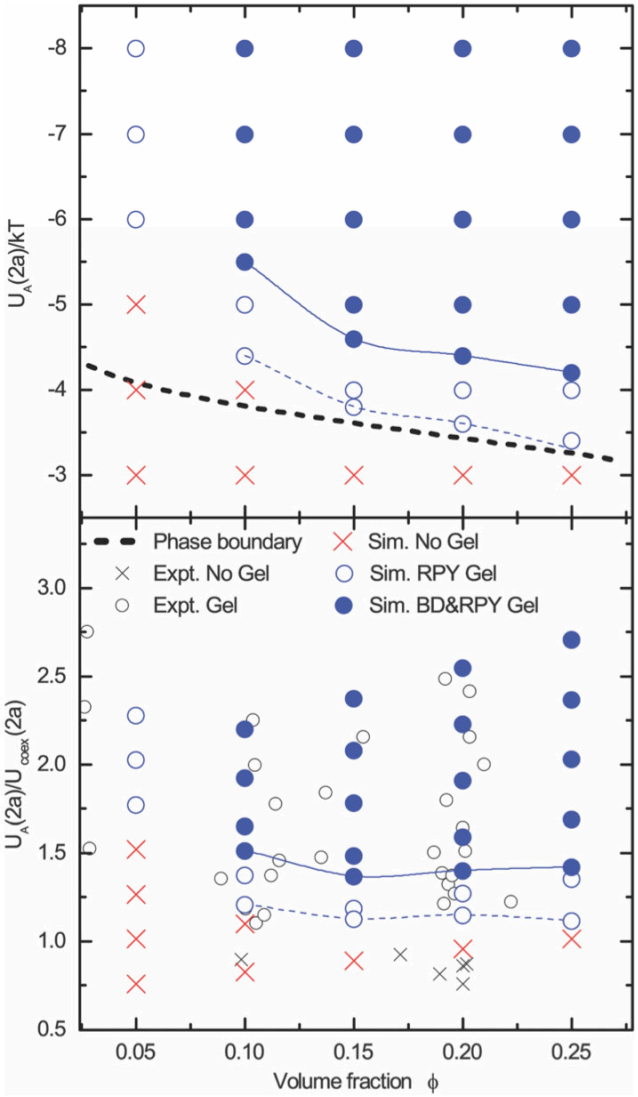
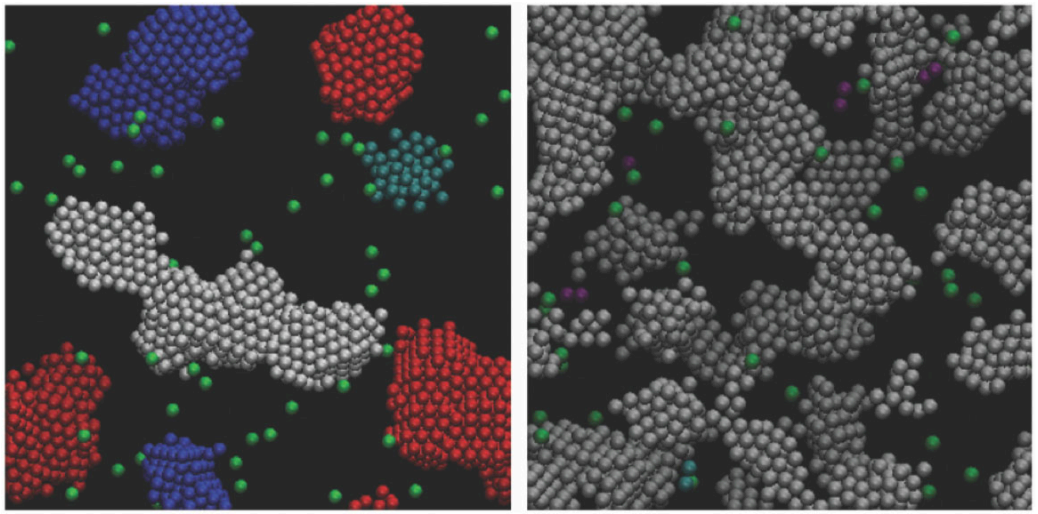
# Structure in flows

# Hydrodynamic interactions

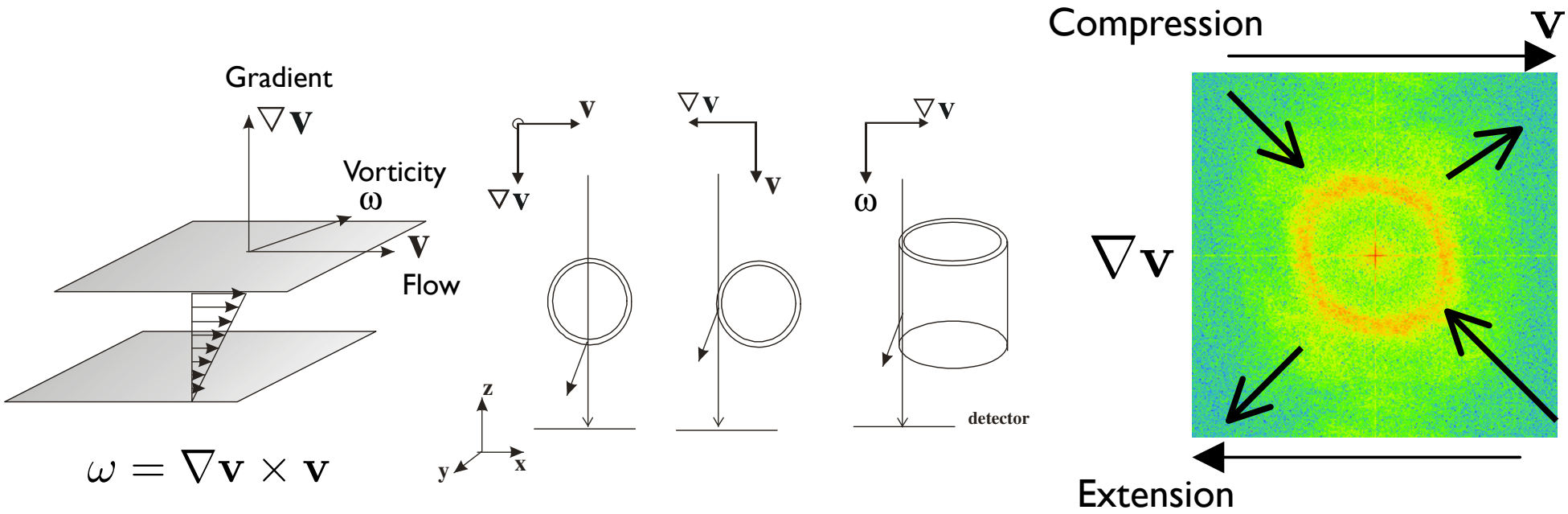
Varga, Z., Wang, G. & Swan, J. The hydrodynamics of colloidal gelation. Soft Matter 11, 9009–9019 (2015).



# Structure in flow

J. Vermant and M. J. Solomon, J. Phys.: Condens. Matter 17, R187 (2005).

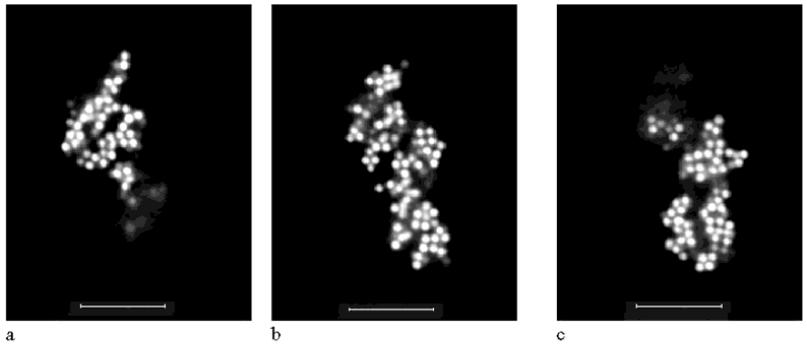


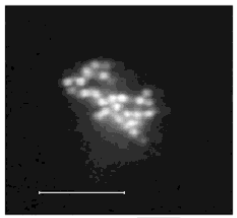

Microstructure subjected to compression and extension in shear flow.

# Effect of flow on structure

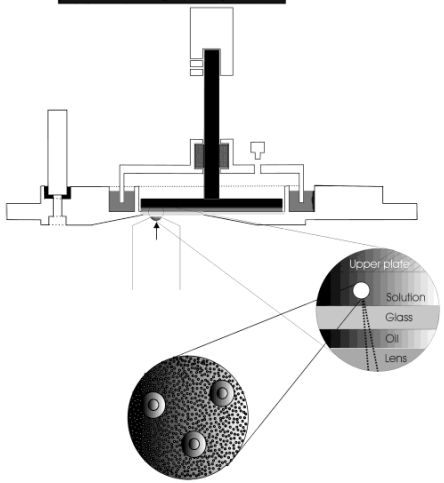
## Flow affects the size, density and structural organization.

V. A. Tolpekin, M. H. G. Duits, D. van den Ende, and J. Mellema,
Langmuir 20, 2614 (2004).

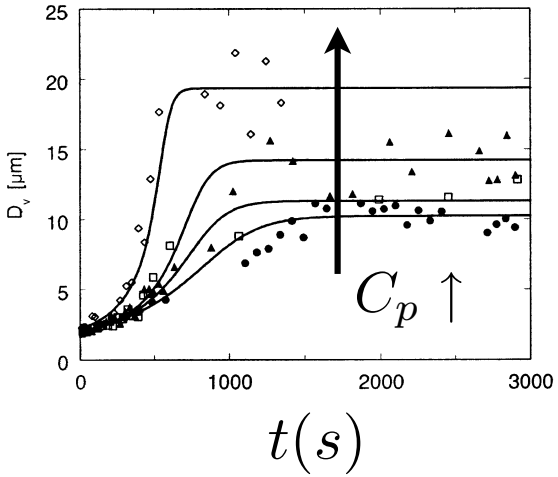


$\phi = 0.001 \quad d_f \approx 2.0$




Average aggregate size

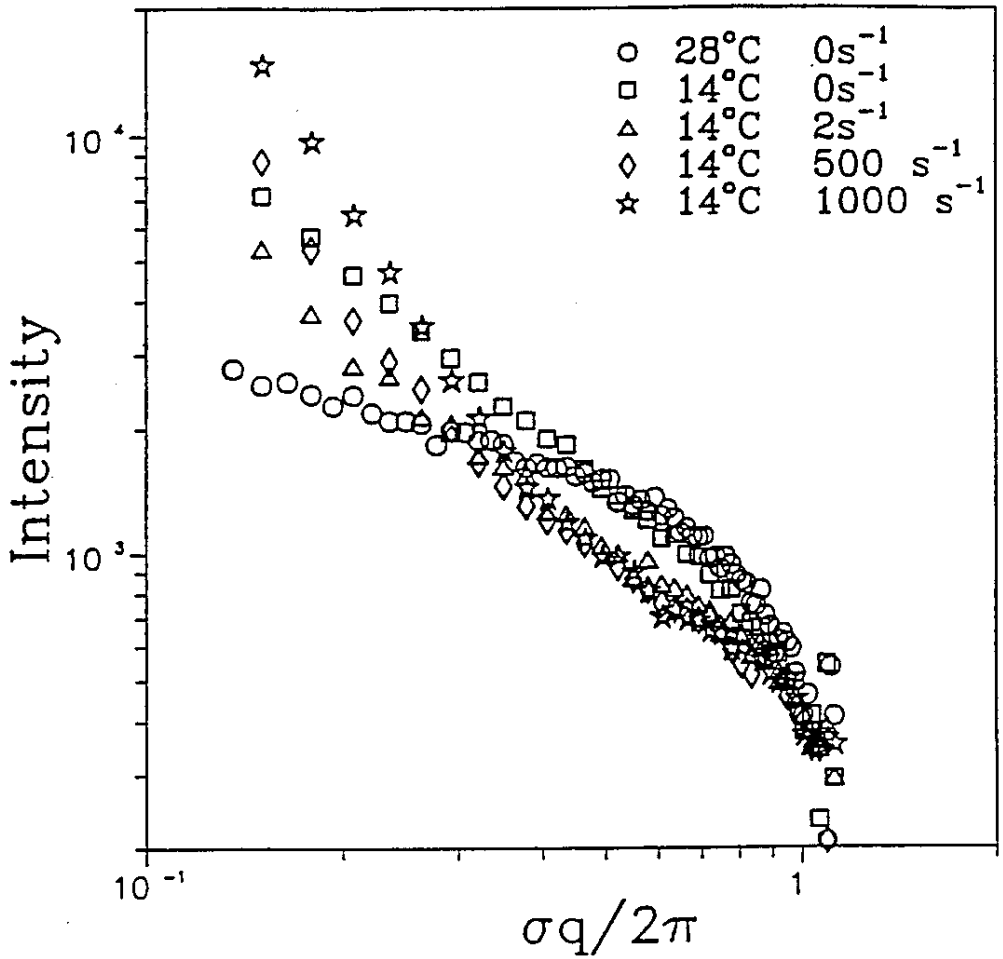



- Aggregate size determined by competition between attractive forces and hydrodynamic stresses.
- Aggregates larger with higher attraction, smaller with stronger shear.
- Fractal structure enables prediction of aggregation curve.

