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Microrheology of a sticking transition

Prerna Sharma

Tata Institute of Fundamental Research
Mumbai
India

Microrheology Of Sticking Transition

Prof. S. Bhattacharya
Dr. SHANKAR GHOSH
Mr. Atul Varshney
Mr. Atul Raut
Mr. Anit Sane
Ms. Smita Gohil

Prerna Sharma

TIFR, Mumbai,

India

Sticking of a colloid to a plate

What happens when a colloidal particle suspended in a medium approaches a wall(plate)?

1. *Hindered diffusion* near to the wall(distance between the wall and the particle less than that of the particle's diameter).

2. The colloid may *stick* to the wall if it approaches the wall close enough.

Hindered diffusion

$$D_\perp$$

$$D_\parallel$$
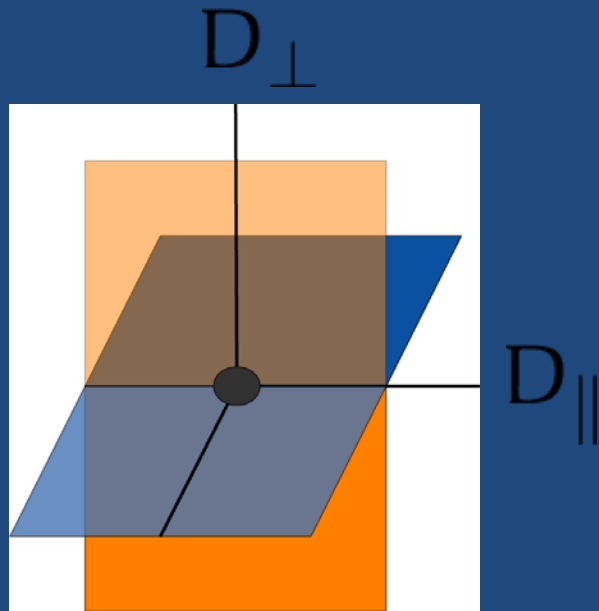
Far away from the plate

$$D_\perp = D_\parallel = D_0$$

As the particle comes close to the wall the diffusion of the particle becomes

(a) Anisotropic : $D_\parallel \neq D_\perp$

(b) Hindered: $D_\parallel, D_\perp << D_0$

In the absence of sticking, on the plate, $D_\perp \rightarrow 0 \quad D_\parallel \rightarrow D_0/3$

When the particle sticks to the plate, $D_\perp \rightarrow 0 \quad D_\parallel \rightarrow 0$

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Stokes-Einstein equation

Einstein showed that the diffusion coefficient of a particle undergoing Brownian motion is
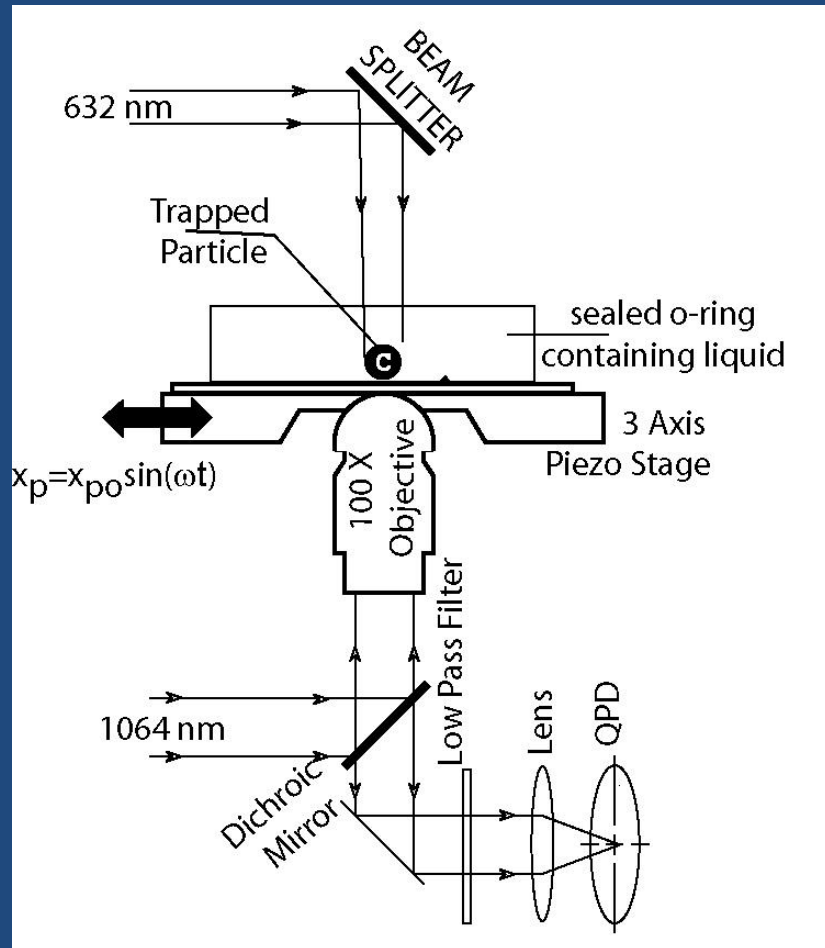
$$D = \frac{\text{Thermal Energy}}{\text{Frictional Coeff.}} = \frac{K_B T}{\xi}$$

