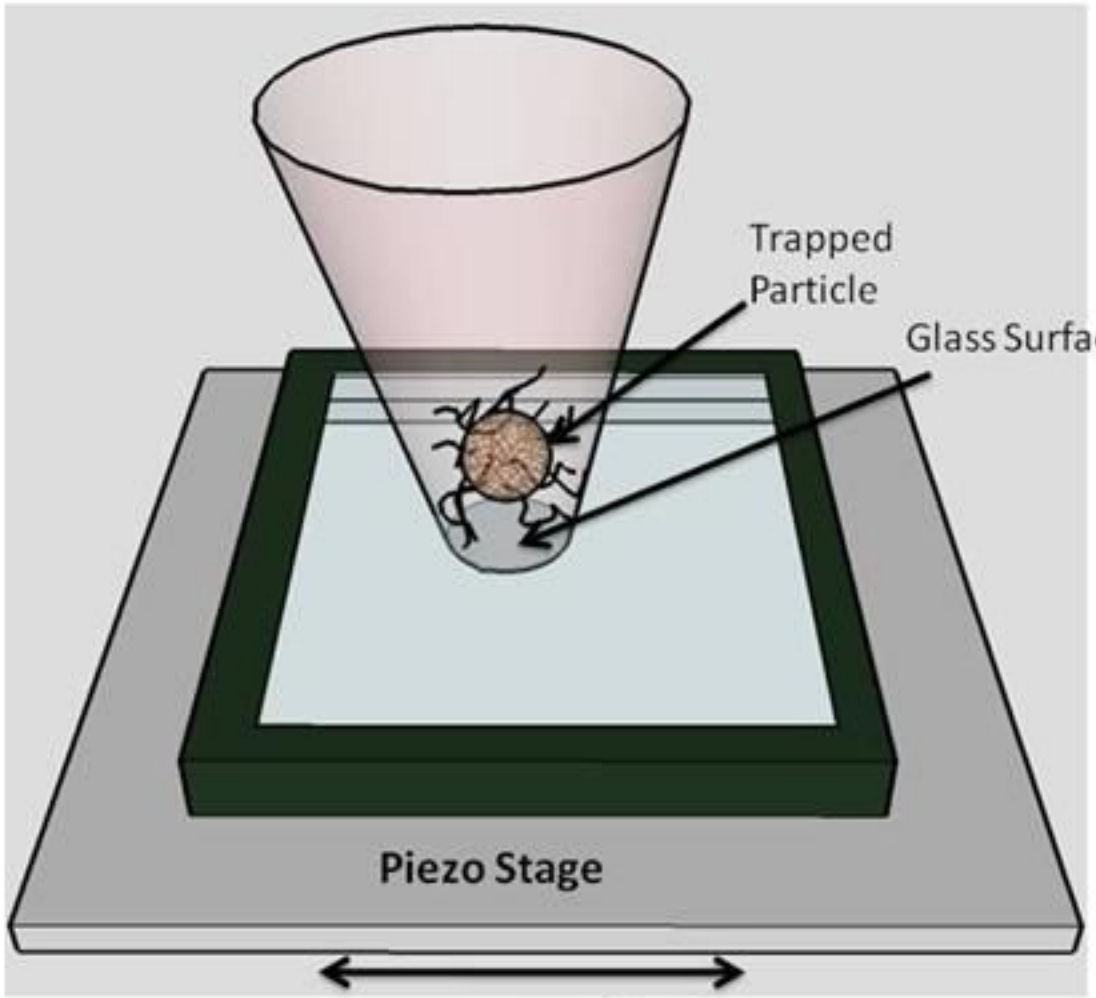
Types of spheres

Silica

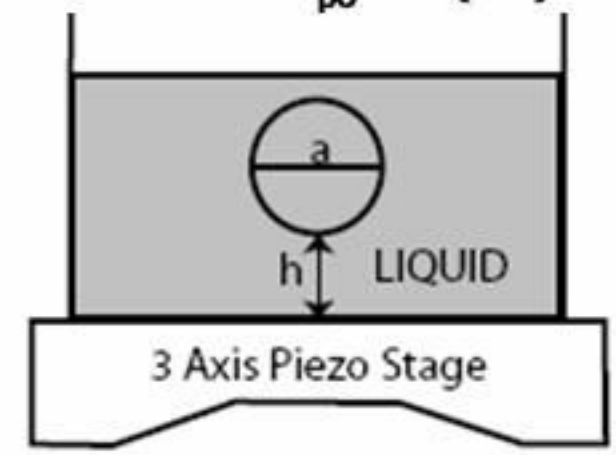
Polystyrene



Experimental details



$x = x_{po} \sin(\omega t)$



1. Trap the particle.

2. Approach the trapped particle to the bottom surface.

3. Two types of measurement:

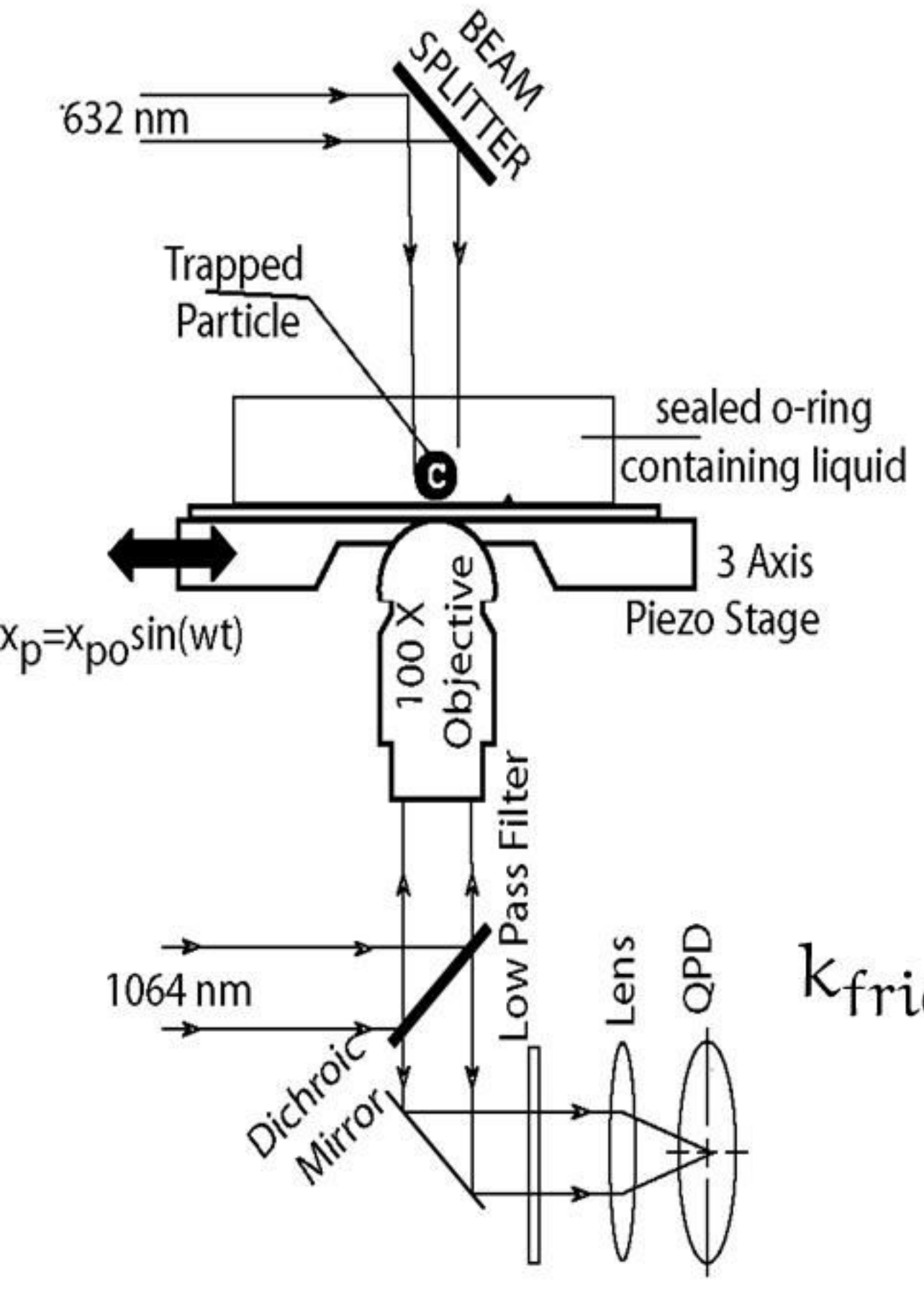
   a) ~~Fluctuations of the motion of the trapped particle.~~

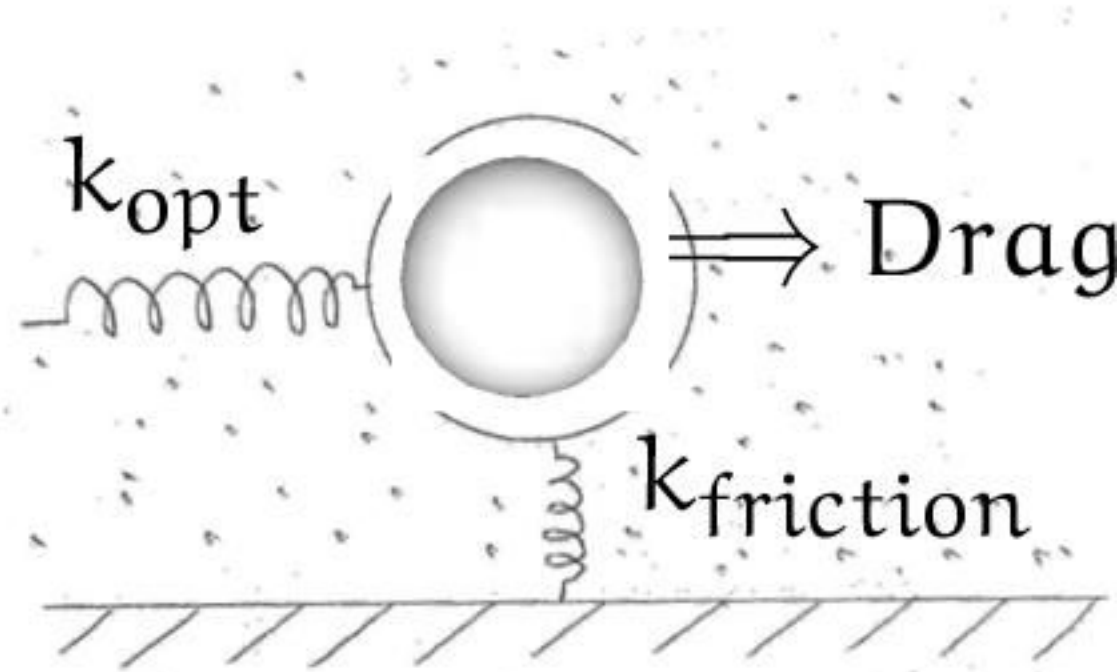
   b) AC response function for a sinusoidal x-y oscillation of the container.

AC response function for a sinusoidal x-y oscillation of the container.

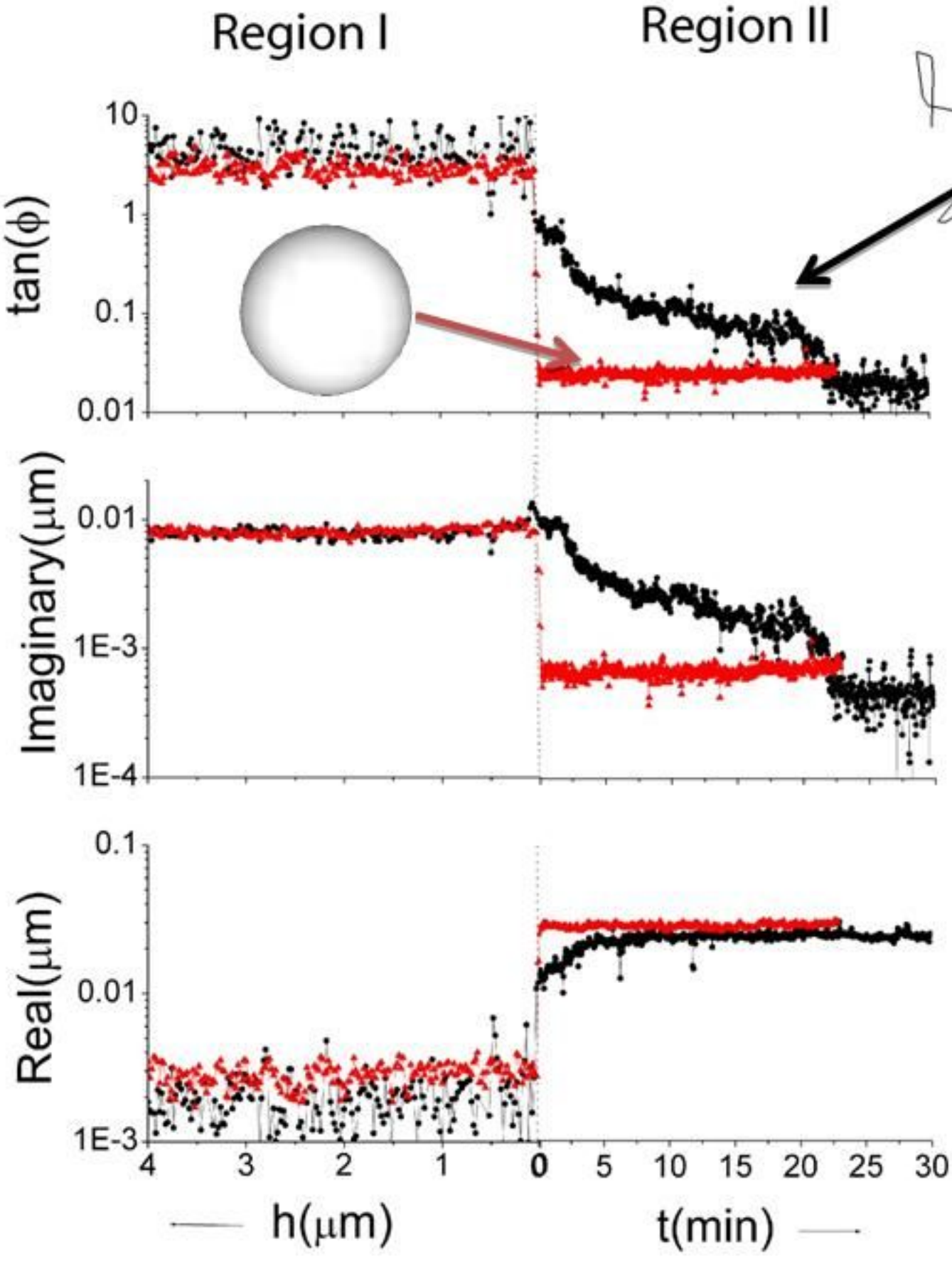
1. Oscillate the container sinusoidally in x-direction.
2. Measure the phase difference between the motion of the trapped particle and that of the container.