# Compaction in flow

C. Rueb and C. Zukoski, J. Rheol. 41, 197 (1997).

Organophilic silica in tetradecane



# Higher concentrations

## "Butterfly" pattern

P. Varadan and M. Solomon,
Langmuir 17, 2918 (2001).

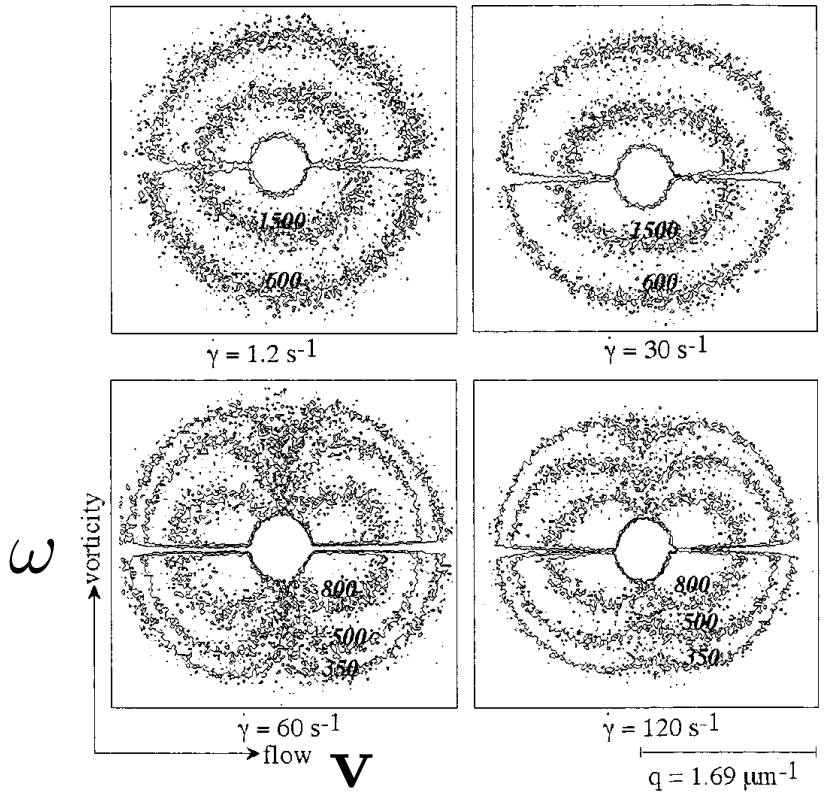
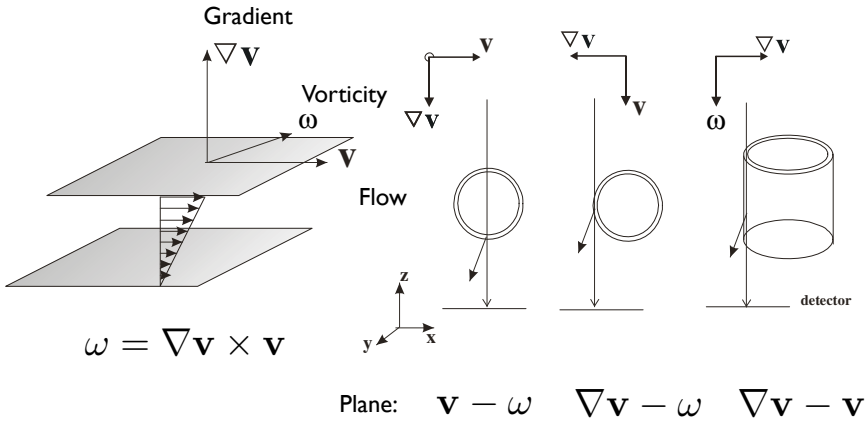
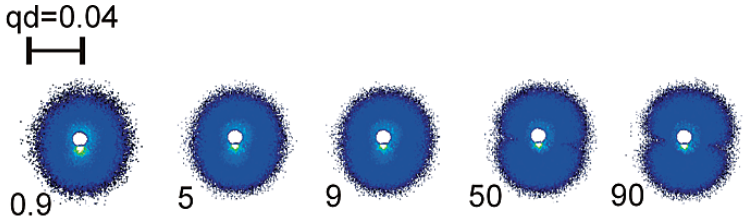



Figure 6. Isointensity contours showing the evolution of the anisotropy in the flow−vorticity plane at high shear rates for $\phi = 0.1$. The intensity values of the contours are shown in each image.

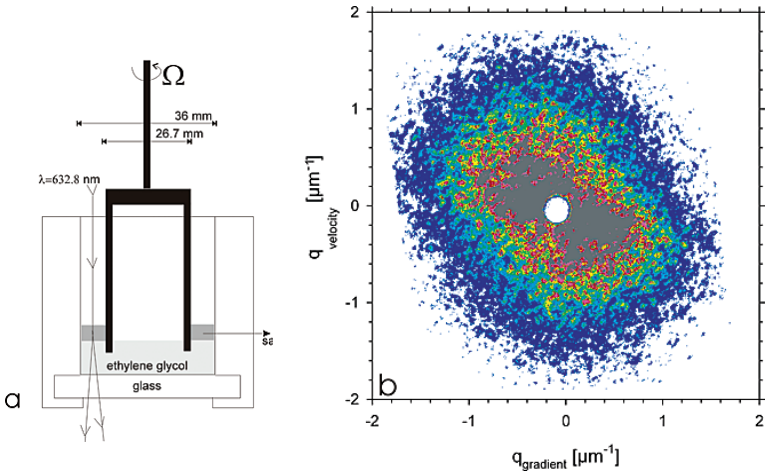



- Higher volume fractions, size reduction and flow densification are still observed.
- Self-similarity of the structure breaks down during shear flow.
- The microstructure becomes anisotropic.

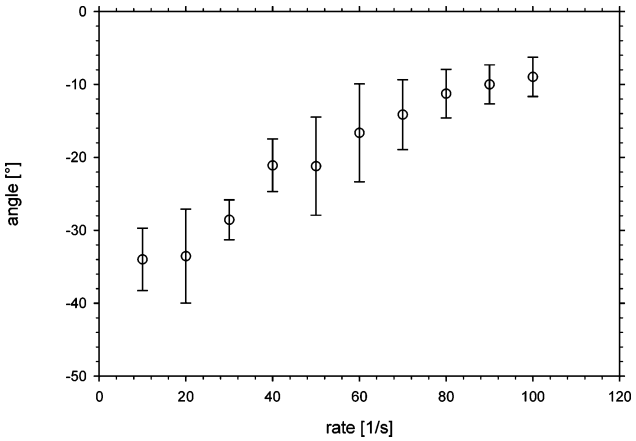
## Scattering in gradient direction




## Scattering in vorticity direction




## Orientation in vorticity plane




## Combined scattering results

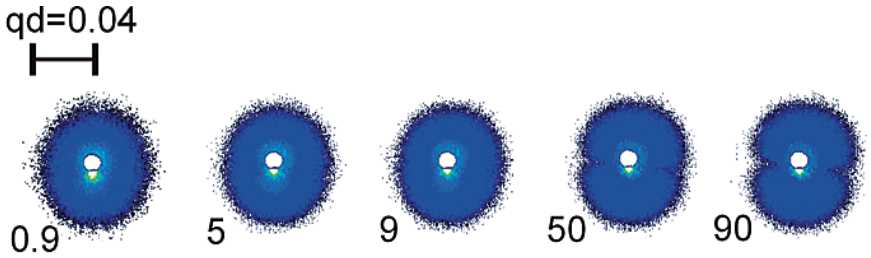
| | SAXS | USAXS | SALS |
|---|---|---|---|
| ω, v | | X | |
| ω, γ̇ | | X | X |
| γ̇, v | X | $I_{\dot\gamma} \neq I_v$ | |

**Figure 13.** Overview of the structural information from the different scattering techniques during shear flow for a sticky sphere suspension. In the scattering planes marked with an X no information is available for the given scattering technique.

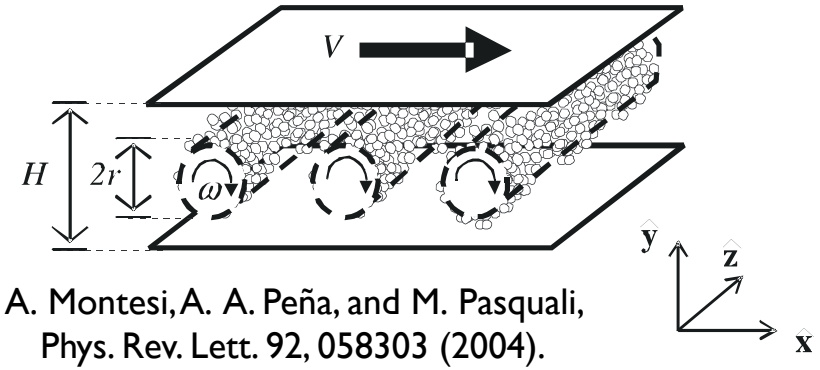
# Structure is complex and hierarchical

# Proposed mechanisms

## Velocity gradient direction

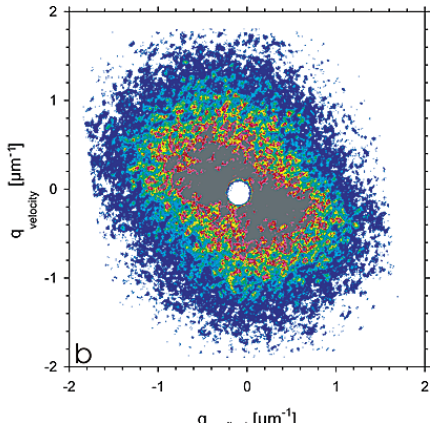


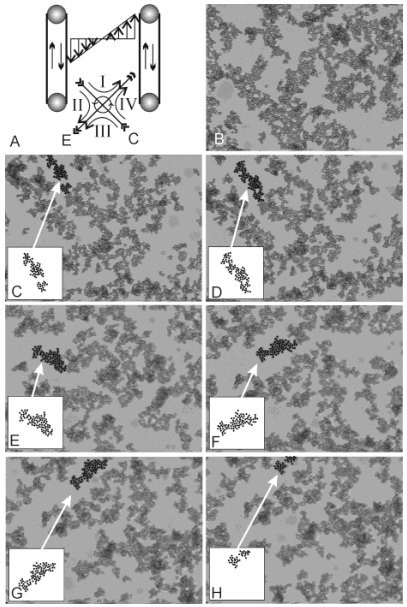

## Rolling




A. Montesi, A. A. Peña, and M. Pasquali,
Phys. Rev. Lett. 92, 058303 (2004).

## Vorticity direction




## Extension and compression

H. Hoekstra, et al. Langmuir,
19:9134–9141, 2003.

# Structure in shear flow

H. Hoekstra, et al. Langmuir, 19:9134–9141, 2003.

- Apparent aggregate size during flow reveals weak dependence on shear rate and is direction dependent. A hierarchy of structures is present.
- Large scale structural inhomogeneity is induced by flow which leads to an anistropic scattering patterns in the velocity gradient and vorticity planes. The magnitude of the anisotropy increases with increasing shear rate.
- The average orientation in the vorticity plane evolves from an orientation close to -45° toward the flow direction with increasing shear rate. The large length scale anisotropy and the anisotropic aggregate shape are explained by the directional dependence of aggregation and break-up processes.
- The direction dependent assembly and subsequent rupture also result in aggregates which are anisotropic in size, larger structures existing along the compression axis of the flow field, as shown by the USAXS measurements.
- The observed densification of the aggregates on a more local scale combined with the reversal of the local scale anisotropy observed in SAXS measurements, are consistent with the mechanism of structure formation. The aggregates are internally compressed when these larger scale structures are formed by compressing aggregates together.