In case of purely viscous coupling, ξ in the bulk is given by Stoke's law.
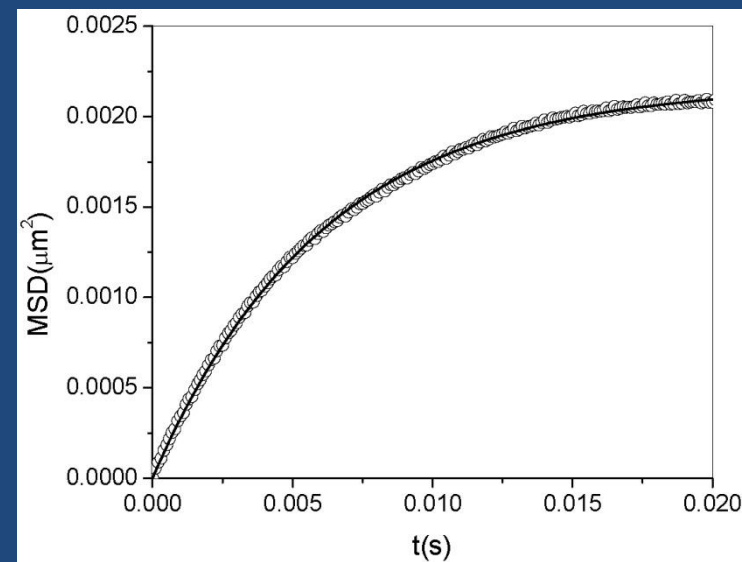
$$\xi = 6\pi\eta a$$

In general, the coupling can be viscoleastic.

Technique: Optical tweezer

$$\gamma \dot{x}(t) + k_{opt} x(t) = f_{random}(t)$$

$$\gamma = 6\pi\eta a$$

Sharma etal, Nature Physics, 4, 960-966 (2008)

Computation of viscoelastic moduli from ac technique

Master equation

$$6\pi\eta a(\dot{x} - \dot{x}_p) + k_{opt}x = 0$$

Substitute

$$x_p = x_{p0}e^{i\omega t} \quad x = x_0 e^{(i\omega t + \phi)} = x_{res}e^{i\omega t}$$

$$\eta = (G'' - iG')/\omega$$

$$G' = \left(\frac{k_{opt}}{6\pi a}\right)\frac{(Re(x_{res})x_{p0} - |x_{res}|^2)}{(x_{p0} - Re(x_{res}))^2 + Im(x_{res})^2}$$

$$G'' = \left(\frac{k_{opt}}{6\pi a}\right)\frac{x_{p0}Im(x_{res})}{(x_{p0} - Re(x_{res}))^2 + Im(x_{res})^2}$$

Protocol to study sticking

1. Hold the particle in an optical trap.

2. Change the distance between the particle and the plate by moving the plate towards the trapped particle in steps of 20nm using piezo stage.