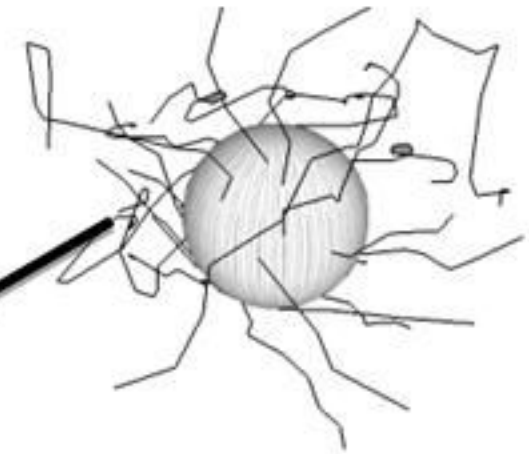
- Stuck particle will move in phase(zero phase difference) with the container.
- Non stuck particle will slip, finite phase difference.
- Can this be modeled by an effective coupling between the particle and the plate?
- Expect elastic coupling from sticking and viscous coupling from slipping.





$$k_{friction} \begin{cases} G' : \text{Elasticity} \\ + \\ G'' : \text{viscosity} \end{cases}$$





Sphere far in the liquid

Viscous coupling

$$\mathrm{Re}(x_0) \neq 0$$

$$\mathrm{Im}(x_0) \neq 0$$

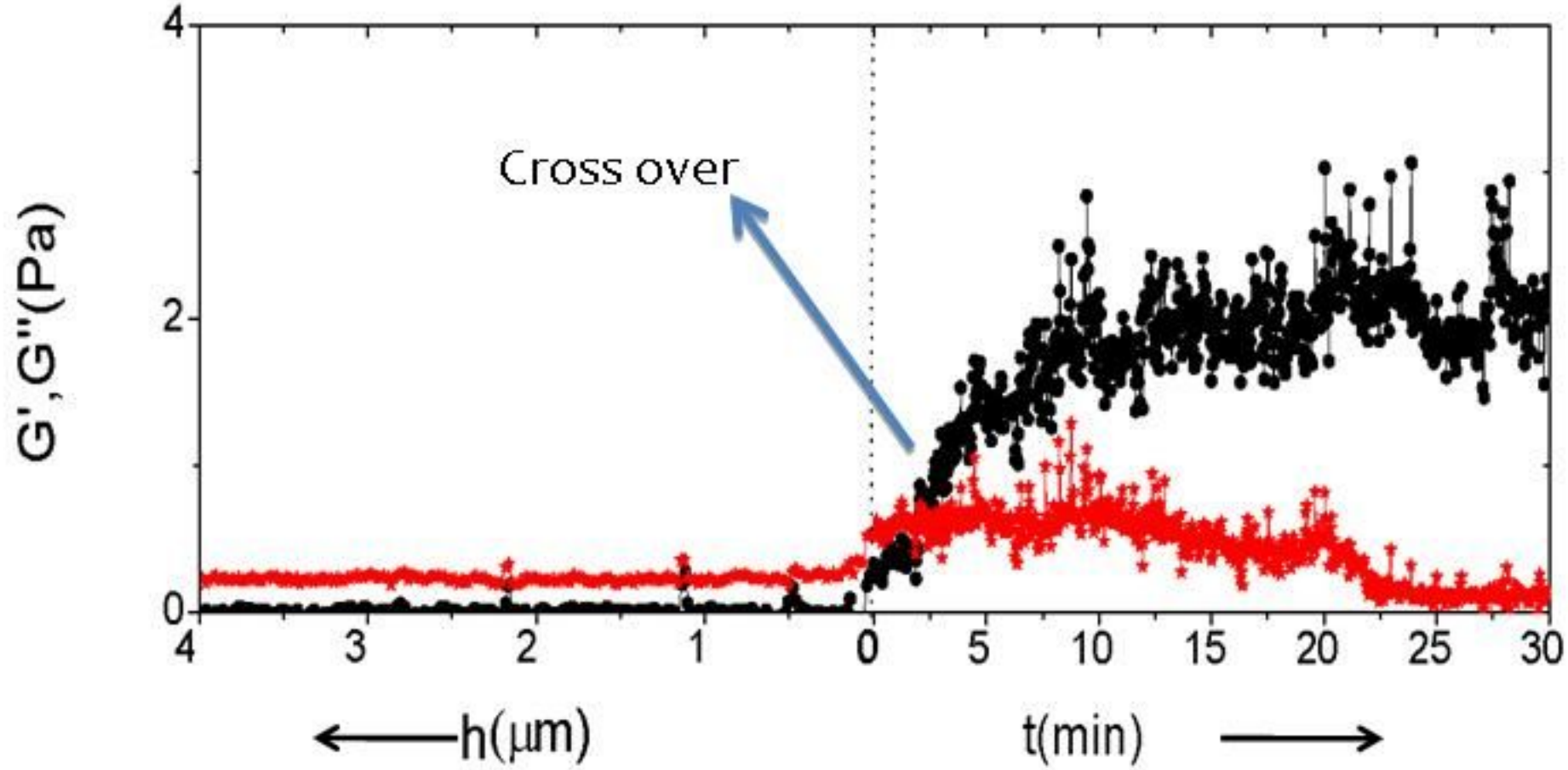
Sphere near to the plate

Elastic coupling

$$\mathrm{Re}(x_0) \neq 0$$

$$\mathrm{Im}(x_0) = 0$$

Typical results for G' and G''



$$G' = \frac{\mathrm{Re}(x)x_{p0} - |x|^2}{(\mathrm{Re}(x) - x_{p0})^2 + (\mathrm{Im}(x))^2}$$

$$G'' = \frac{\mathrm{Im}(x)x_{p0}}{(\mathrm{Re}(x) - x_{p0})^2 + (\mathrm{Im}(x))^2}$$

Upon contact, G'' reaches a peak and decreases with increasing time G' rises from zero, crosses G'' at the peak of G'' and saturates with time. Exactly what the Maxwell model does as function of increasing frequency

Aging and slow dynamics

- **Time dependence in polystyrene spheres is an effect of "tethers", acting as internal degrees of freedom.**
- **Tethers explore environment until sinks into a deep enough well to be stuck.**
- **Explore different types of sticking by changing particle-plate interaction, strength of the drive and strength of the optical trap.**

Control Parameters for tuning the sticking

Salt Concentration	Interaction Potential High salt concentration stronger interaction potential
Frequency	Different Configuration (??)
Optical Trap stiffness	Force (?)

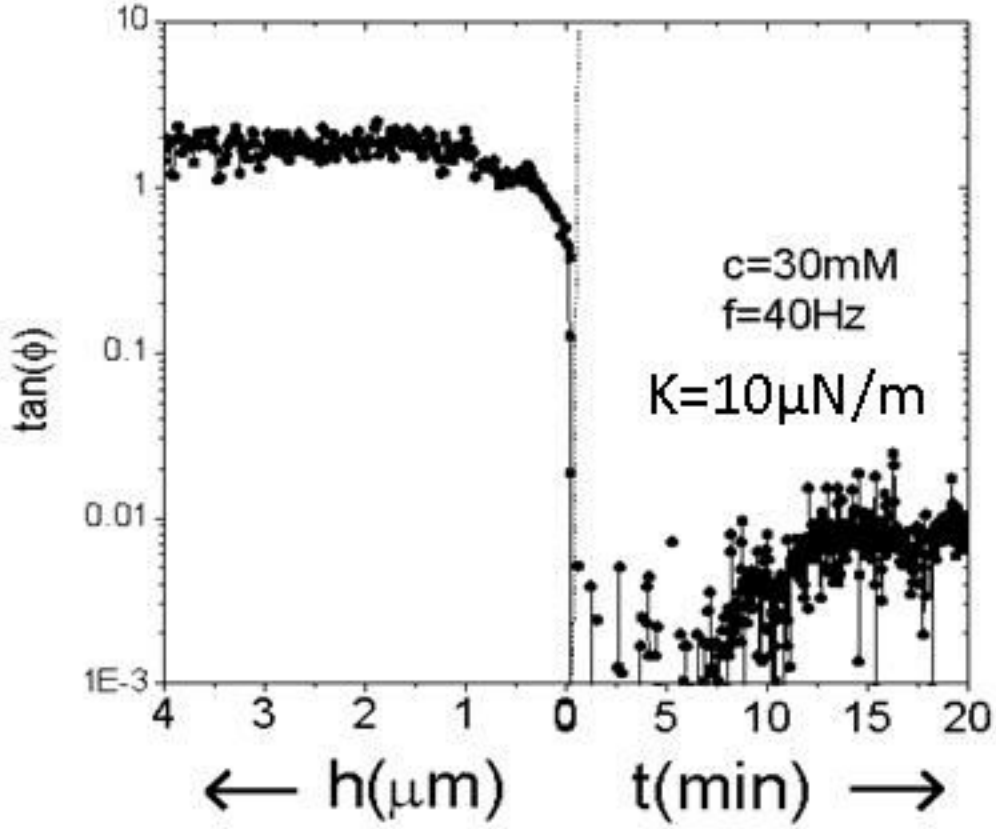
Depending on the magnitude of these three parameters, three regimes of sticking can be explored