Hierarchy and simple mechanism for many systems

# Startup of steady shear

A. Mohraz and M. J. Solomon, J. Rheol. 49, 657 (2005).

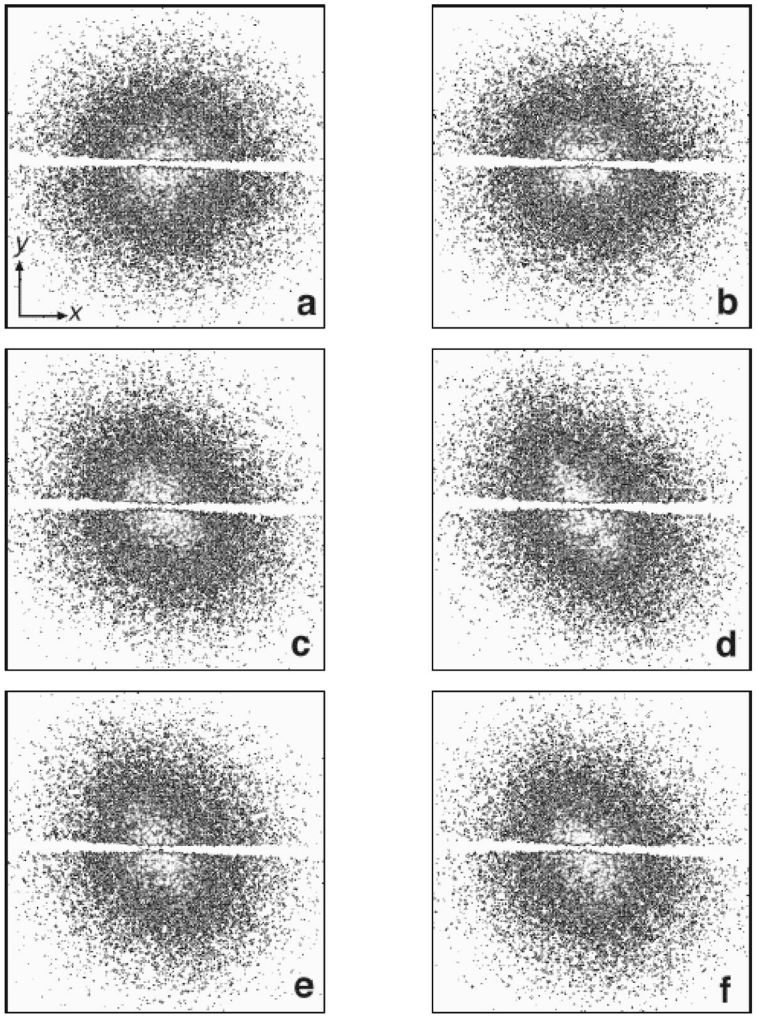
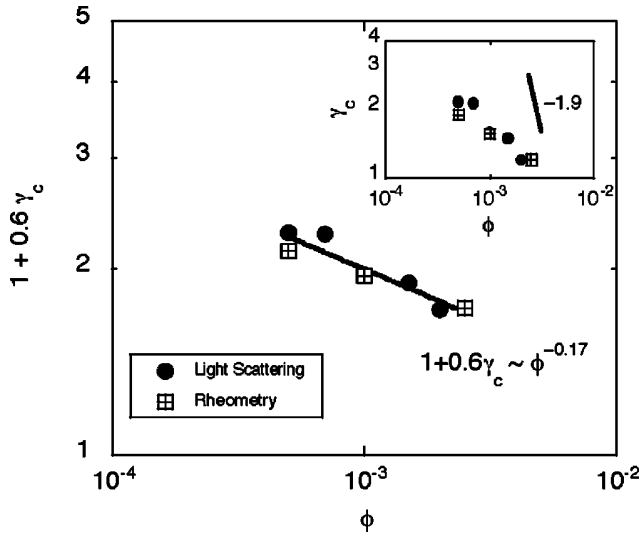



**FIG. 4.** Contour plots of a representative cascade of scattering patterns collected during start-up of steady shea flow of DLCA polystyrene gels with $\phi=1.0\times10^{-3}$ and $\dot{\gamma}=0.56\ s^{-1}$, and $t$= (a) −0.1, (b) 1.1, (c) 2.2, (d) 3.5, (e 6.3, (f) 8.3 s. The time $t$=0 corresponds to the inception of shear. Maximum anisotropy is observed at ~3.5 s. The low-intensity region in the middle of images is due to the beam stop.

$$1 + 0.6\gamma_c \sim \phi^{(1-d_b)(3-d_f)}$$




- Scaling agrees with the simple model of a gel network that ruptures after the cluster backbone is extended affinely to its full length.
- Rheological measurements demonstrate that the maximum anisotropy coincides with a maximum in shear stress

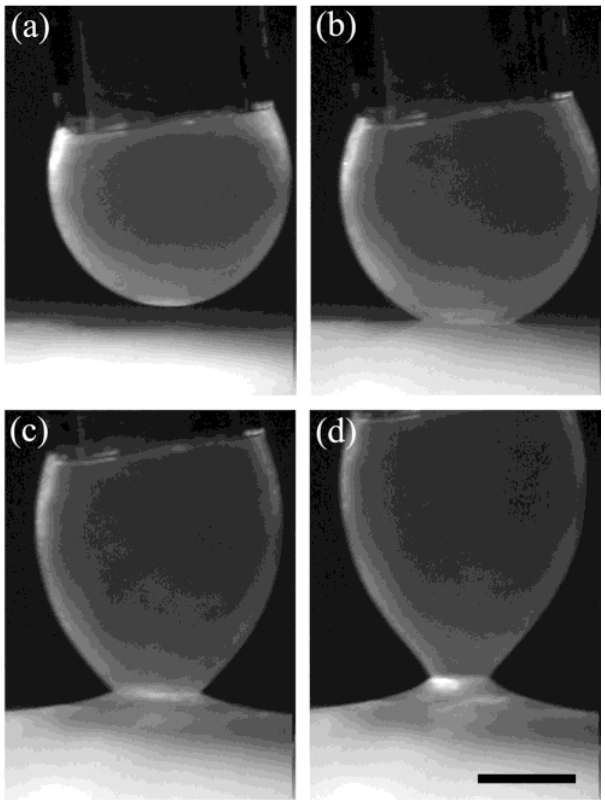
# Gels at interfaces

# Particles at interfaces

## Stabilization of incompatible materials (blends, emulsions, foams)

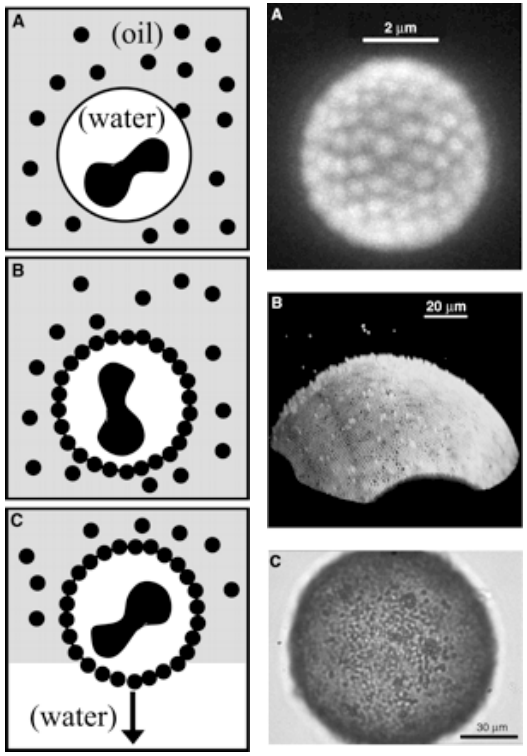
Pickering, J. Chem. Soc. 91, 2001, 1907

### Interfacial mechanics



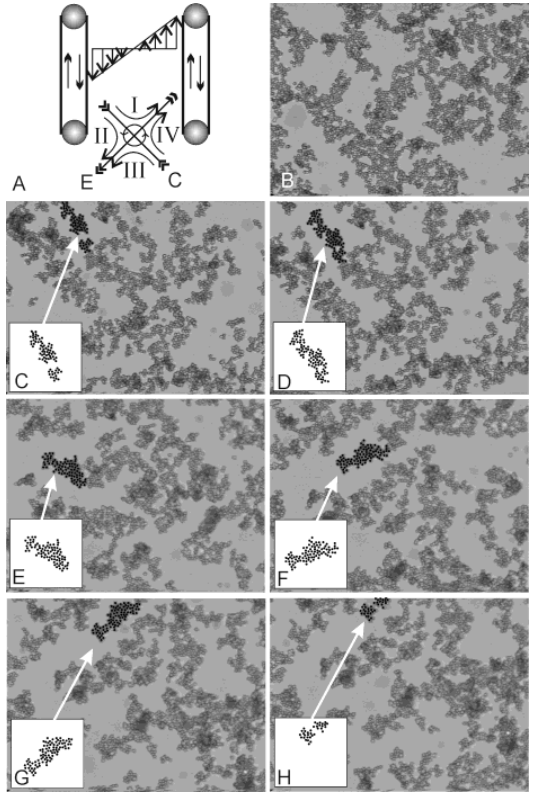

Stancick, et al. Langmuir, 20:90–94, 2004.

### Structured materials




Dinsmore, A.D. Science, 298: 1006-1009 (2002).