3. At each displacement of the plate measure $D_{\parallel}$ of the particle using both Rms as well as AC technique.

4. When $D_{\parallel} \sim D_0/3$ stop moving the plate up and measure $D_{\parallel}$ as a function of time.

Raw data from ac technique
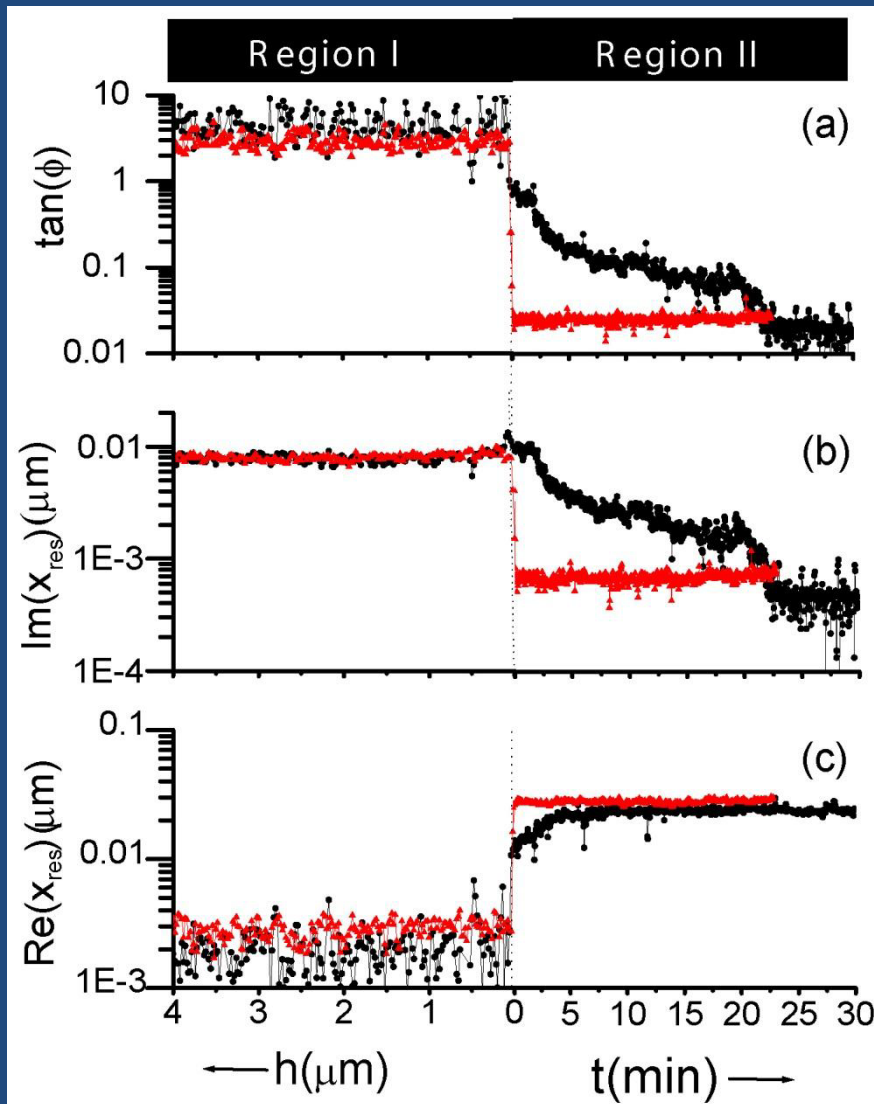
$$tan(\phi) = \frac{k_{opt}}{6\pi\eta_{eff}a\omega} = \frac{k_{opt}D}{K_bT\omega}$$