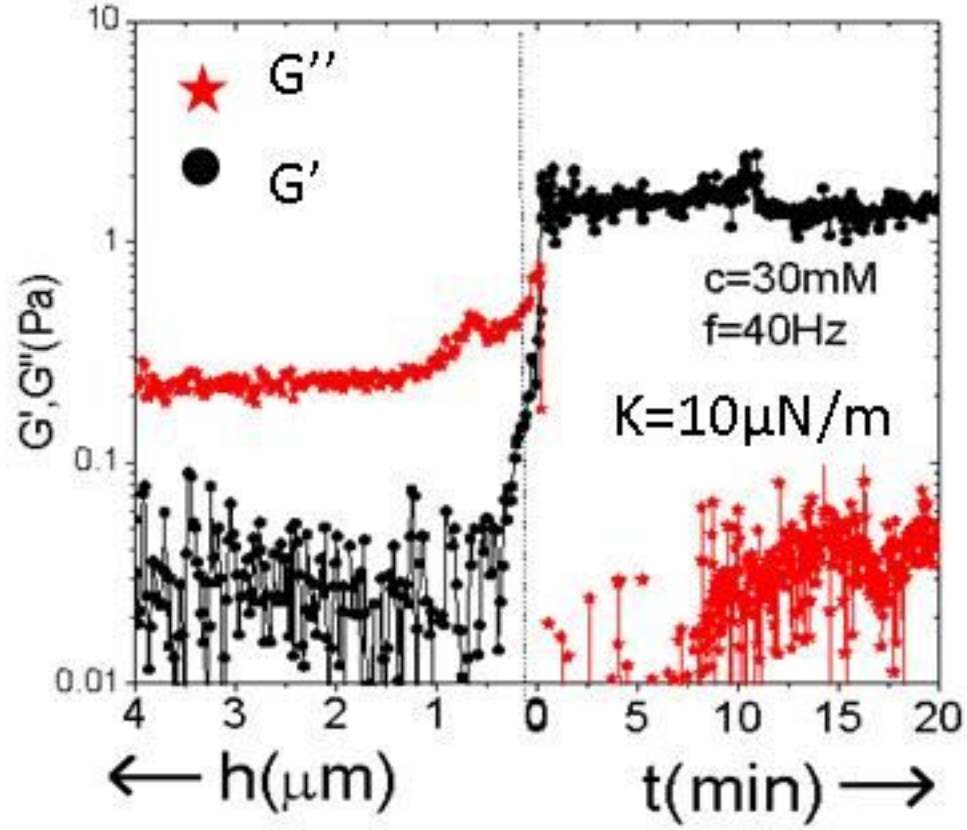
1. Well stuck

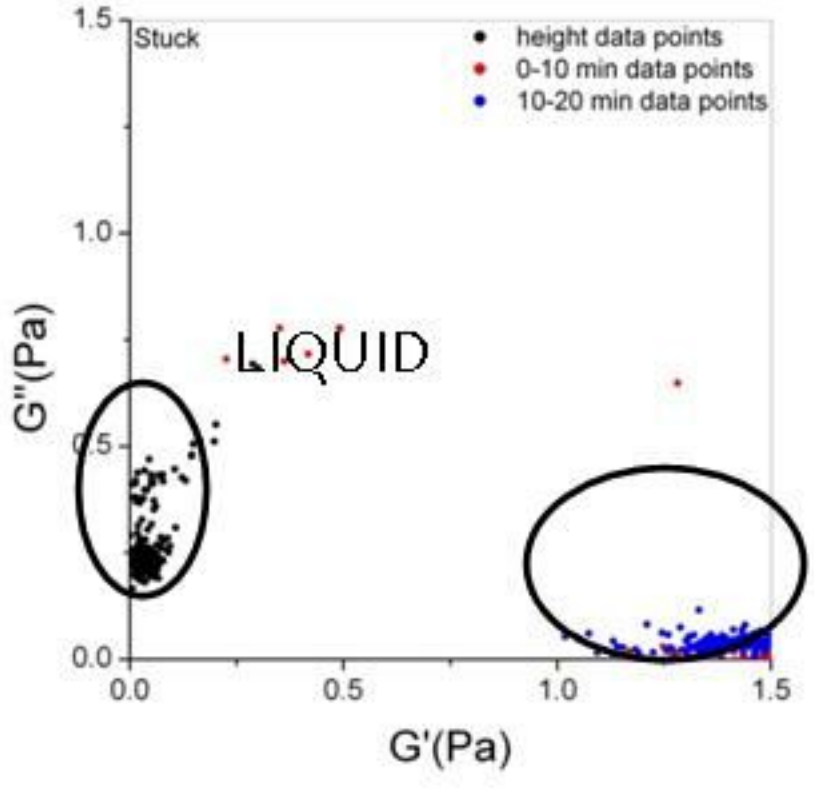
2.Aging/Slow relaxation

3.Slip/ Non-stuck

Well Stuck

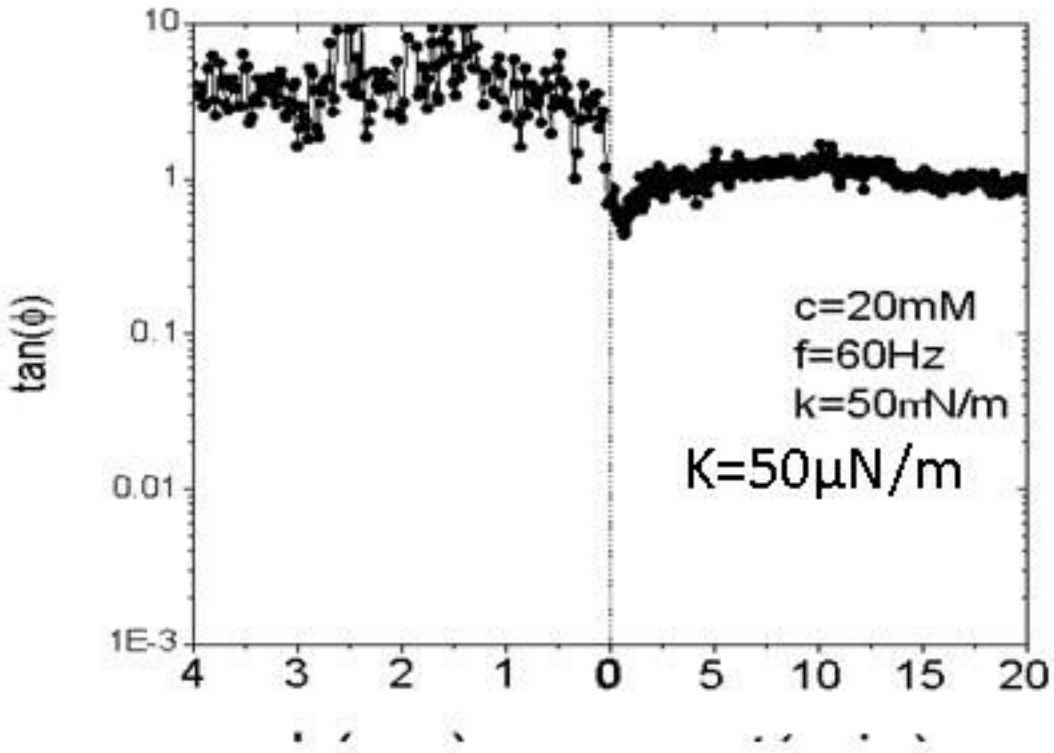


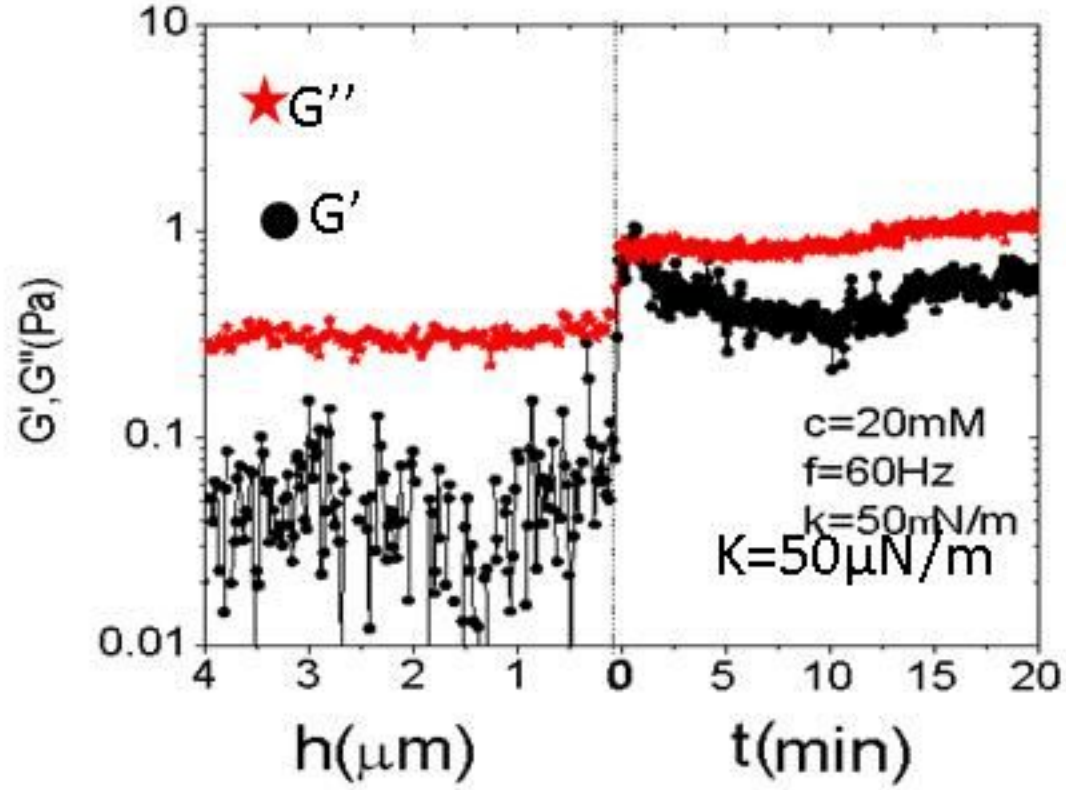


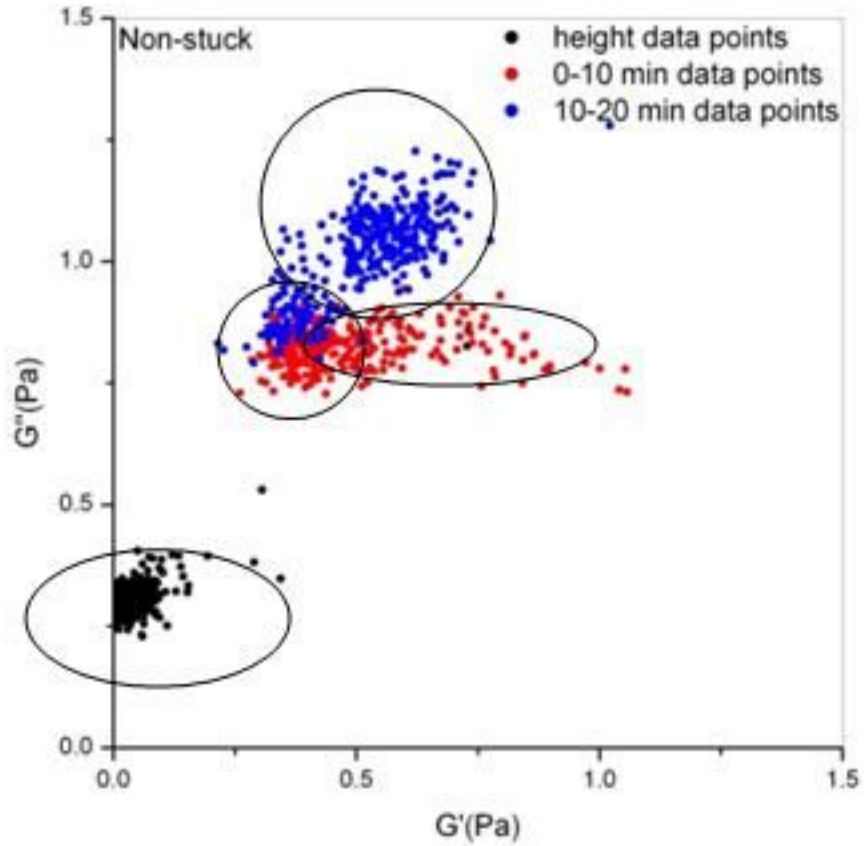


Sticking , phase goes to zero, implies G' >> G'', more elastic than viscous

Slip/Non-stuck