### Surface rheology

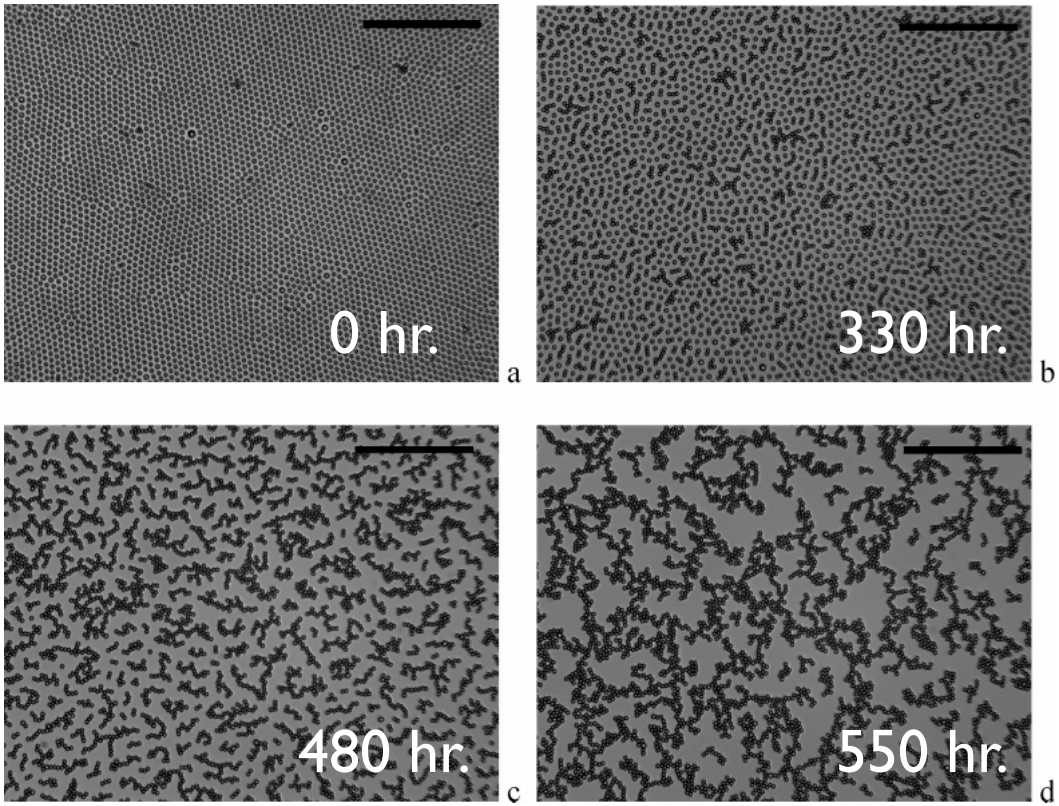



H. Hoekstra, et al. Langmuir, 19:9134–9141, 2003.

# Aggregation phenomena

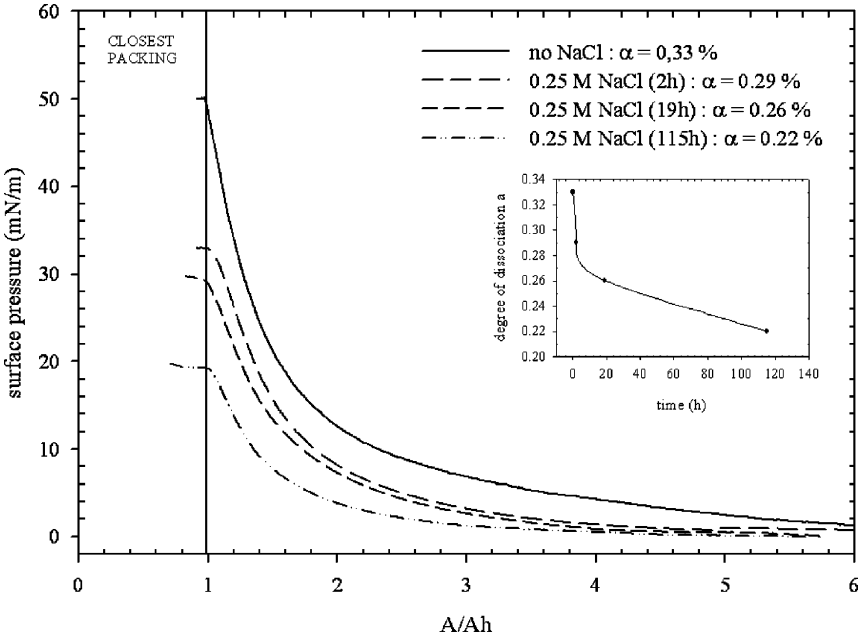
## Decane-water (0.25M NaCl)

Reynaert and Vermant, Langmuir 22, 4936, 2006.




$$D_f = 1.58 \pm 0.03$$

Surface pressure isotherms



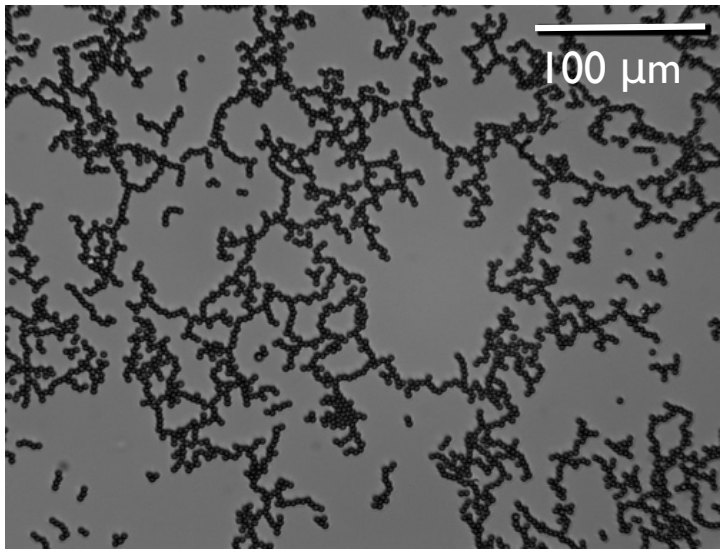

System becomes less repulsive with time

B. J. Park, et al. Langmuir 24, 1686 (2008).

# Aggregation in presence of surfactants

Reynaert and Vermant, Langmuir 22, 4936, 2006.

Decane-(water + 0.5 mM SDS + 0.5 M NaCl) interface.



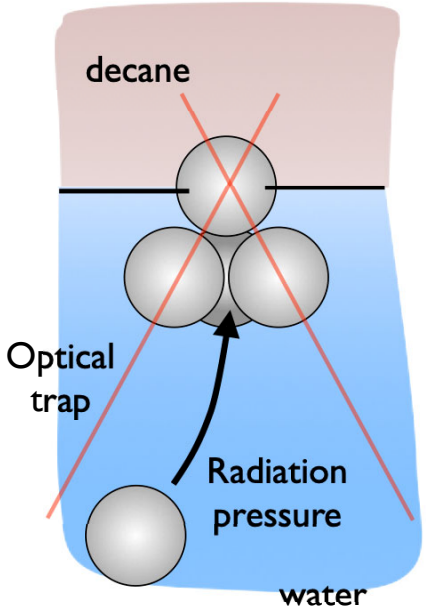

- Faster aggregation kinetics (hours instead of days)
- Lower fractal dimension (consistent with DLCA)

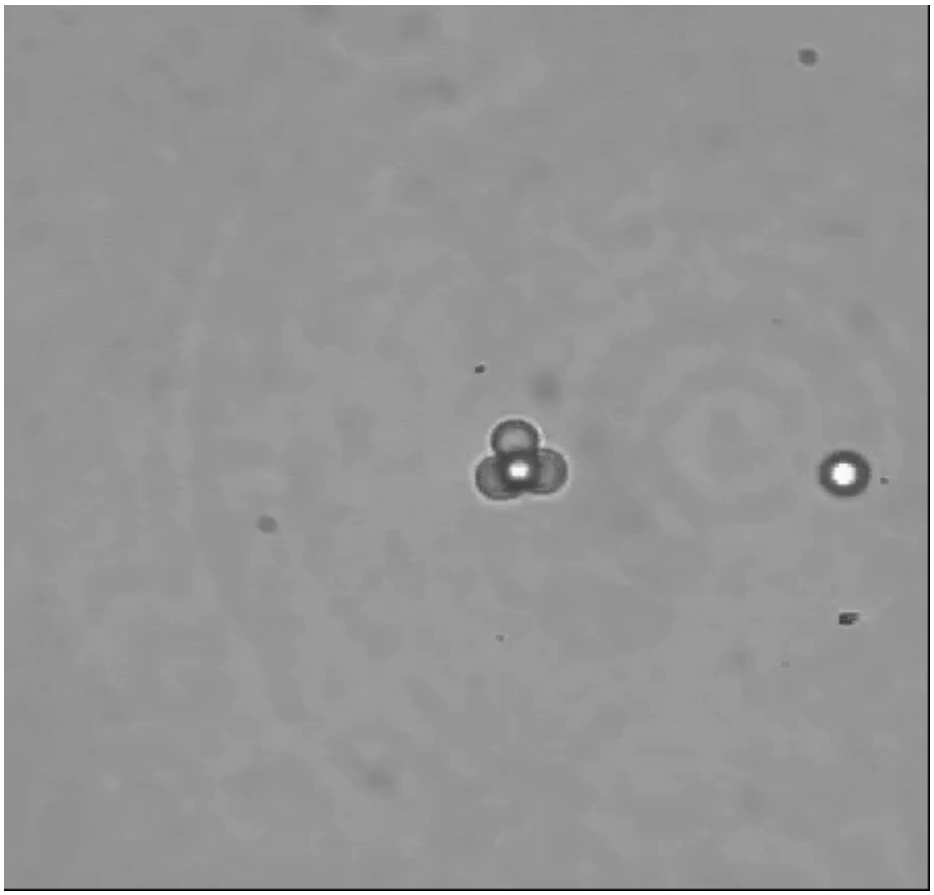
| $C_{SDS}$[mM] + $C_{NaCl}$[M] | $\phi$ | $t_{IND}$ (min) | $D_f$ | $\tau$ | $\omega$ | $z$ |
|---|---|---|---|---|---|---|
| 0.5 + 0 | 0.04 | >6000 | | | | |
| 0.5 + 0.1 | 0.1 | 330 | 1.44 ± 0.04 | 1.1 ± 0.1 | 2.8 ± 0.3 | 3.4 ± 0.4 |
| 0.5 + 0.3 | 0.05 | 275 | 1.45 ± 0.03 | 1.2 ± 0.1 | 2.1 ± 0.1 | 3.0 ± 0.1 |
| 0.5 + 0.5 | 0.11 | 40 | 1.46 ± 0.03 | 1.7 ± 0.1 | 0.5 ± 0.1 | 1.3 ± 0.1 |
| 0.1 + 0.25 | 0.08 | 1000 | 1.47 ± 0.03 | 1.49 ± 0.05 | 3.7 ± 0.4 | 4.9 ± 0.5 |
| 0.9 + 0.3 | 0.08 | 290 | 1.46 ± 0.04 | 0.9 ± 0.1 | 2.7 ± 0.2 | 2.8 ± 0.5 |

# Electrostatic interactions

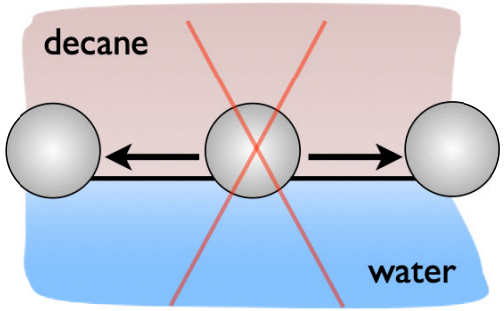
Polystyrene particles at decane-water interface
$2a = 3.1 \pm 0.1\ \mu m$, $\sigma = 7.4$ or $9.1\ \mu C/cm^2$

Electrostatic interactions in bulk aqueous phase



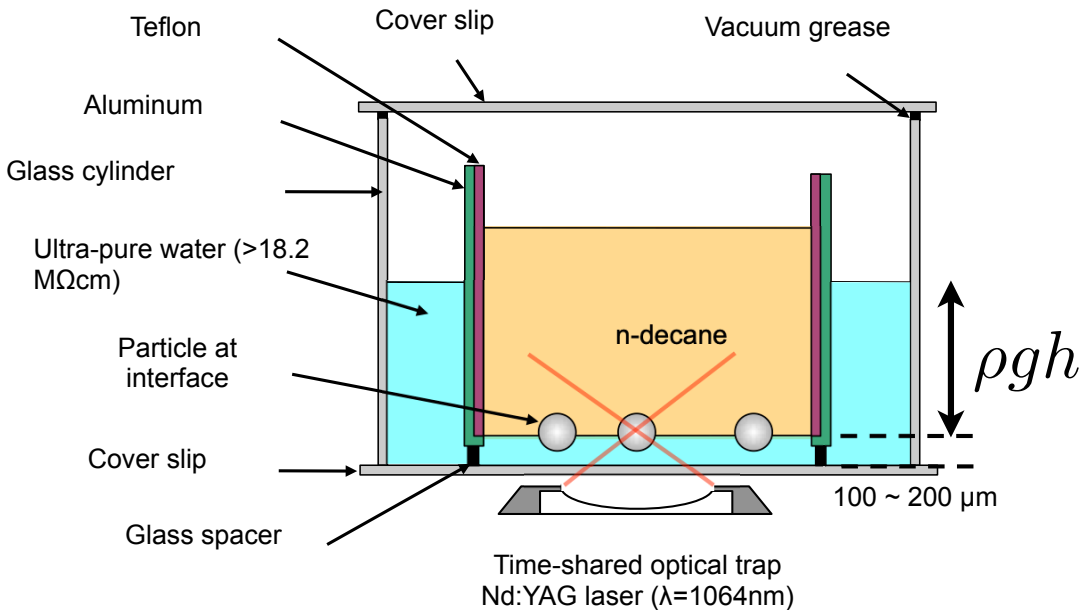




Long-range repulsion at interface



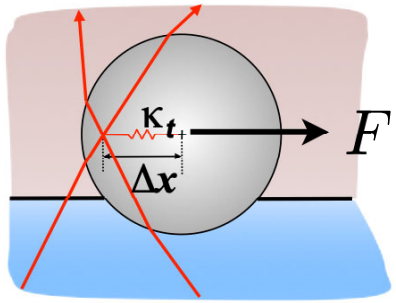
# Particle pair interaction measurements using laser tweezers