▲ Silica

● Polystyrene

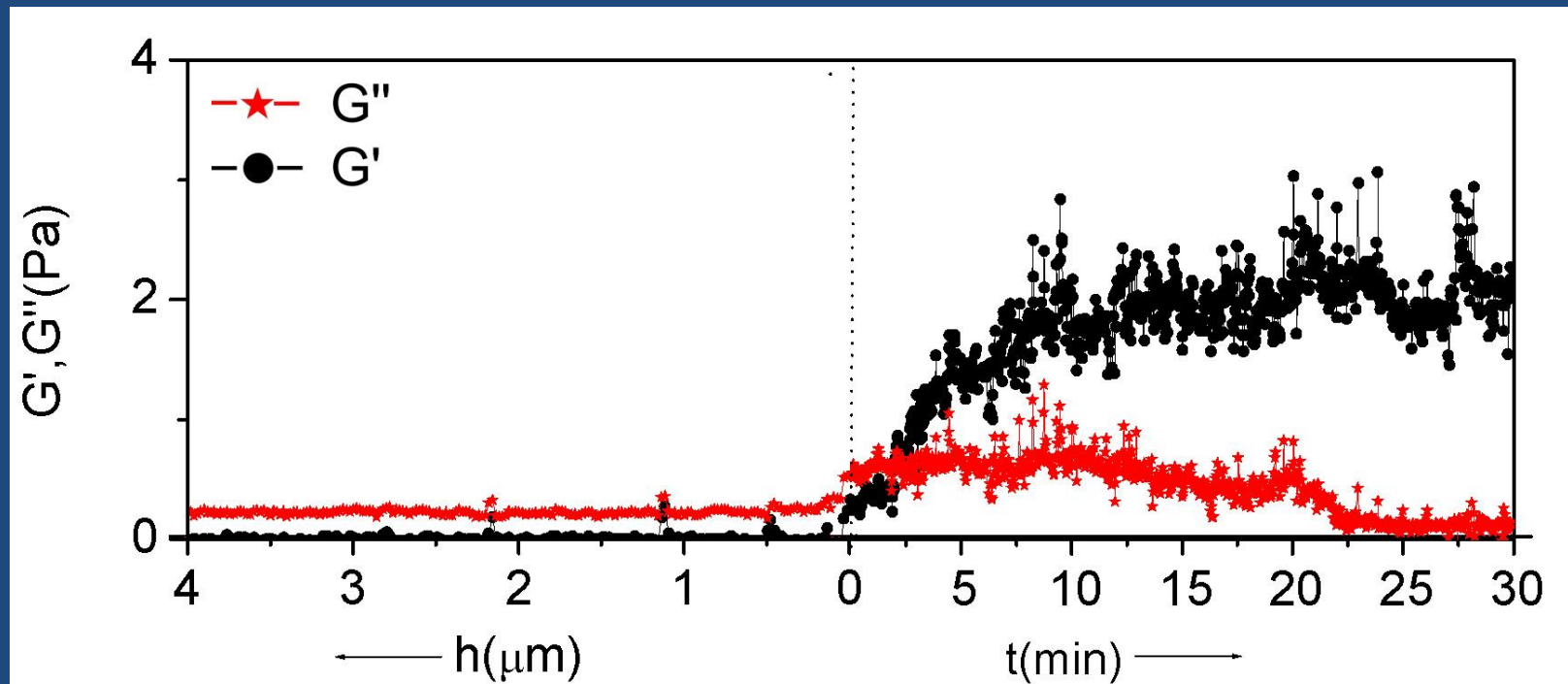Sphere far in the liquid
Viscous coupling

$$Re(x_0) \neq 0$$

$$Im(x_0) \neq 0$$

Sphere near to the plate
Elastic coupling

$$Re(x_0) \neq 0$$

$$Im(x_0) = 0$$

Sharma etal, Nature Physics, 4, 960-966 (2008)

Typical results from G',G''

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.

Sharma etal, Nature Physics, 4, 960-966 (2008)

Slow dynamics

Why is there a time dependence for polystyrene and not for silica?

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.