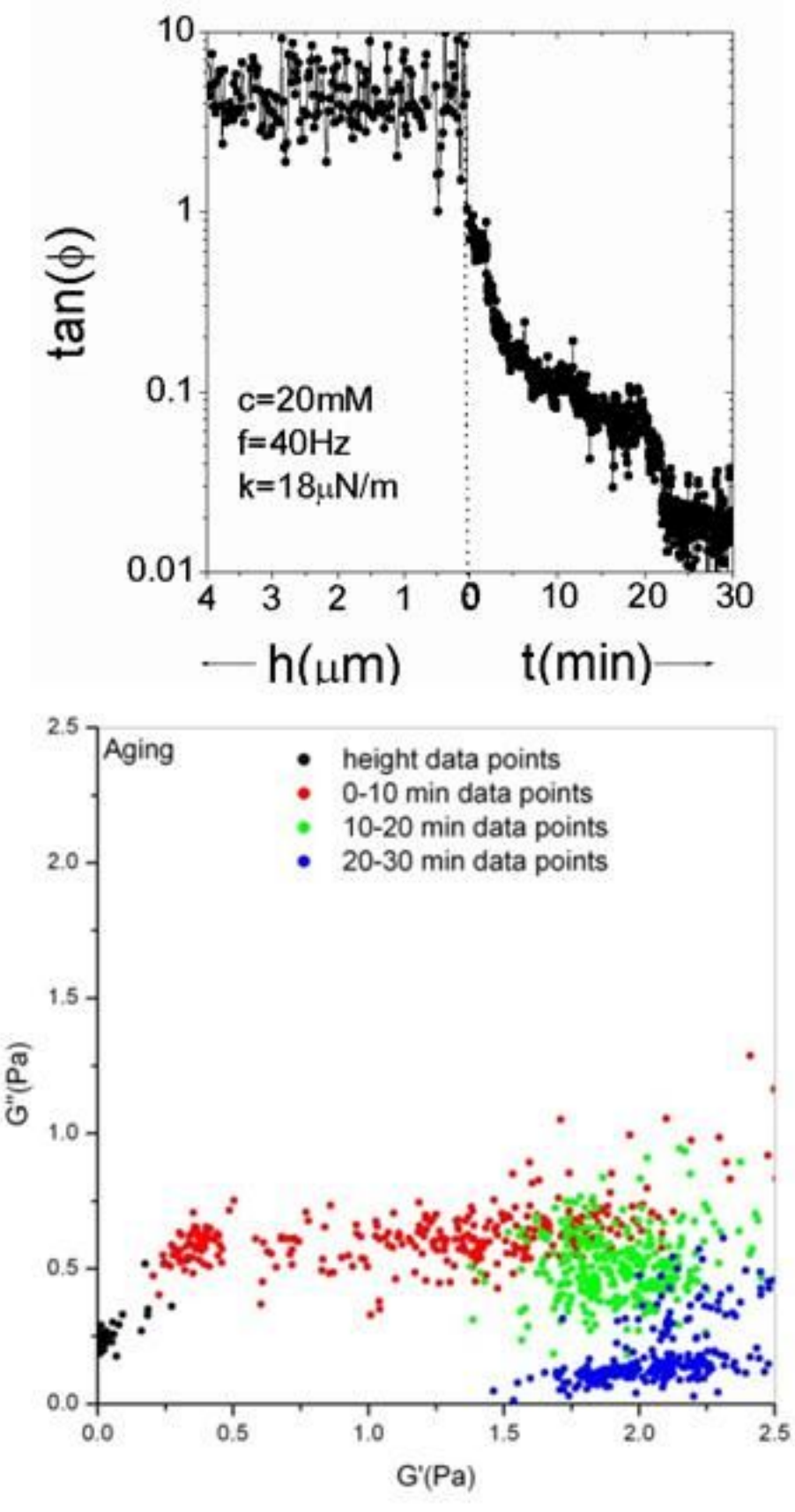


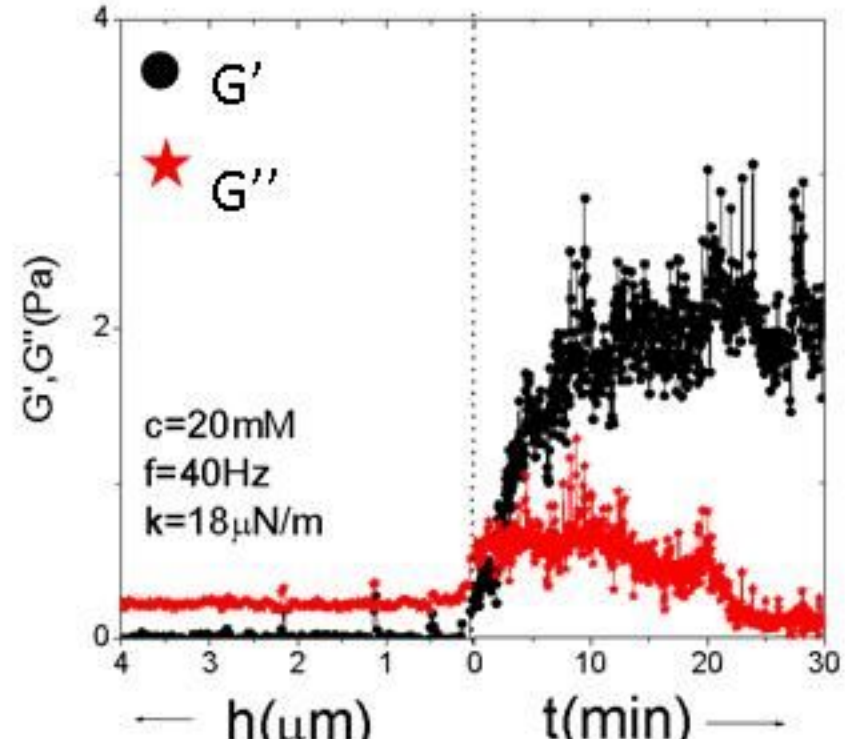




Non-sticking, phase does not go to zero, but to a terminal value: implies larger viscosity than bulk but G' ~ G", more viscous than elastic

Aging/Slow Relaxation

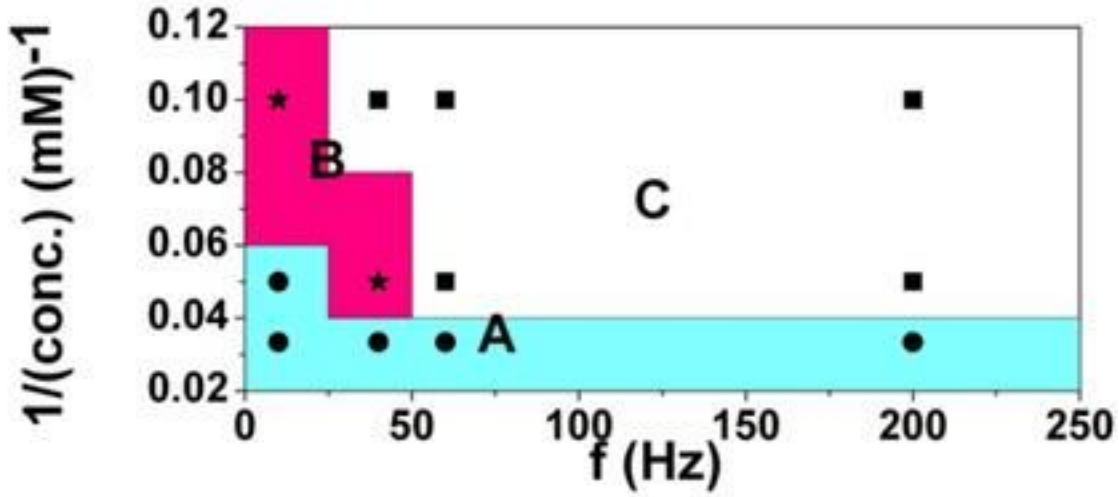




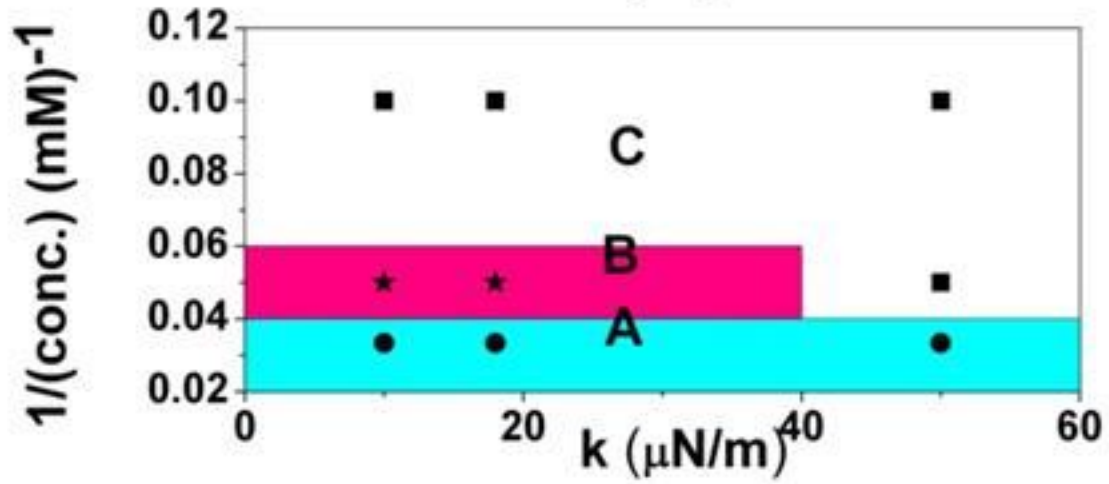
Sticking , phase goes to zero, implies G’ > G”, more elastic than viscous