## Experimental setup




## Interaction measurements

Active

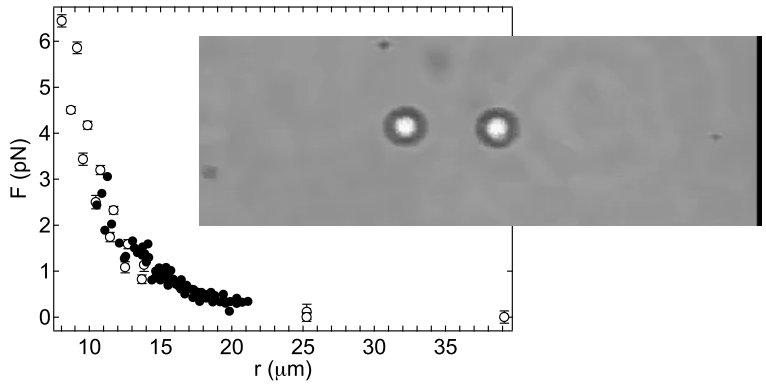

Trapping force at the interface:

B. J. Park and E. M. Furst. Langmuir, 24(23):13383–13392, 2008.

## For reproducibility:

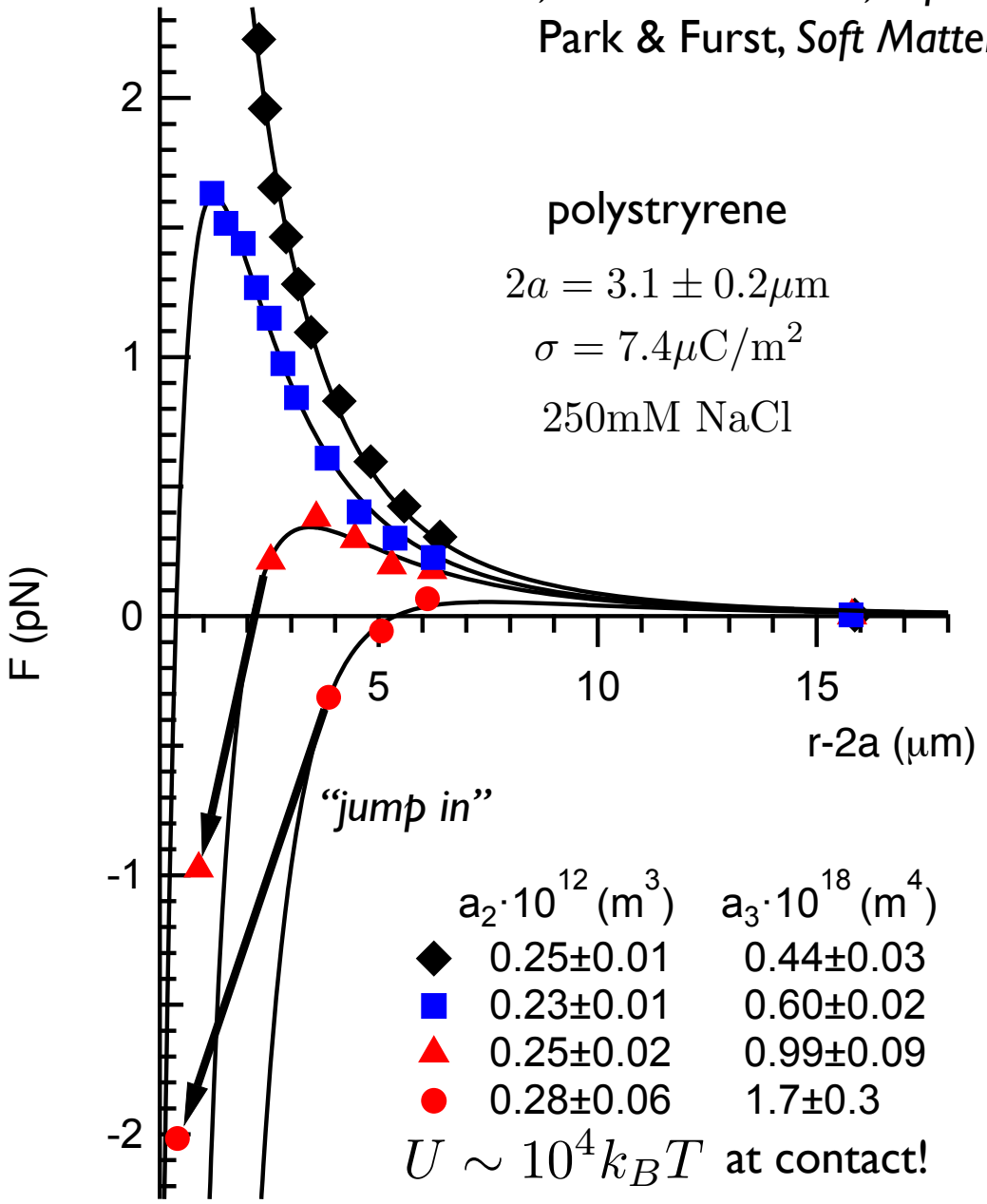
1. n-decane: rinsed over aluminum oxide support
2. Particles: repeated centrifugation and re-dispersion
3. Cover slip flame treated: contact angle ~0 degrees

Passive: Force from trajectories



# Interaction potential & force

Park, B. J. et al. *Langmuir* 24, 1686–1694 (2008).
Park, Vermant & Furst, *Soft Matter* 6, 5327–5333 (2010).
Park & Furst, *Soft Matter* 7, 7676–7682 (2011).




$$\frac{U(r)}{k_B T} = \frac{a_2}{r^3} - \frac{a_3}{r^4}$$

$$F(r) = \frac{3a_2 k_B T}{r^4} - \frac{4a_3 k_B T}{r^5}$$

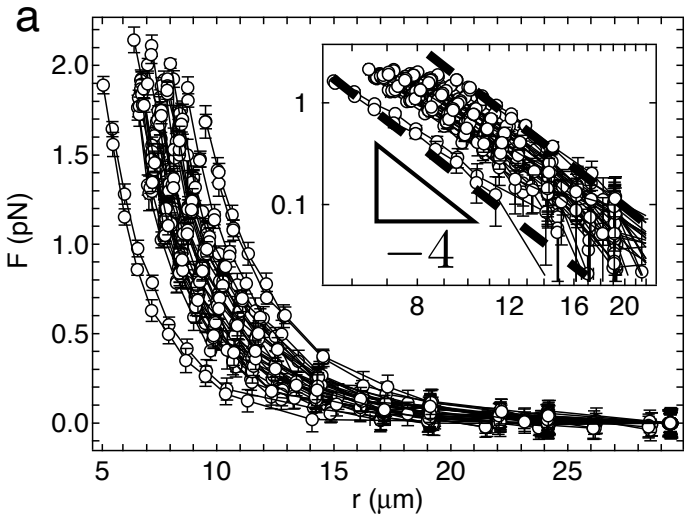
"Heterogeneous" – depends on particle pair
Sensitive to salts, surfactants, and particle prep

# Variation of interaction

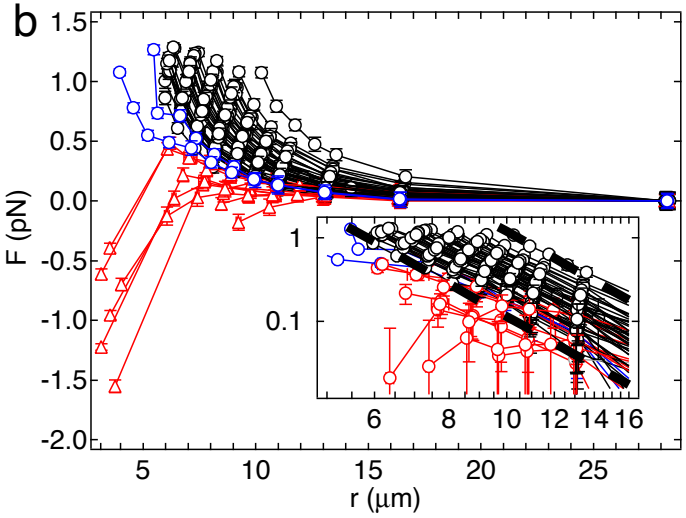
Park, Vermant & Furst, Soft Matter 6, 5327–5333 (2010).
Park & Furst, *Soft Matter* 7, 7676–7682 (2011).

Neat (no salt or surfactant)