Can we tune the sticking behavior of polystyrene spheres?
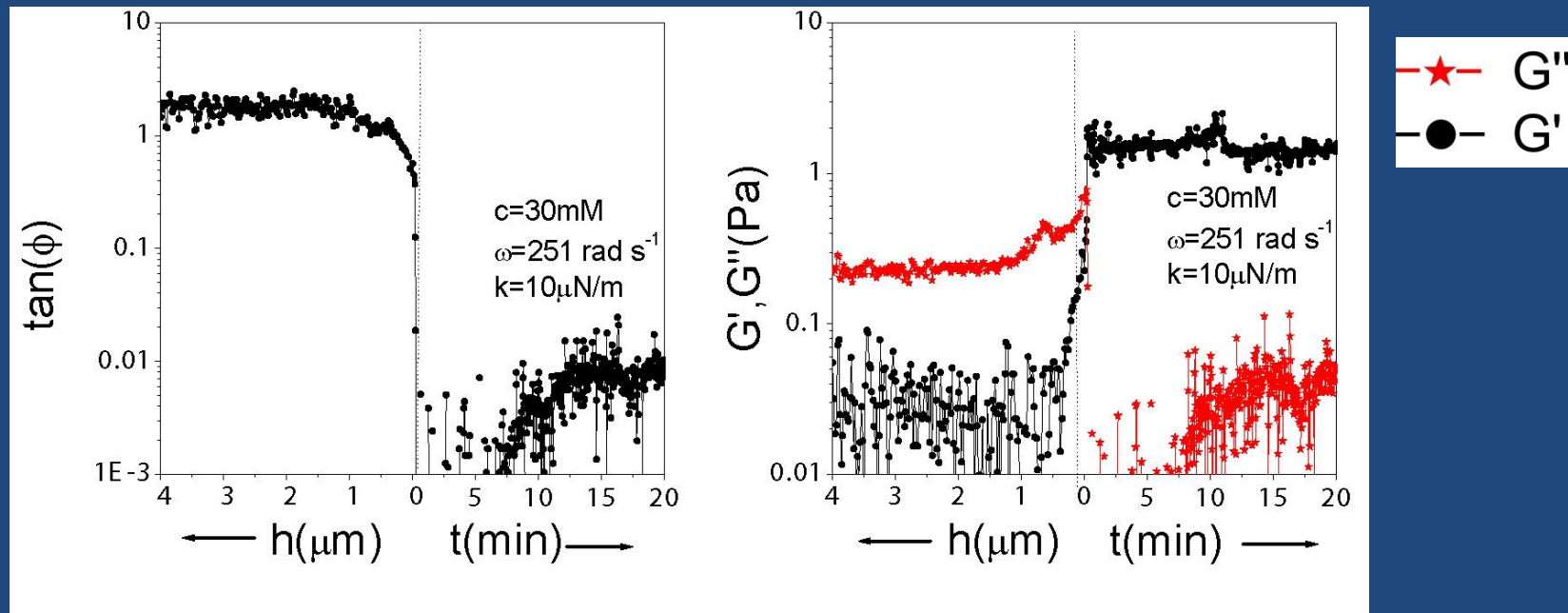
Tuning the sticking behavior of the colloid