Phase Diagram

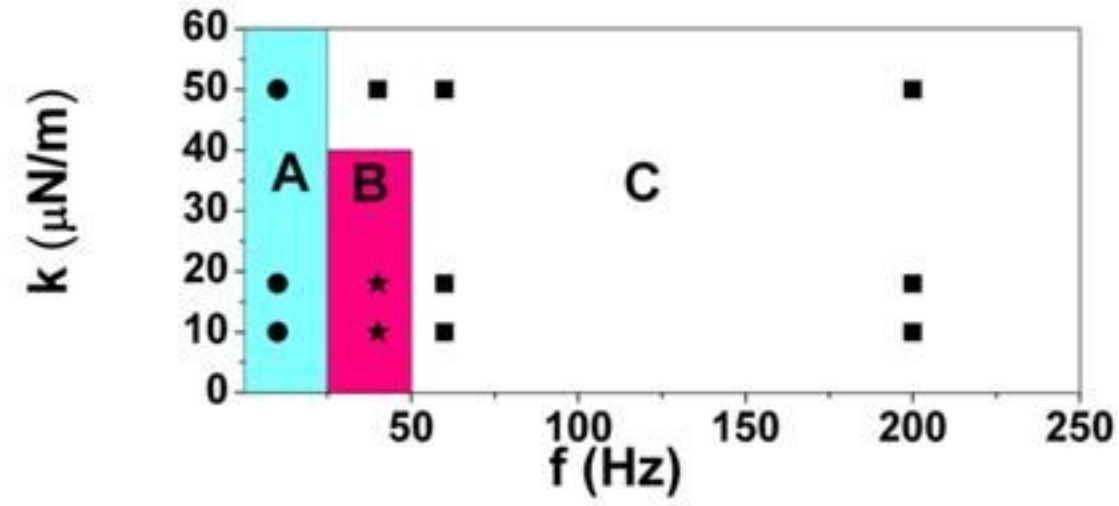
k=18μN/m



f=40Hz



conc=20mM

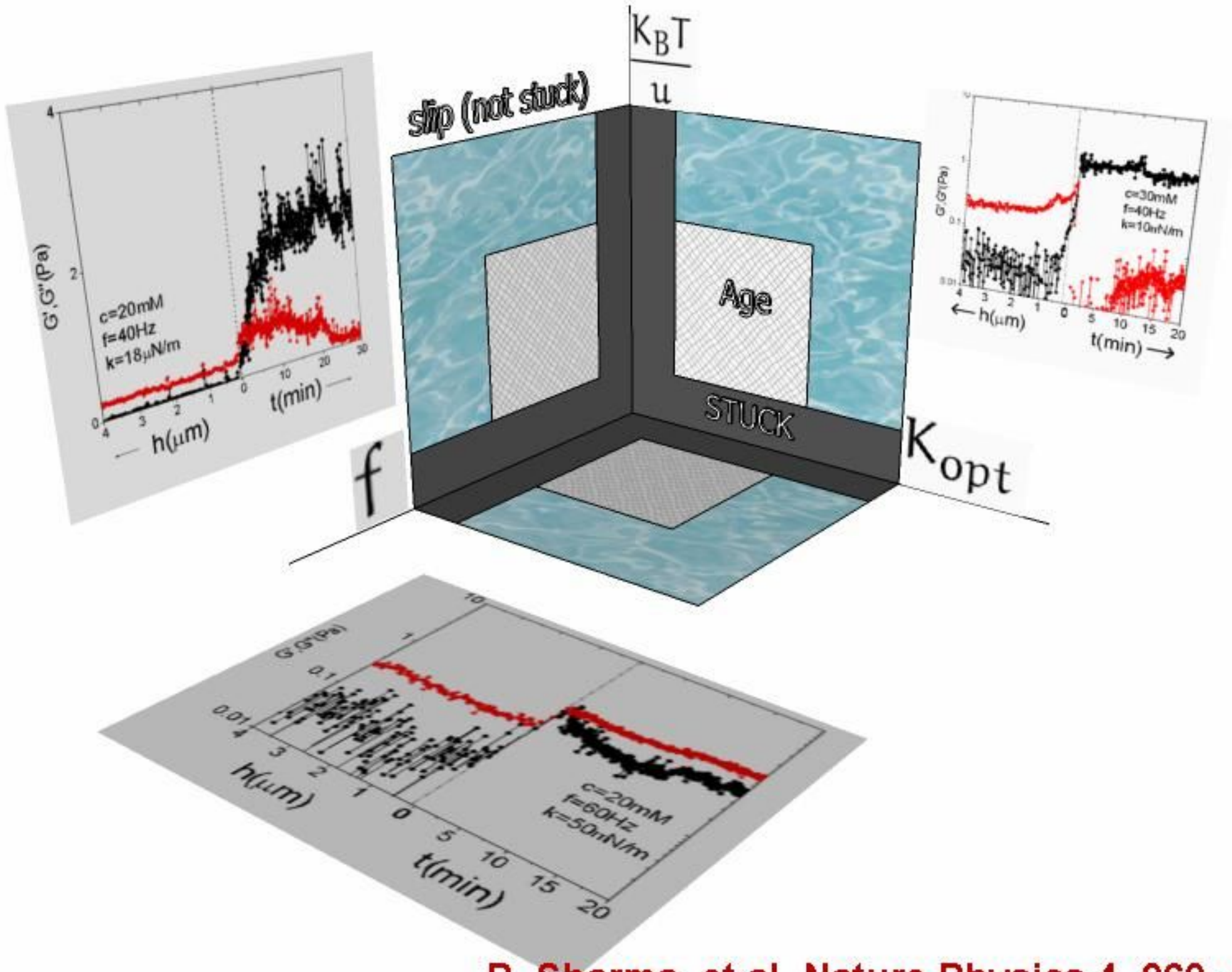


Stuck

Age

Non Stuck

Combined phase Diagram

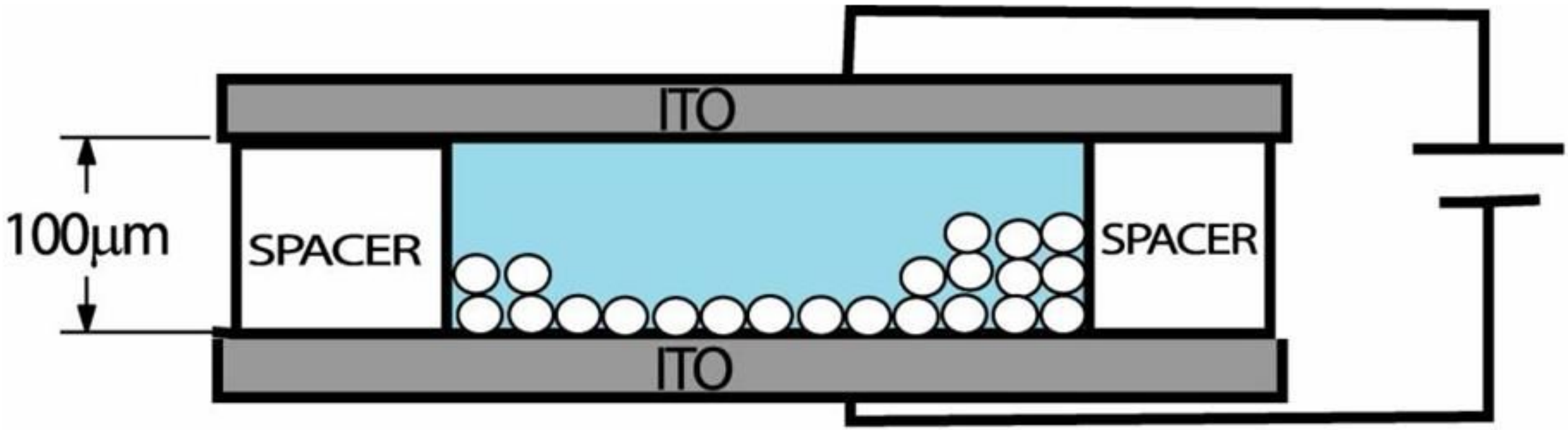


P. Sharma et al. Nature Physics 4, 960 - 966 (2008)

Many particle events

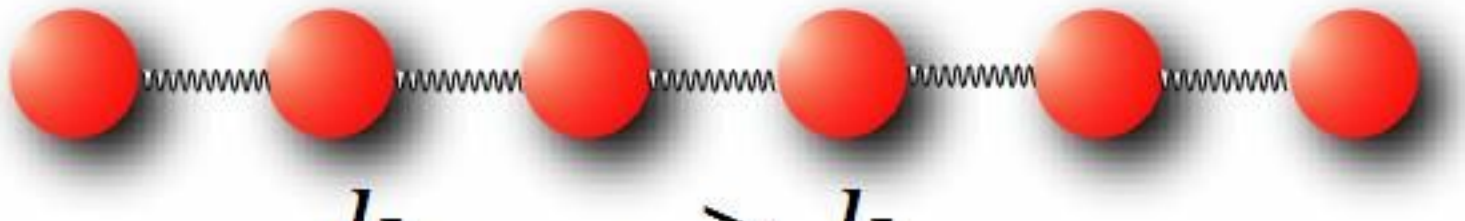
Desorption of colloidal layer from a glass plate as chunks of particles (achieved by altering rigidity).

Experiments

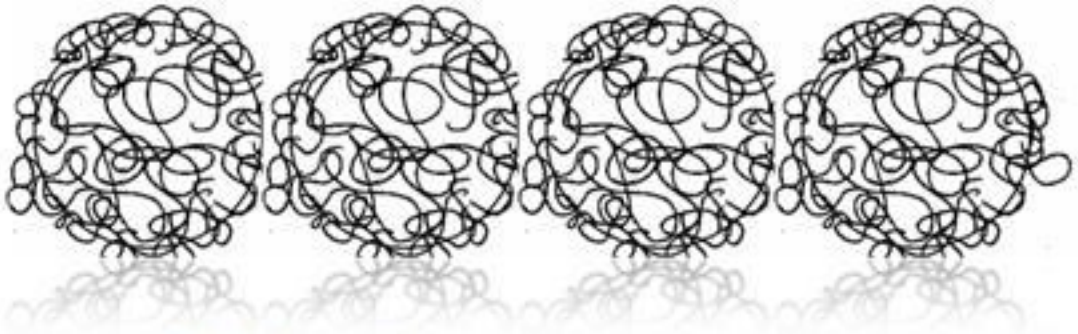


The external mechanical stress to the films was applied in the form of a dc electric field between two ITO electrodes separated by an oil-filled insulating space of thickness ~100 μm. For all experiments reported here, the field was ramped in steps of 0.01 V/μm with a waiting period of 2 sec between steps.

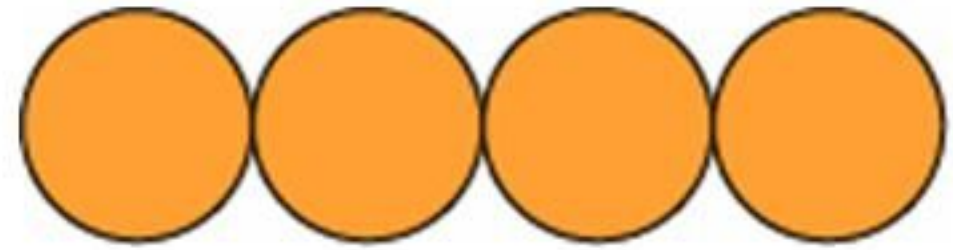
Changing Rigidity



$$k_{si-si} > k_{p-p}$$



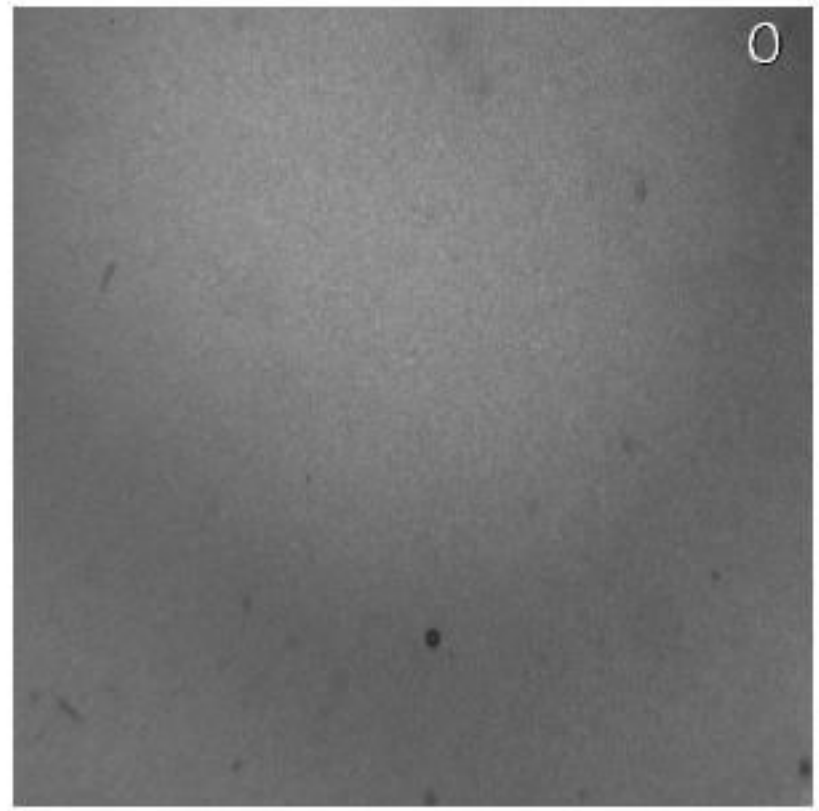
Soft **Polystyrene** particle network $G \sim 1\ Pa$

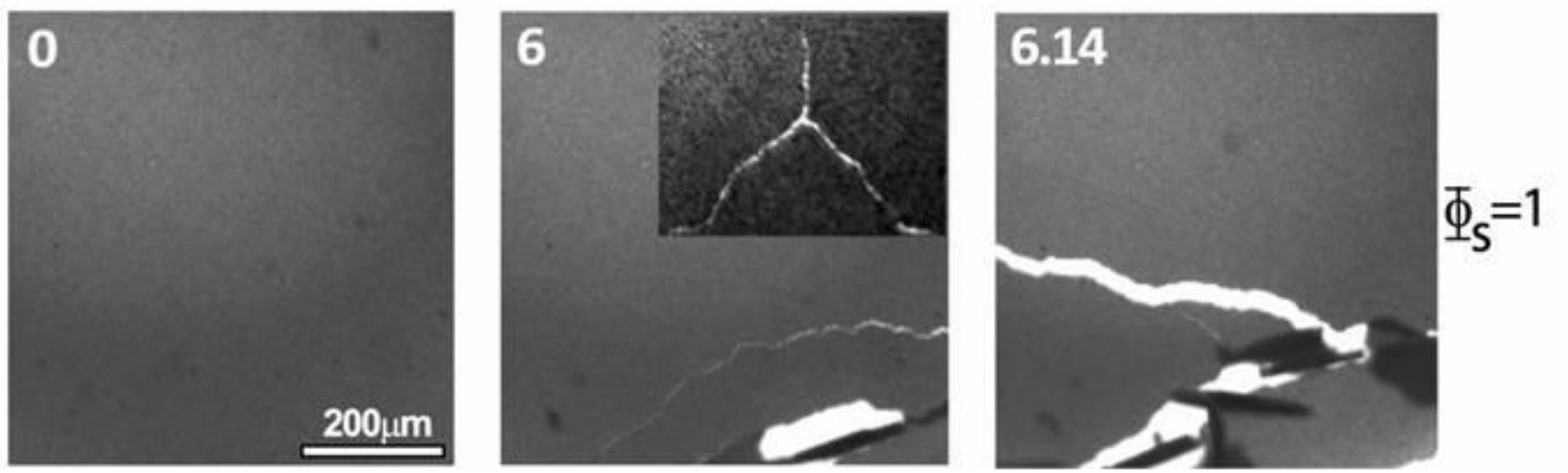


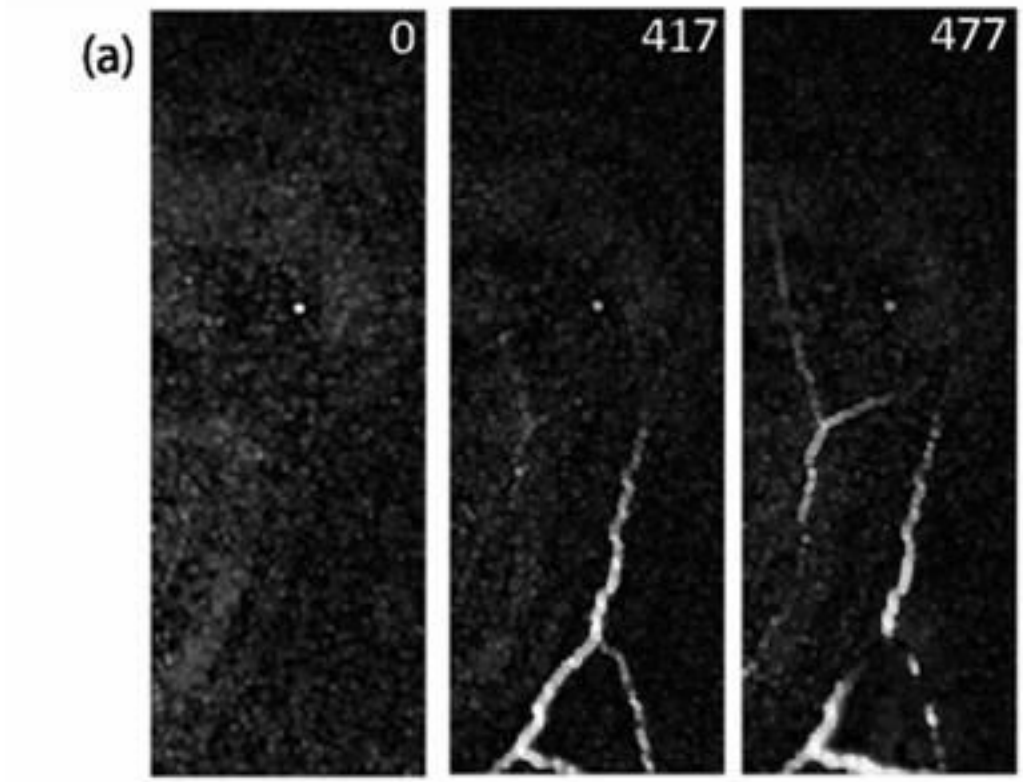
Rigid **Silica** particle network $G \sim 100\ Pa$

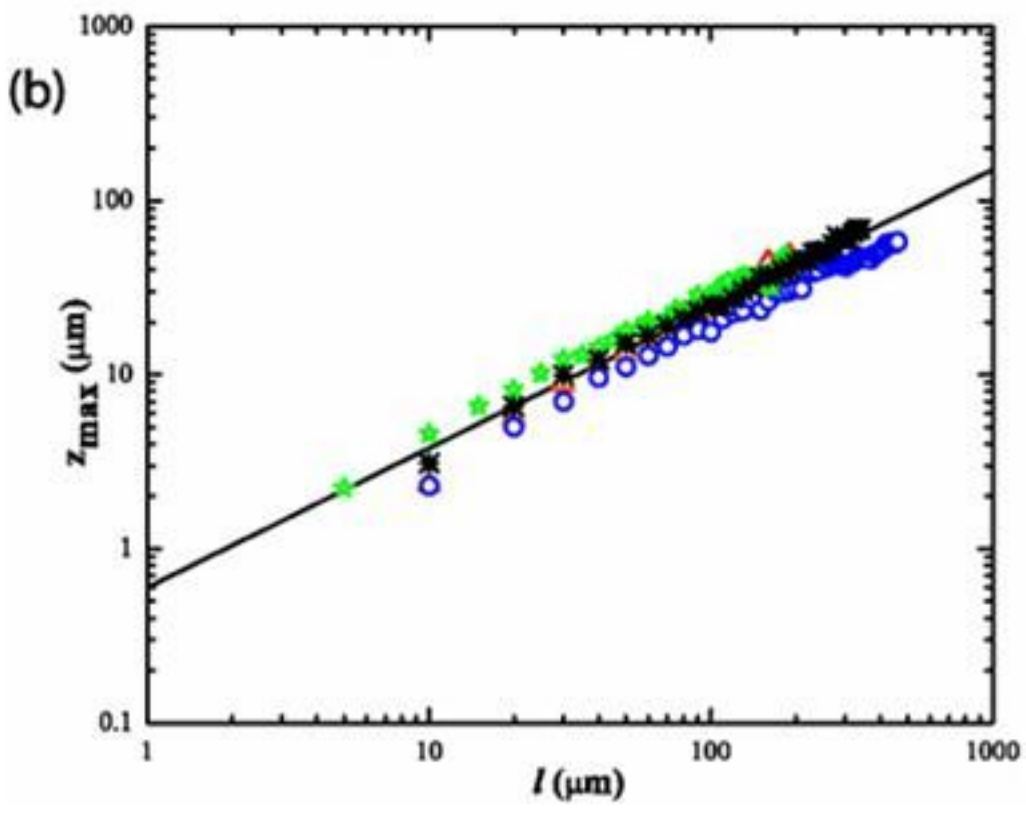
The covalent-type interaction between sililca particles (Si-O-Si) is stronger than the van der Waal type interaction between polystyrene particles