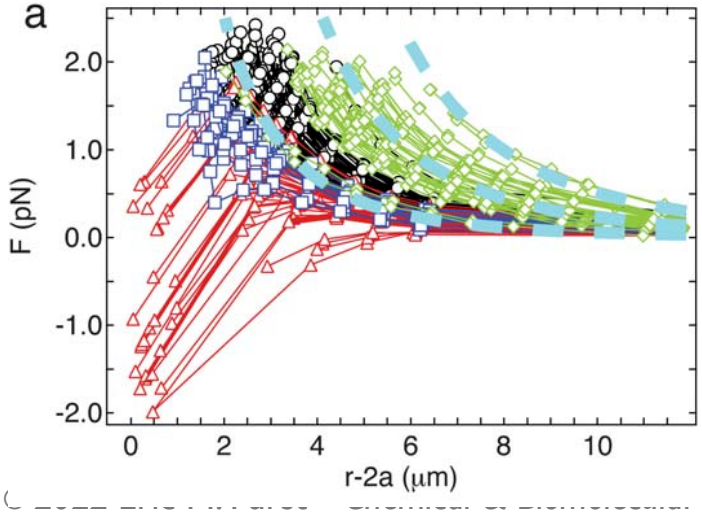
*Cleaned*



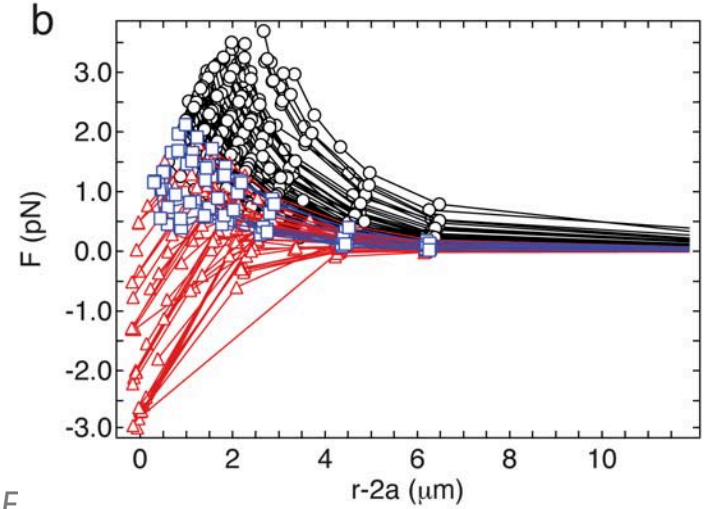

*Used as received*



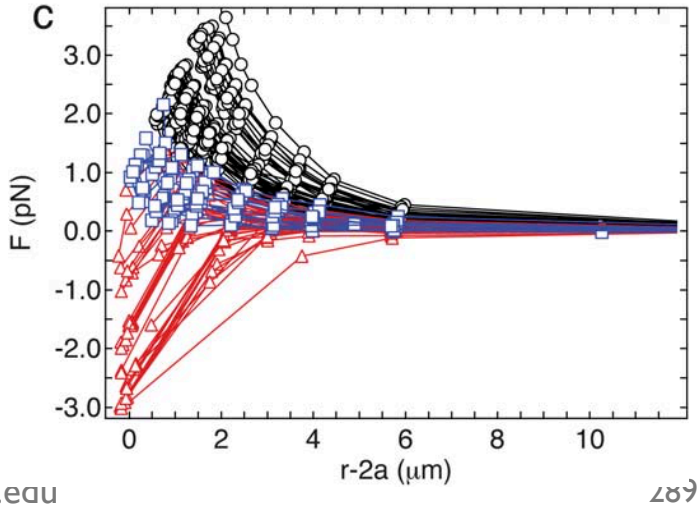

Neat (green) or 0.25 M salt




0.25 M salt + 0.1mM SDS



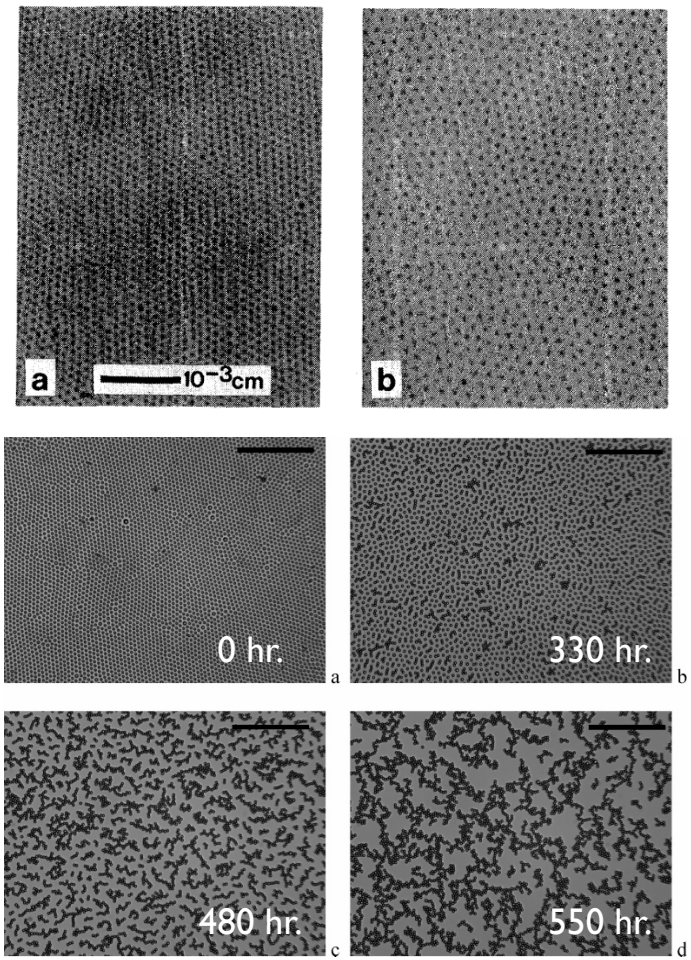

0.25 M salt + 25μM SPAN 80



# Electrostatics at the interface: Dipole repulsion

## 2D crystal

Pieranski, Phys. Rev. Lett. 45, 569, 1980.

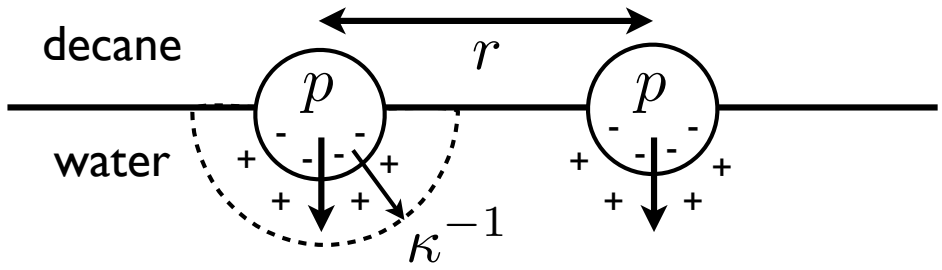



Reynaert and Vermant, Langmuir 22, 4936, 2006.

Stable for weeks–large kinetic stability barrier

## *Charge dissociation model*

Hurd, J. Phys. A, 18, 1055, 1985.



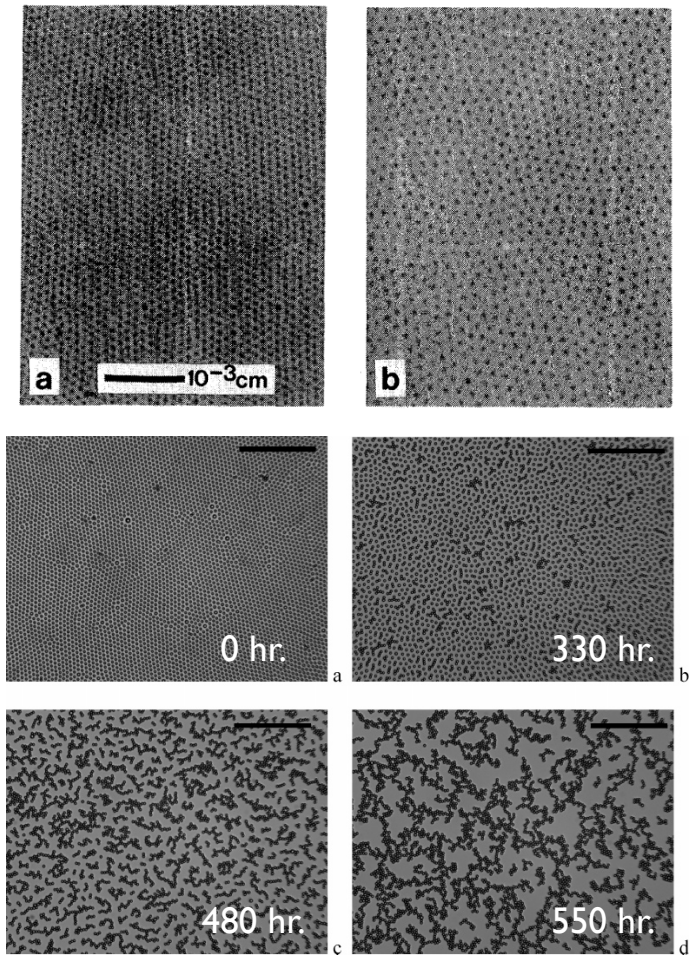

$$U(r) = \frac{\epsilon_{oil} q^2_{water}}{2\pi\epsilon_0 \epsilon^2_{water} \kappa^2 r^3}$$

# Charge renormalization

*Weaker salt dependence than Hurd model*

## 2D crystal

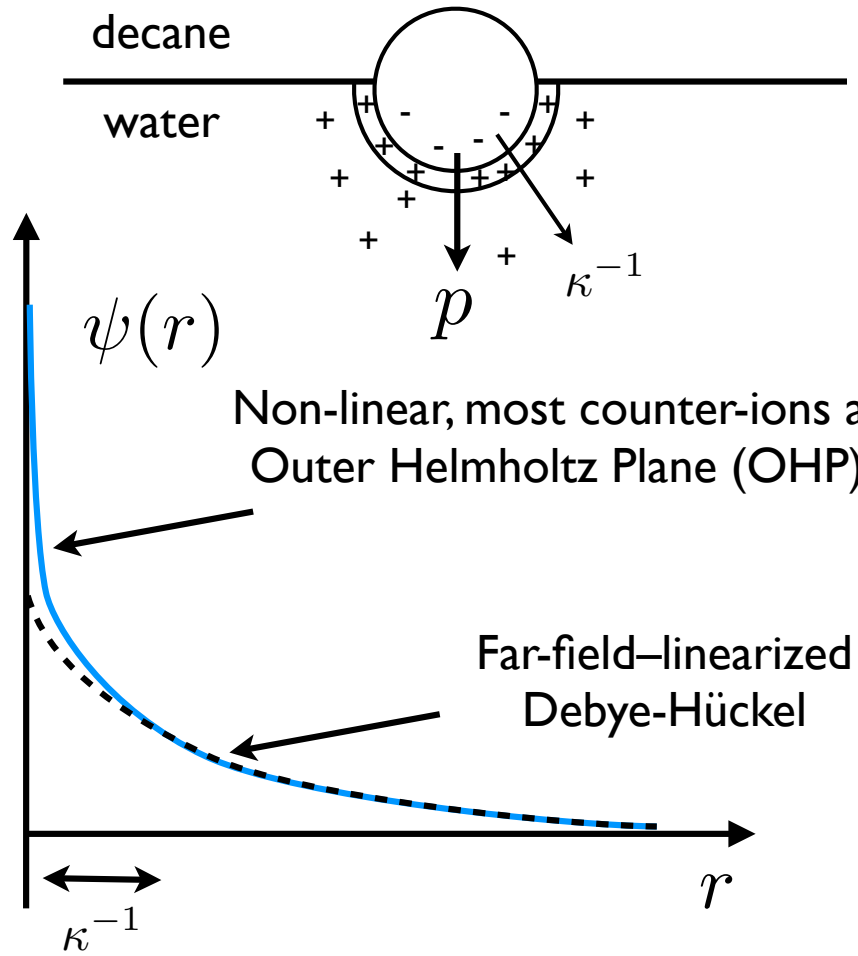
Pieranski, Phys. Rev. Lett. 45, 569, 1980.




Reynaert and Vermant, Langmuir 22, 4936, 2006.