Control Parameters
1. Salt concentration
2. Optical trap stiffness
3. Frequency of oscillation of the container.
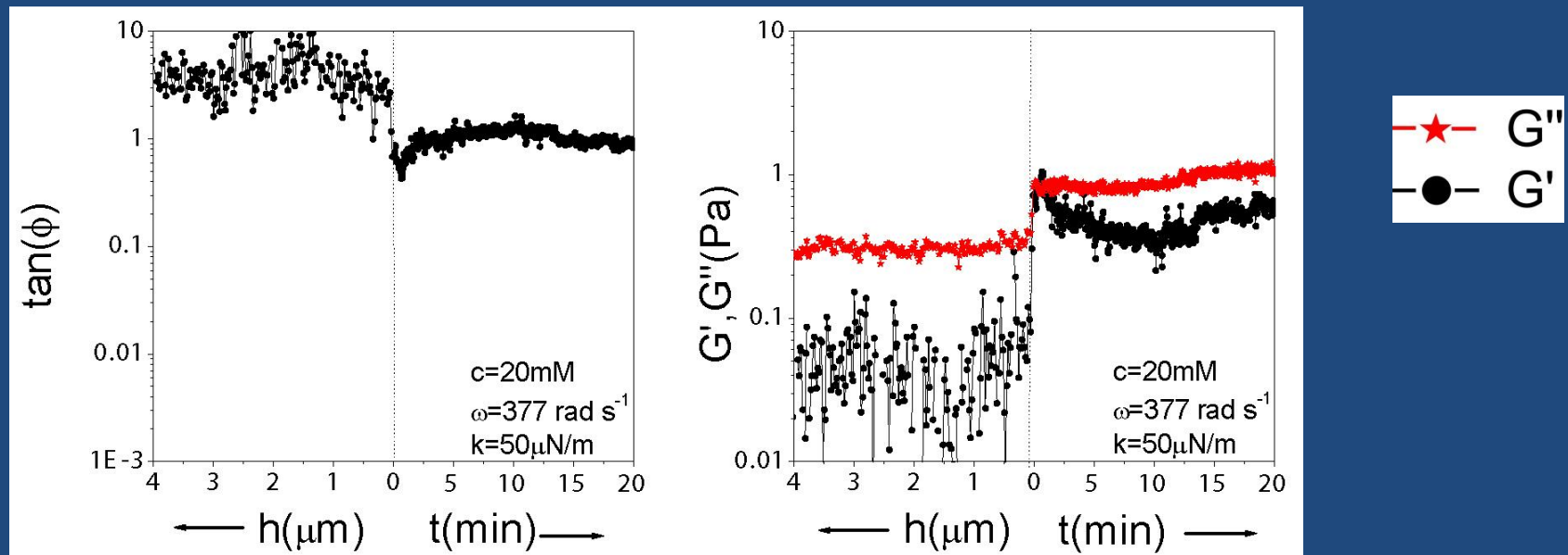