$\varphi_s = 1$







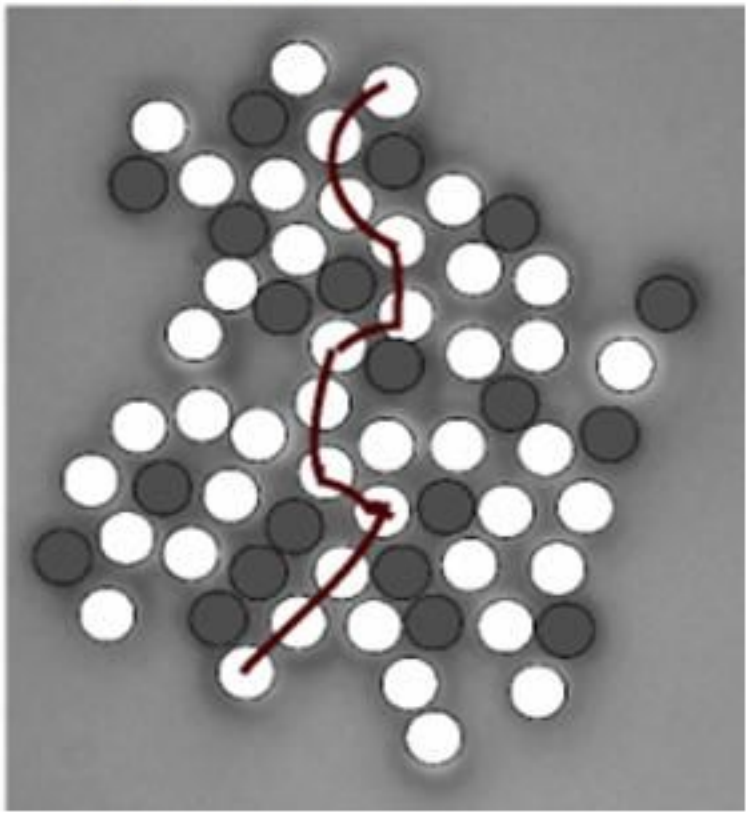


$$z_{max} \sim l^{\kappa},$$

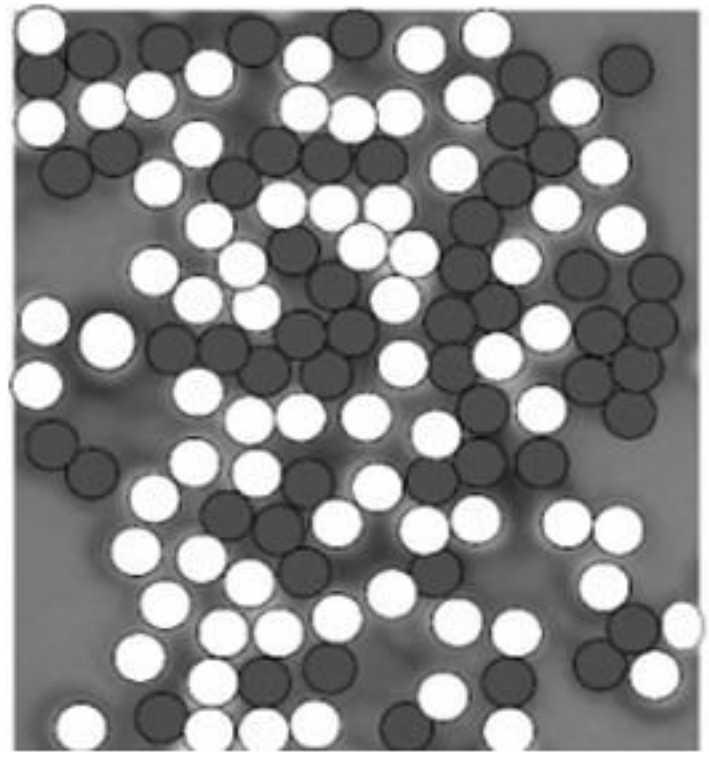
χ=0.8

Silica- Polystyrene mixture

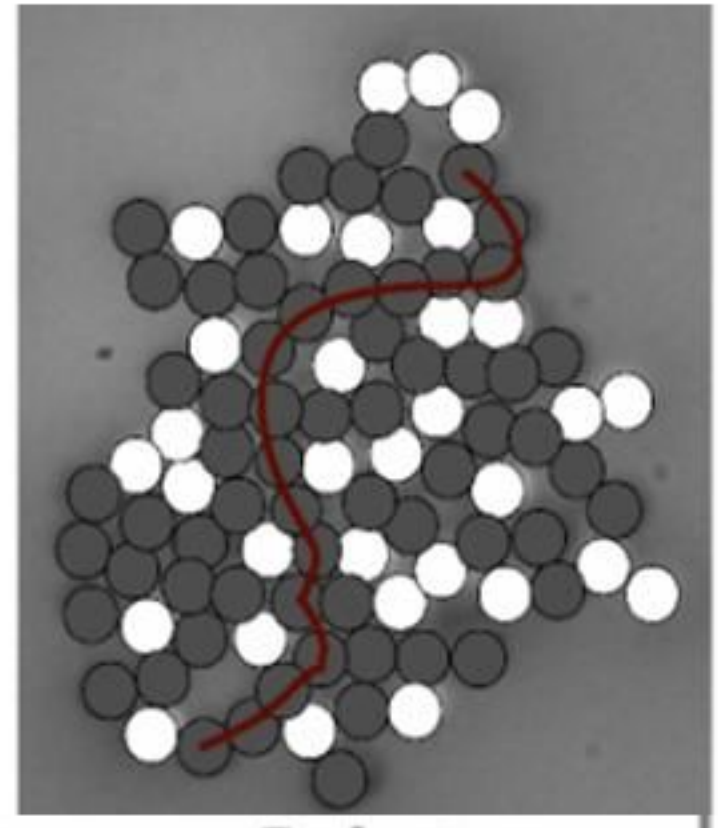
$\varphi(\mathrm{Si}) = 0.2$



$\varphi(\mathrm{Si}) = 0.5$



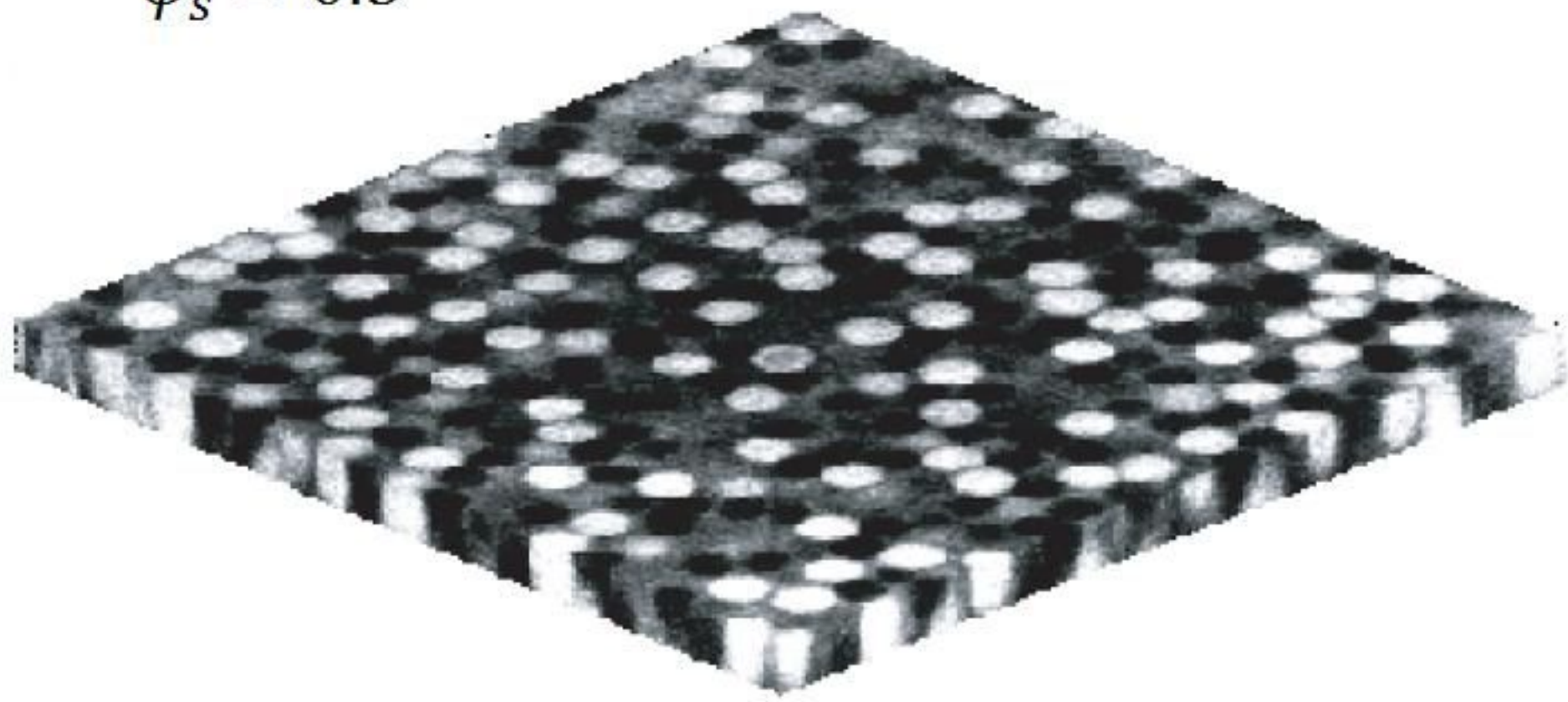
$\varphi(\mathrm{Si}) = 0.8$

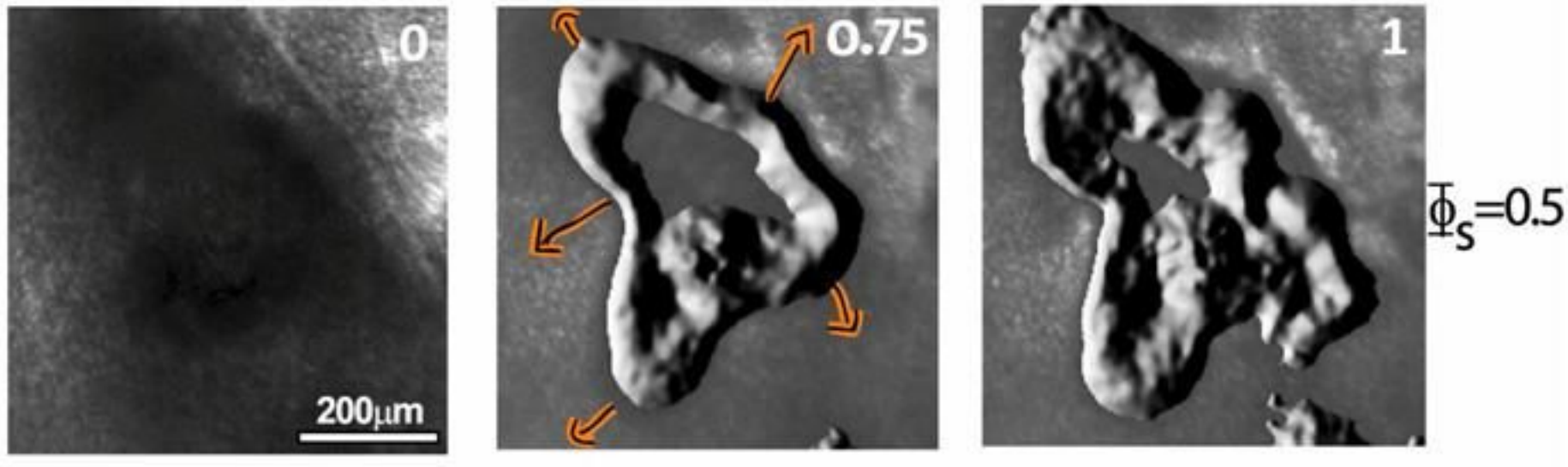


Increasing the silica fraction in the mixture increases the density and connectivity of the mechanically stronger silica clusters, thereby enhancing the rigidity of the film