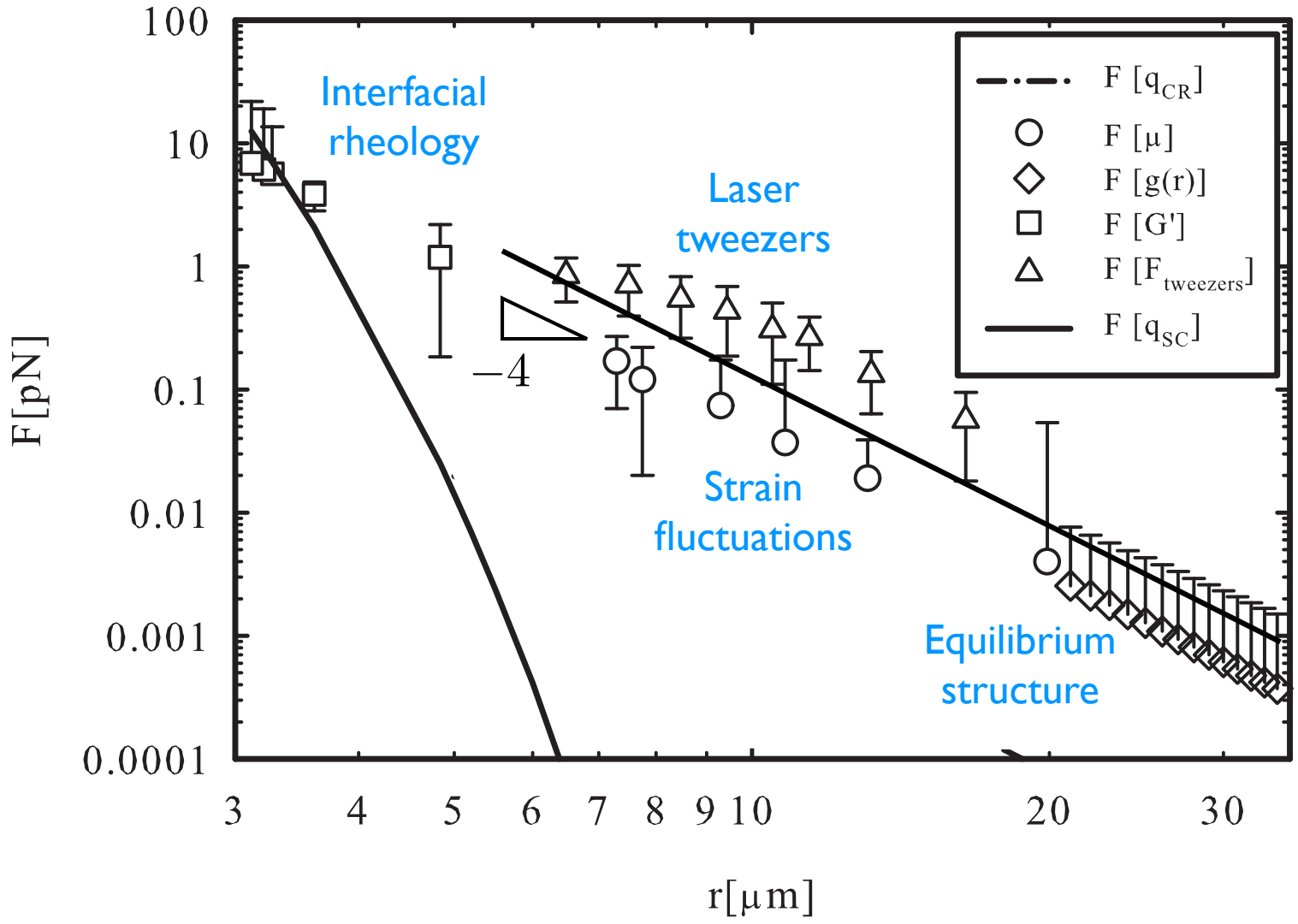
D. Frydel et al. *Phys. Rev. Lett.* 99, 118302, 2007.

$$q_{\text{eff}} = g(\kappa R)q$$



# Consensus experiments

Masschaele, Park, Fransaer, Furst and Vermant, *Phys. Rev. Lett.*, 105:048303, 2010.

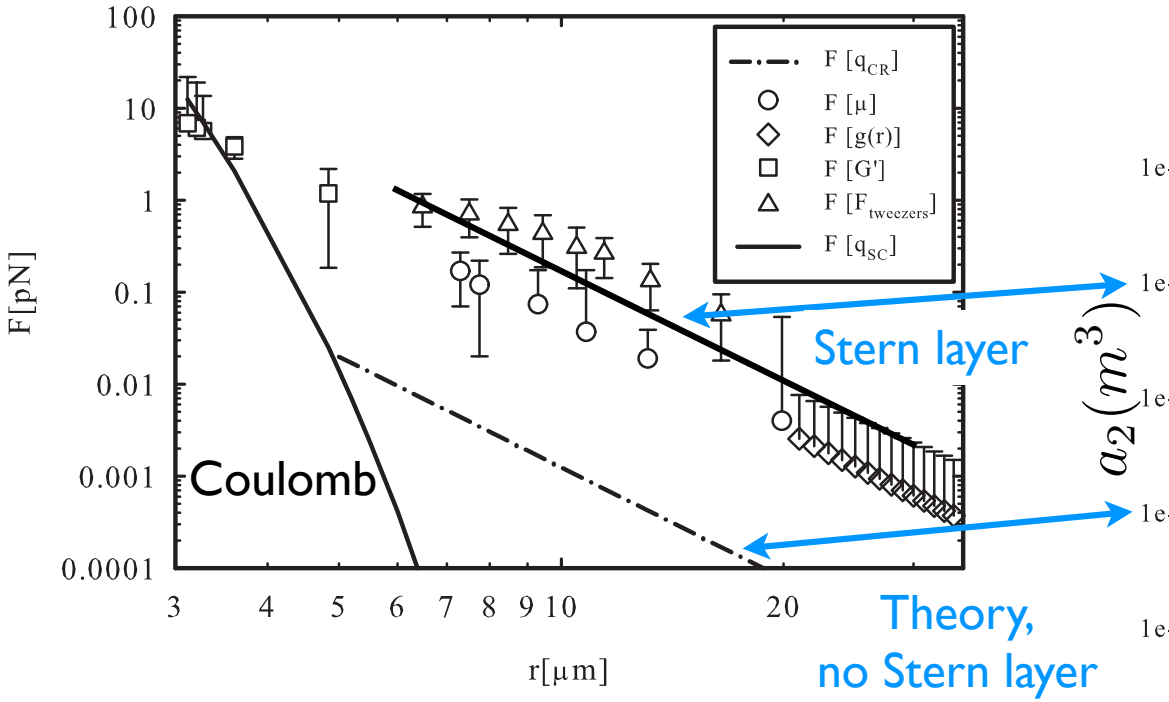


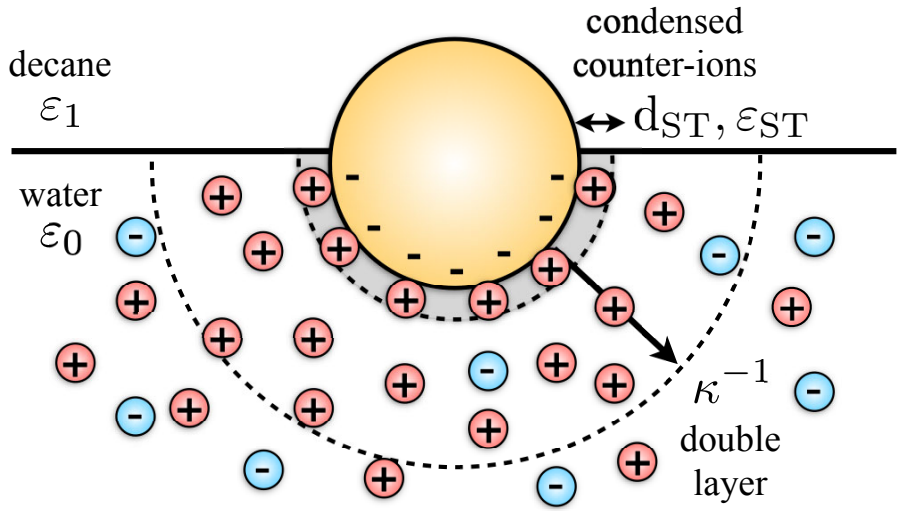
# Contribution of Stern layer

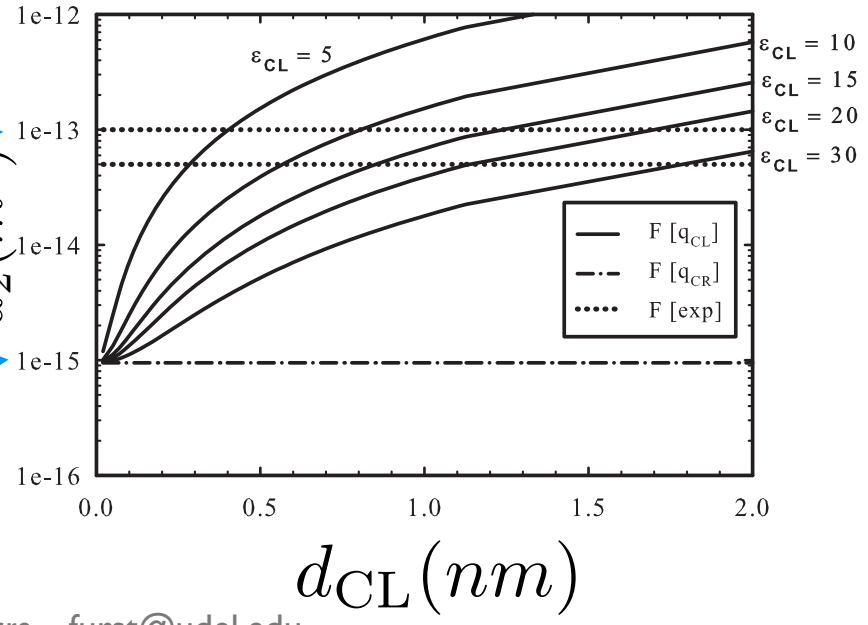
Masschaele, Park, Fransaer, Furst and Vermant, *Phys. Rev. Lett.*, 105:048303, 2010.

$$F = \frac{3a_2 k_B T}{r^4}$$

Four independent measurements:
*Tweezers, equilibrium structure, surface rheology, dynamics*

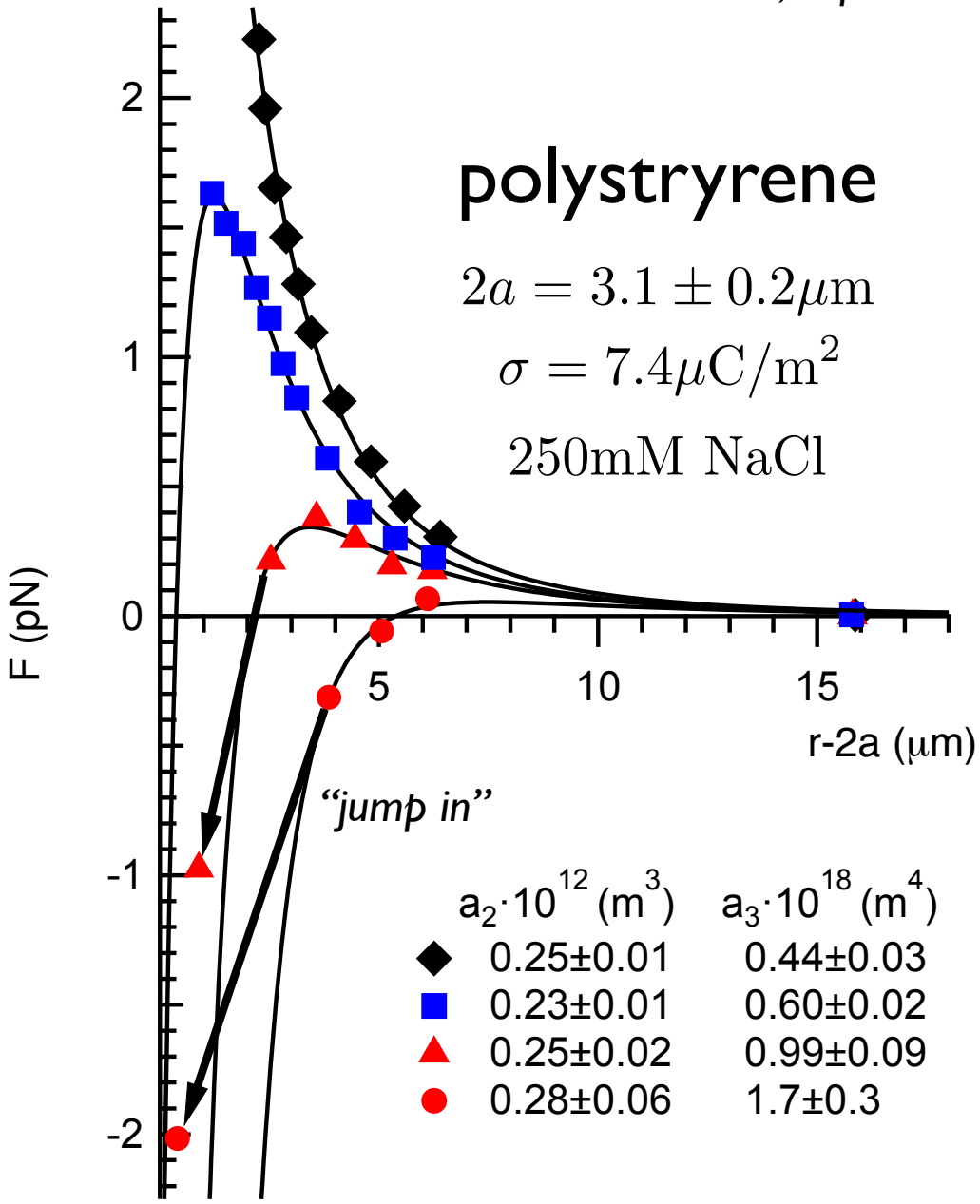


# Attractive interaction

Park & Furst, *Soft Matter* 7, 7676–7682 (2011).