Regimes of sticking
1. Slow Relaxation/Aging
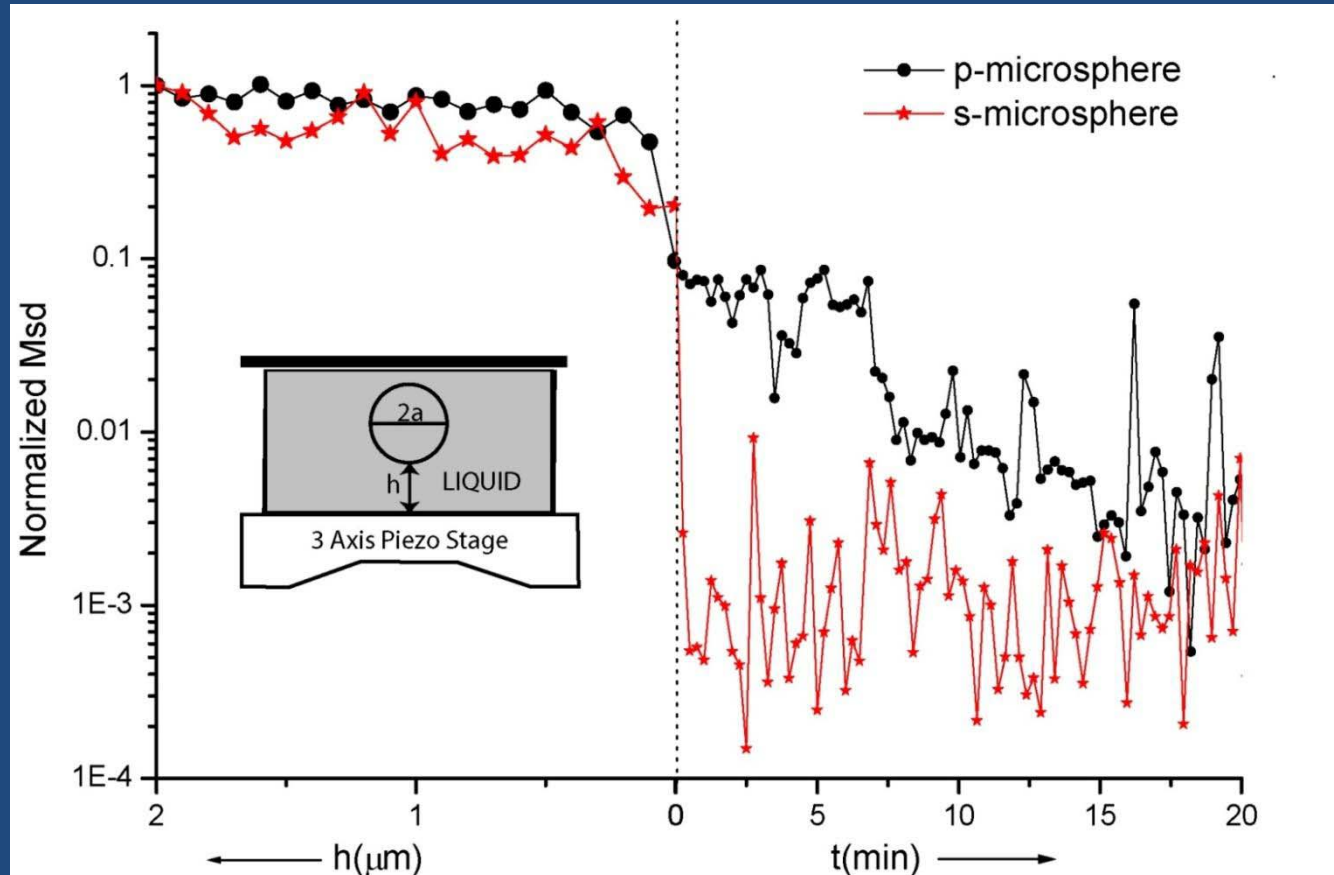2. Well-Stuck
3. Non-stuck/Slip