$$0.3 < \phi_s < 0.8$$

$\varphi_s = 0.5$





Vapor-like for small silica fraction , ($\phi(s)<0.3$),

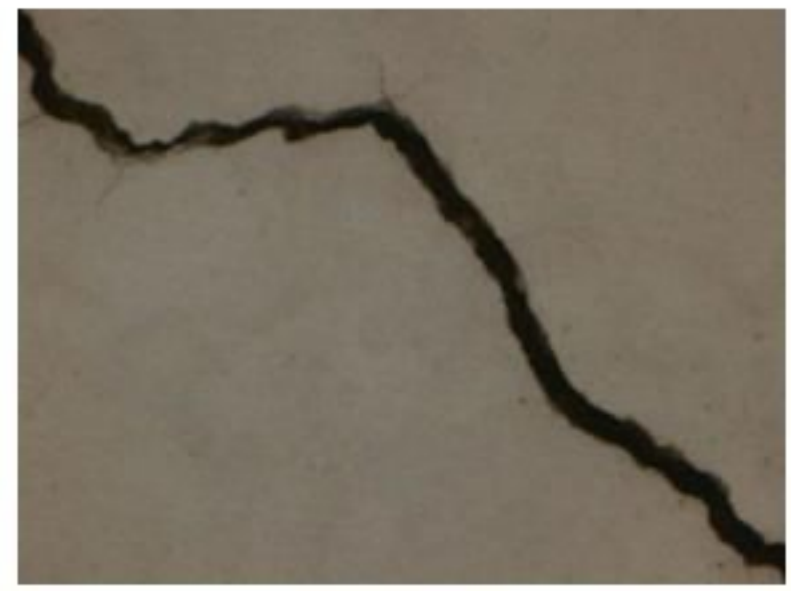
In the vapor-like regime, the micrographs show that spatially uncorrelated particles evaporate individually with increasing E,

Mixed type in the intermediate regime ($0.3<\phi(s)<0.8$)

delamination proceeds in the form of larger spatially contiguous areas with irregular boundary, reminiscent of, for example, correlated flow of liquids in blisters

Solid-like for large silica fraction ($\phi(s)>0.8$)

delamination proceeds by nucleation of cracks and their propagation and eventual delamination as chunks containing 100's of particles

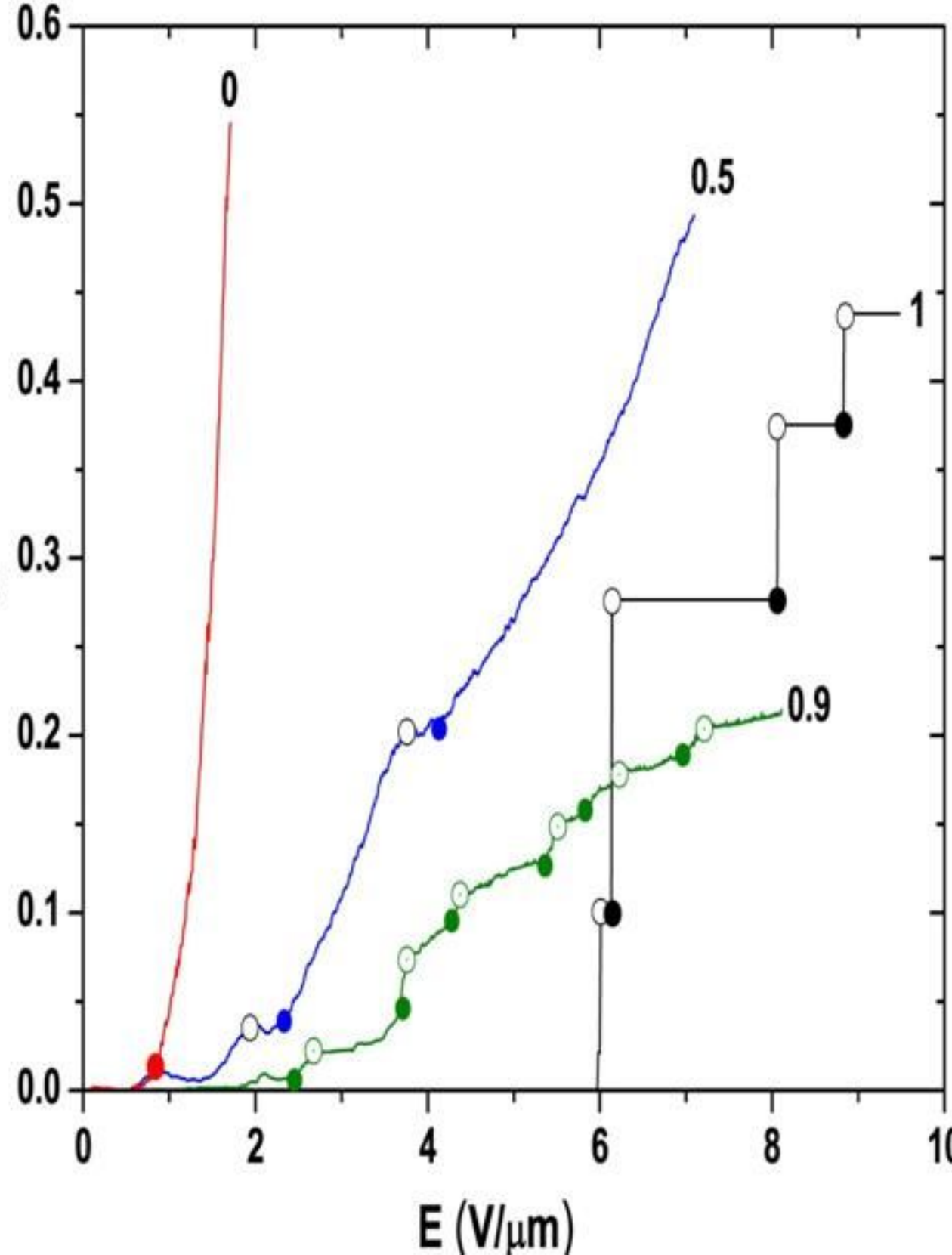


Variation of the fraction of delaminated area (A_d) as a function of electric field

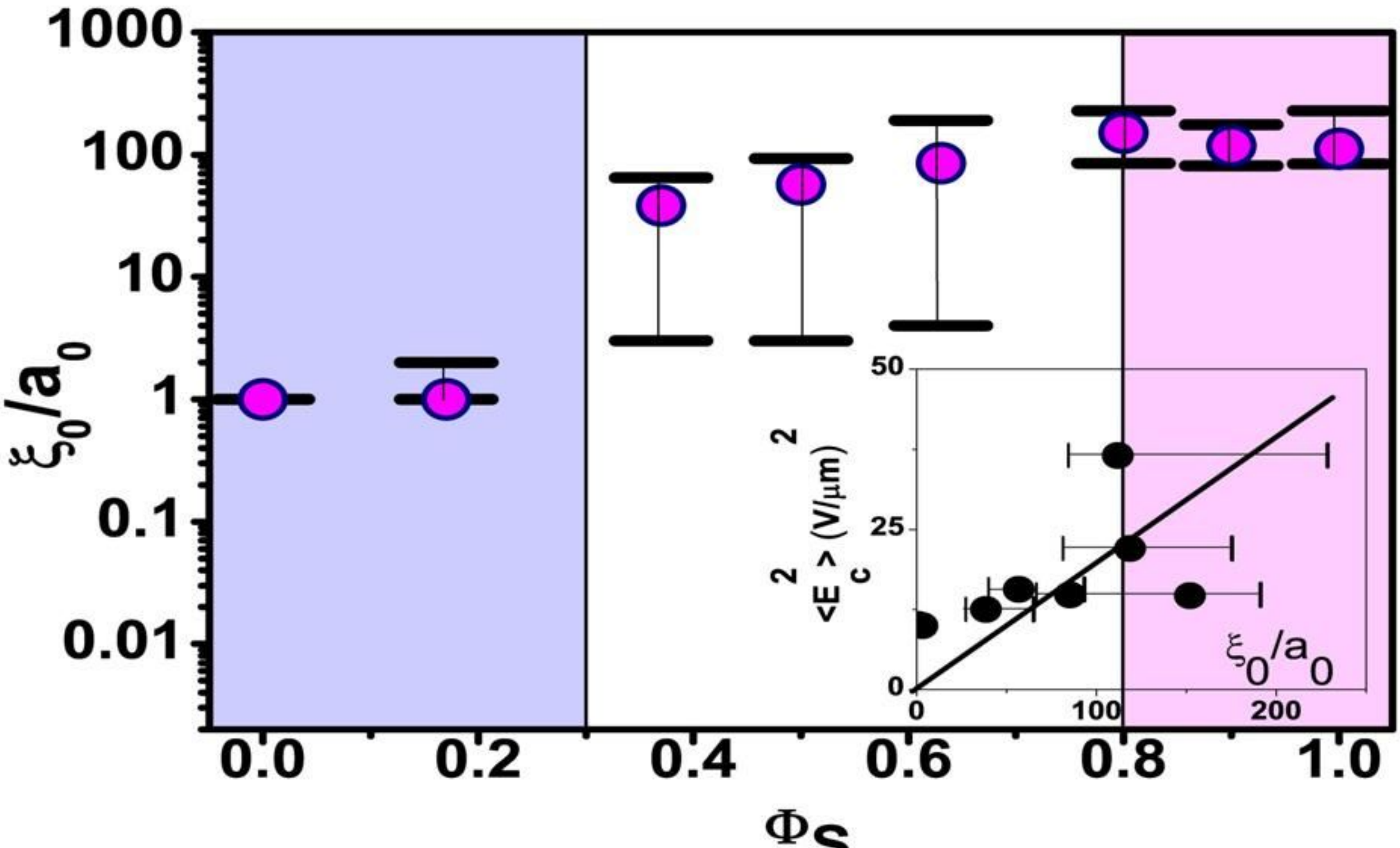
- For soft films, the delamination sets in at low values of the field and A_d grows smoothly, consistent with the observation of sequential evaporation of single particles

- At intermediate rigidity ($\varphi(s)>0.3$), the onset does not change appreciably but the curve begins to display jaggedness.

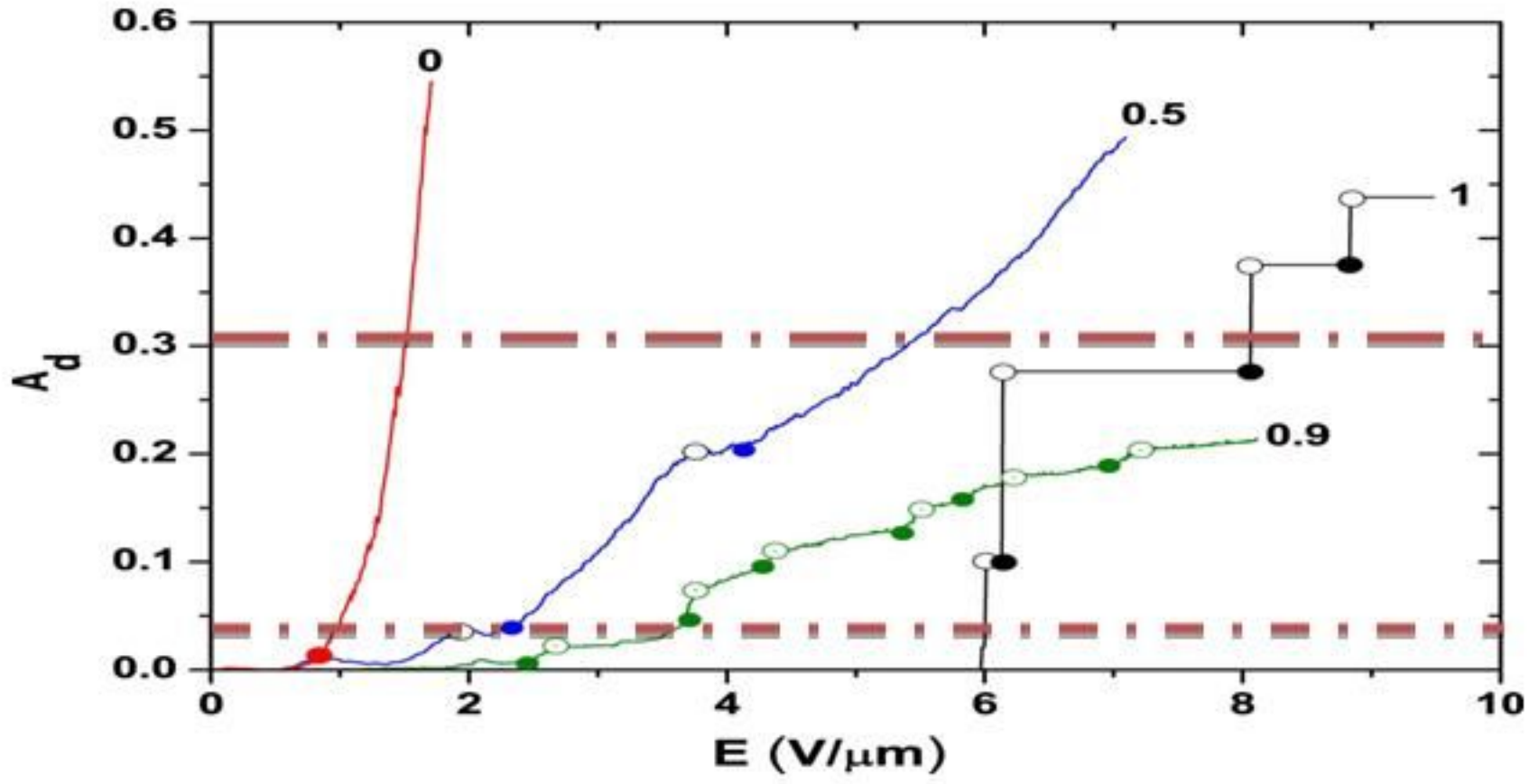
- For purely silica films ($\varphi(s)=0.1$) of larger rigidity, a sequential delamination of large chunks are seen as sharp jumps of A_d, separated by large field intervals where no delamination occurs.