Stuck regime

Stuck : phase goes to zero, implies G' >> G'', more elastic than viscous.

Sharma etal, Nature Physics, 4, 960-966 (2008)

Non stuck

Non-stuck : phase does not go to zero, but to a terminal value G' ~ G'', more viscous than elastic coupling.
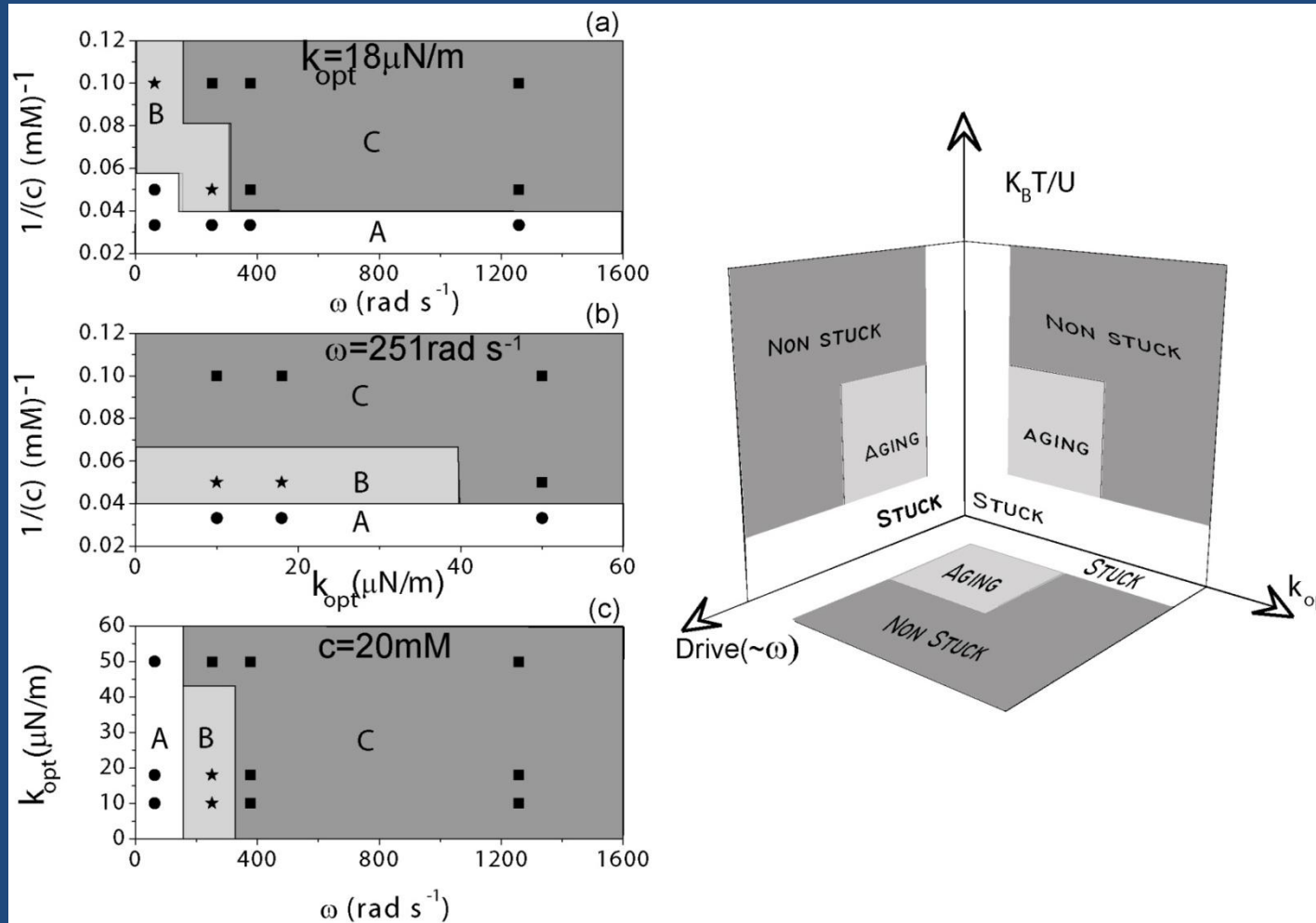
Sharma etal, Nature Physics, 4, 960-966 (2008)

Variations of mean squared displacement

$$\langle x^2 \rangle = \frac{K_B T}{\gamma \pi^2} \int_{f_L}^{f_U} \frac{df}{f^2 + f_c^2} \qquad f_c = \frac{k_{opt}}{2\pi\gamma}$$

Sharma etal, Nature Physics, 4, 960-966 (2008)

Phase diagram

A: Stuck

B: Slow relaxation

C: Non-Stuck

Flexible Bonds between Latex Particles and Solid Surfaces

1. Flexible bonds. We observed that a large fraction (sometimes up to 50%) of the latex particles deposited on a collector surface executed a type of oscillatory or "dancing" motion, especially when subjected to turbulent flow. Typically a latex particle moves irregularly over a certain site; its lateral motion can vary from a fraction of a micrometer to several micrometers. This motion was observed with all latices and all collectors used. In contrast, TiO$_2$ particles of diameter 0.1–0.2 μm did not show these flexible bonds, although some aggregates were able to rotate about an axis, however, without translational motion. Single TiO$_2$ particles usually moved for a short time ($\leqslant$1 sec) in an irregular fashion over the surface before becoming motionless.

From the observed motion of latex spheres tethered to collector surfaces (and to other spheres), it must be concluded that long chain-like structures exist in latex systems. The fact that flexible bonds were only observed with latices and not in TiO$_2$ systems makes it highly unlikely that impurities in water or other artifacts could be responsible for this phenomenon.

Whatever the explanation, from the observations reported in this note it seems clear that not all monodisperse emulsion polymerization latices can be uncritically considered model colloidal systems, especially in deposition and stability investigations.

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Conclusions

1. Sticking of polystyrene microspheres is different from that of silica spheres, probably due to the presence of 'polymeric tethers'.

2. A phase diagram of sticking of polystyrene microspheres was obtained by tuning the salt concentration and the drive.