Variation of correlation as a function of silica volume fraction.



Definition of an average critical stress in the system



The average of square critical electric field was calculated as follows

$$\langle {E_c}^2 \rangle = \frac{\sum_i \left({E_i}^2\right) f\left(A_d | E_i, E_{i+1}\right)}{\sum_i f\left(A_d | E_i, E_{i+1}\right)}$$

$0.2 < \sum_i f(A_d|E_i, E_{i+1}) \leq 0.3 \ (\sim W)$

$\sum_d f(A_d|E_i, E_{i+1}) \leq 0.3$

$\sum f(A_d|E_i, E_{i+1}) \leq 0.001 \ (\sim G)$

$\langle E_c^2 \rangle (V/\mu m)^2$

100

10

1

0.0

0.2

0.4

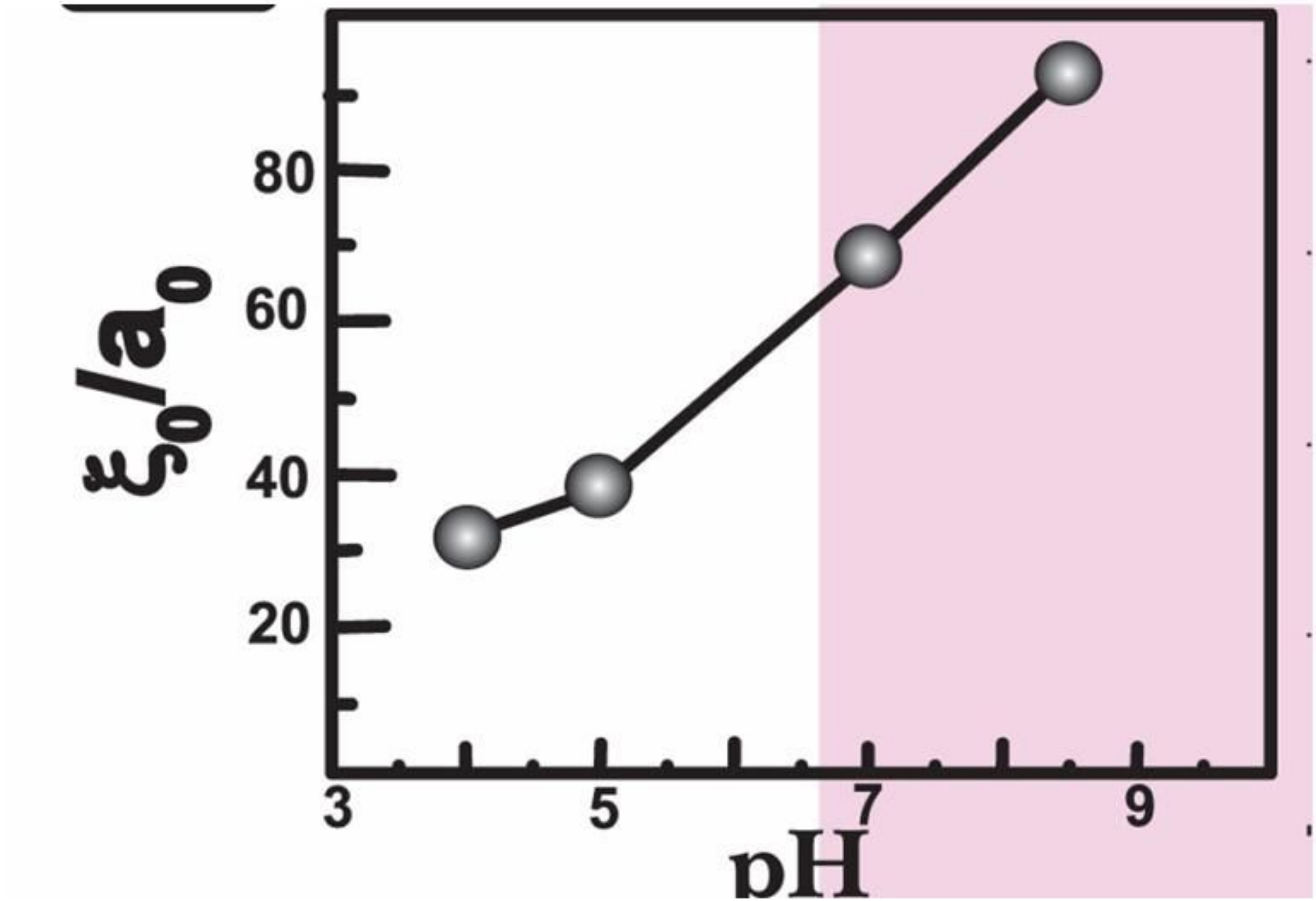
0.6

0.8

1.0

Φ_S

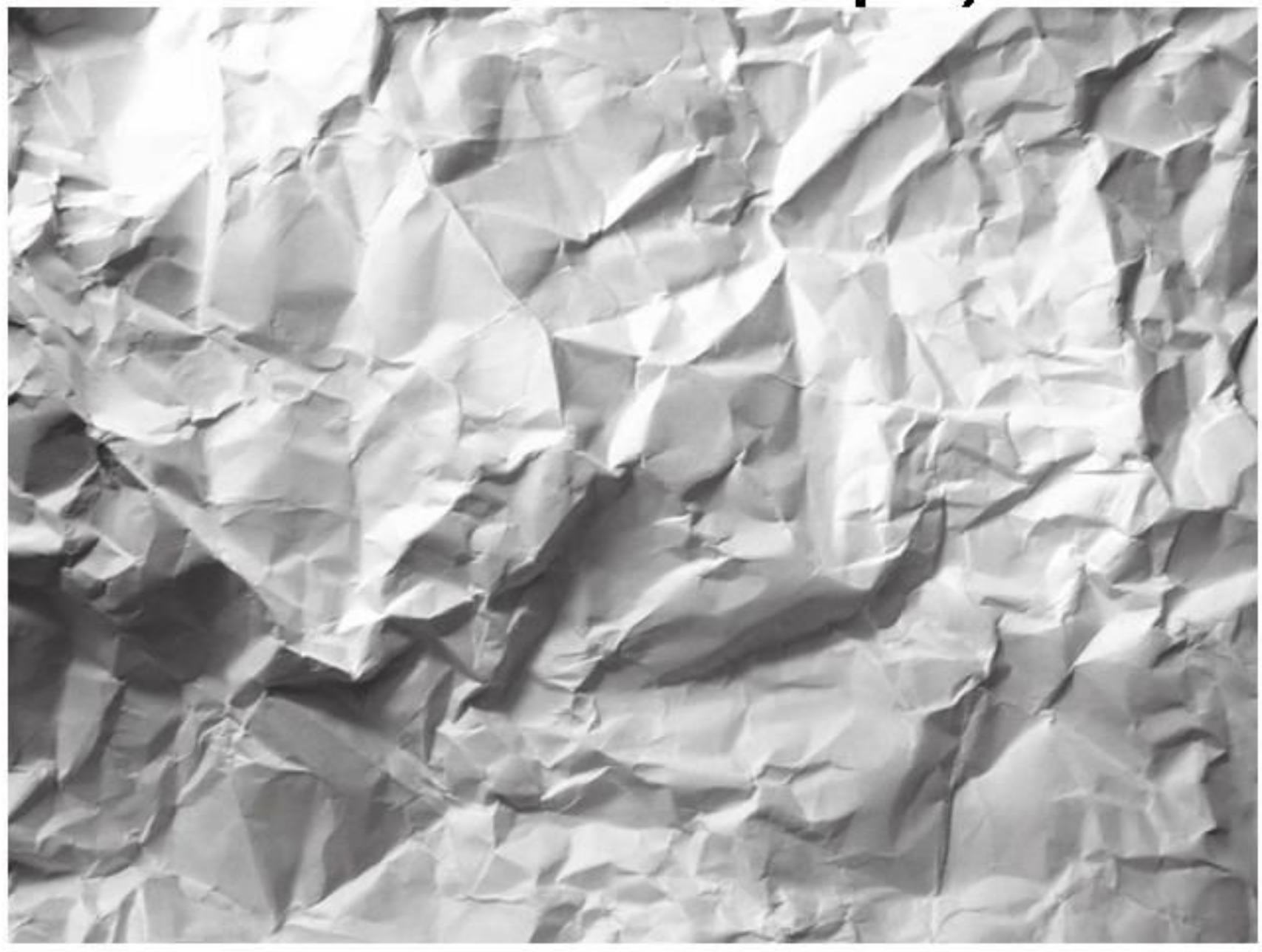
Changing ξ for purely silica films



pH alters the surface charge on silica

What about creep ?

What sets up ξ



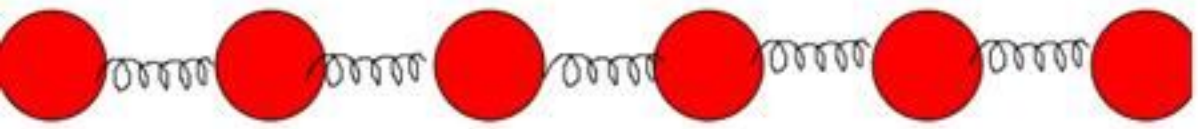
On applying stress the paper rips at the folds

Assumptions

- **Delamination is triggered at the weak spots where defects are located, the collective delamination length is naturally proportional to the correlation length. We assume that when stressed by the electric field beyond a critical strain , the system fails at these weak spots. (ξ(o) is the length scale of failure)**

- **Delamination begins at these locations as the particles overcome not only the in-plane pinning potential but also the sticking potential along the layer-normal .**

Elasticity and Pinning



Lattice without substrate

Long-range order present

Lattice with substrate (Pinning)

Pinning destroys long range orde

$$F = \frac{1}{2} G(u_0/\xi_0)^2 - f_p u_0 \sqrt{\frac{n_p}{V_0}}$$

Elastic energy

$u_o =$ *range of pinning potential*

$G =$ *Rigidity Modulus*

$f_p =$ *pinning force*

$n_p =$ *Volume density of pins*

$V_o = \xi_0^2 a_0 =$ *Correlation Volume*

System in absence of external stress

$$F = \frac{1}{2} G(u_0/\xi\ )^2 - f_p u_0 \sqrt{\frac{n_p}{\xi^2 a_0}}$$

Estimate of the equilibrium elastic correlation (ξ_o) length of the distortion by minimizing F with respect to ξ_o, and is given by:

$$\frac{\partial F}{\partial \xi} = 0 \qquad V_0 = \xi_0^2 a_0$$

$$\xi_0 = G u_0 \sqrt{a_0/W}$$

$$[W = n_p f_p^2]$$

Correlation length (ξ_o) increases with rigidity (G)

Correlation length (ξ_o) decreases with pinning (W)

System in presence of external stress

A critical stress (σ_c), needed to produce a critical strain (γ) above which the system deforms plastically, leading to delamination, is given by

$$\sigma_c = G\gamma_c \qquad\qquad E_c^2 \sim G\gamma_c$$

$$E_c^2 \sim \gamma_c(\xi_0/a_0)\sqrt{\mathrm{W}a_0 \,/\, u_0^2}$$

$$G = (\xi_0/a_0)\sqrt{W a_0/{u_0}^2} \qquad E_c^2 \sim \gamma_c(\xi_0/a_0)\sqrt{W a_0 / u_0^2}$$

- **Both E_c and ξ_0 increase together as the rigidity of the system increases (in the experiment the rigidity (ϕ(s)) of the film increases by increasing).**

- **For a soft film , the particles are individually-pinned, where ξ(0)~a(0) . Naturally, they also delaminate individually. Thus the smooth increase of A_d with E represents a gradual delamination of individual particles and implies the existence of a broad distribution of the local sticking potential.**

- **The appearance of jaggedness in A_d for, say , marks the collective delamination at higher rigidity, as expected.**

Conclusion

- **Detachment of colloidal thin films from a substrate under a controlled external stress such as exerted by an external electric field is an excellent minimal system which captures the essential complexity of the various detachment processes seen in Nature.**

- **Furthermore, the entire process is well-described by using only a few system parameters like the rigidity and the pinning strength. These parameters yield the correlation length over which the system delaminates, an easily measurable quantity in most cases of material failure.**

- **Finally, the observed dynamical phase diagram - illustrating a transition between individual and collective dynamics - its analysis and analogies place the delamination process within a unified conceptual framework of disordered elastic media that include phenomena such as wrinkling, pinning, cracking and**

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