## polystryrene

$2a = 3.1 \pm 0.2\mu\text{m}$

$\sigma = 7.4\mu\text{C/m}^2$

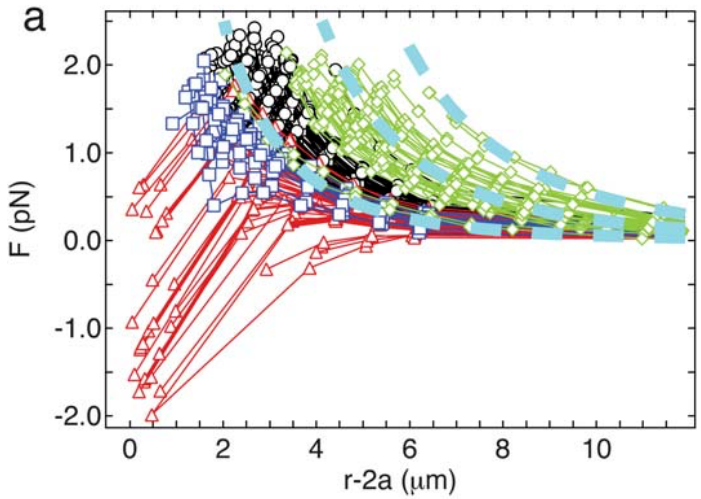
250mM NaCl

| | $a_2 \cdot 10^{12}$ ($m^3$) | $a_3 \cdot 10^{18}$ ($m^4$) |
|---|---|---|
| ◆ | 0.25±0.01 | 0.44±0.03 |
| ■ | 0.23±0.01 | 0.60±0.02 |
| ▲ | 0.25±0.02 | 0.99±0.09 |
| ● | 0.28±0.06 | 1.7±0.3 |

$$\frac{U(r)}{k_B T} = \frac{a_2}{r^3} - \frac{a_3}{r^4}$$

$$F(r) = \frac{3a_2 k_B T}{r^4} - \frac{4a_3 k_B T}{r^5}$$

Neat (green) or 0.25 M salt

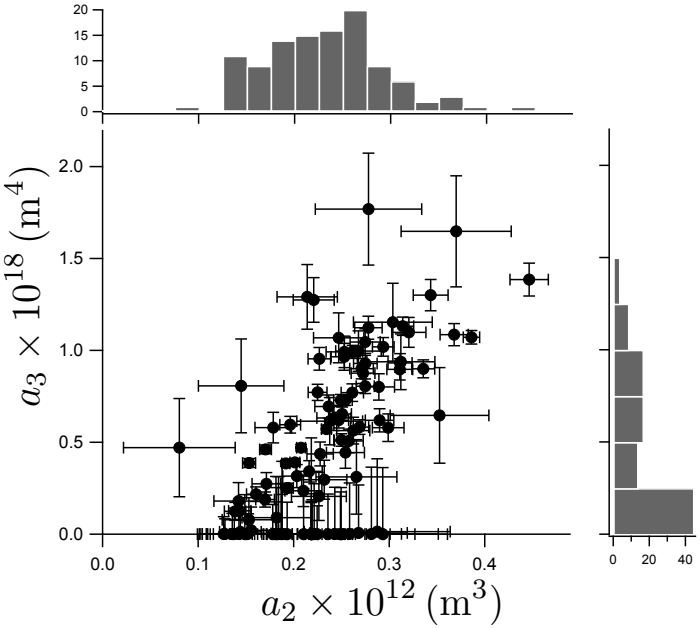


# Interaction parameter distributions

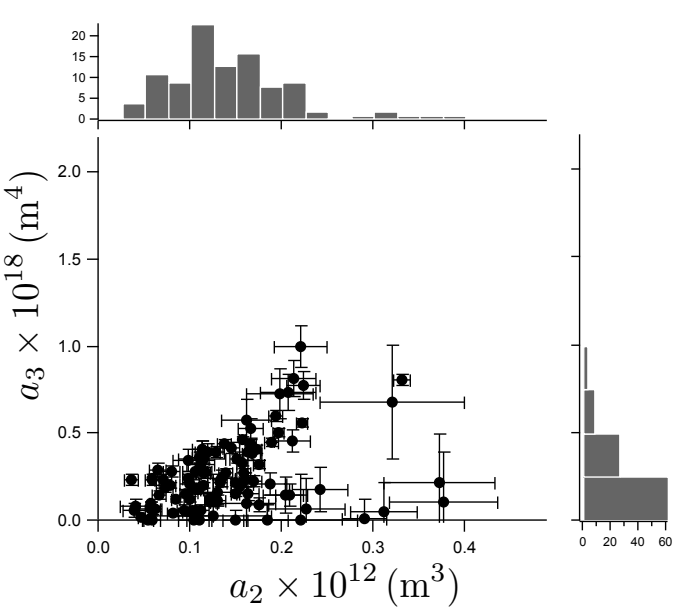
Park & Furst, *Soft Matter* 7, 7676–7682 (2011).

$$F_{\text{cap}} = -\frac{4a_3 k_B T}{r^5} \qquad F_{\text{rep}}(r) = \frac{3a_2 k_B T}{r^4}$$

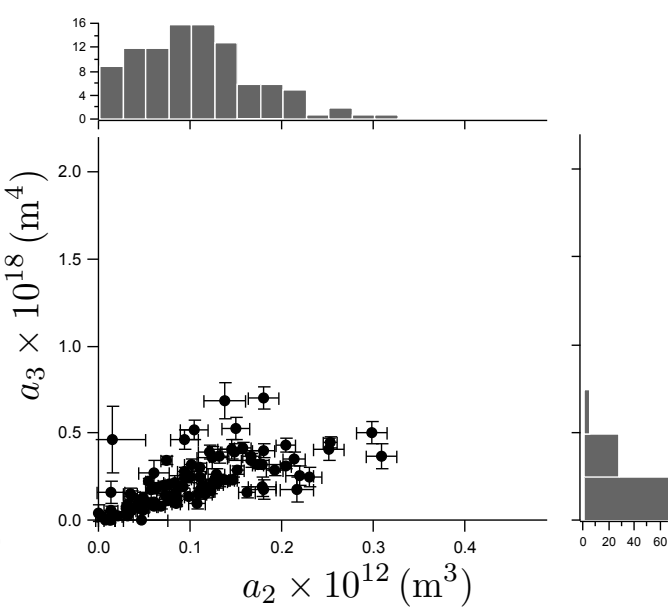
## NaCl

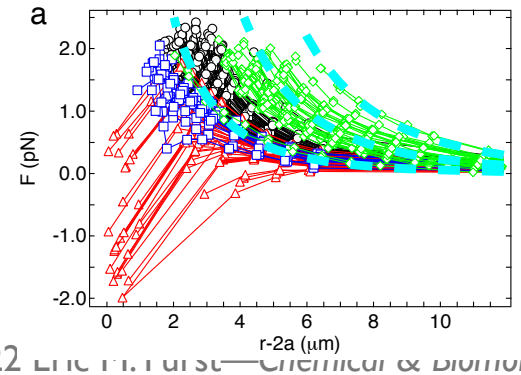


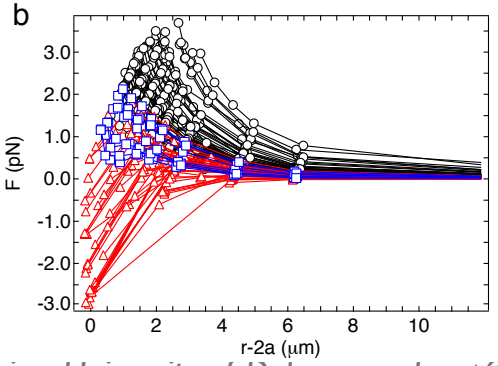

## SDS / NaCl

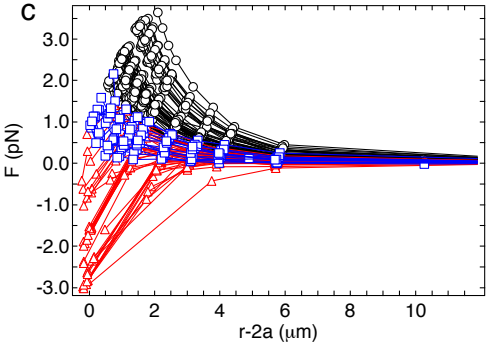



## SPAN 80



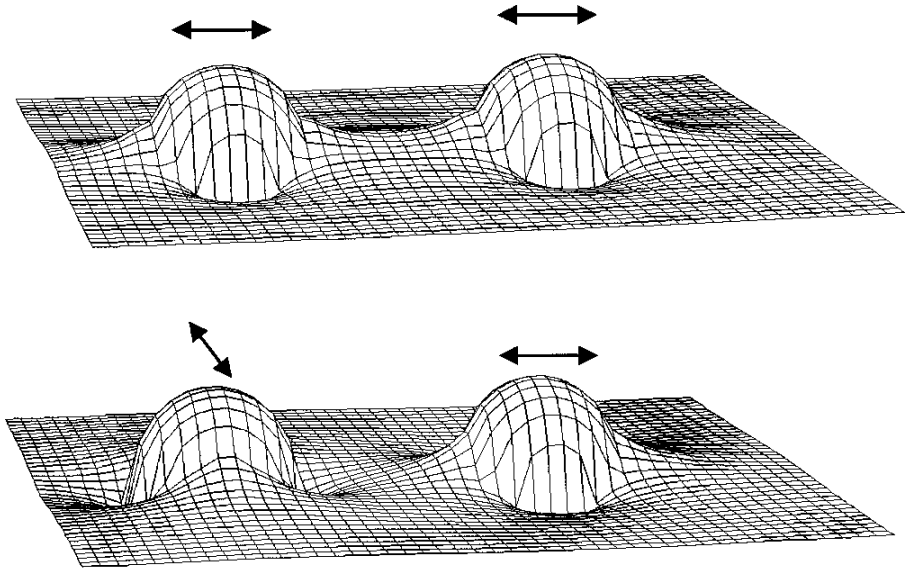



# Capillary forces

D. Stamou, et al. Phys. Rev. E, 62:5263–5272, 2000.

Contact line roughness

Far-field: quadrupolar interaction



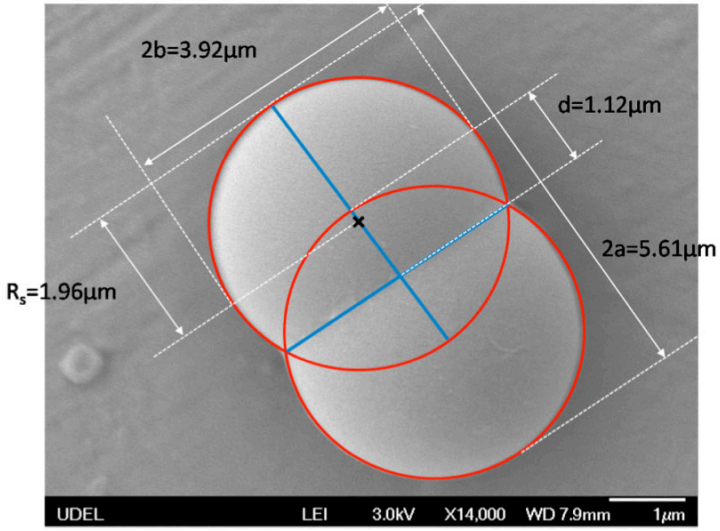
$$U_c = -12\pi\gamma H_2^2 \cos[2(\phi_A + \phi_B)] \left(\frac{r_c}{r}\right)^4$$

$$F(r) = -\frac{4a_3 k_B T}{r^5} \qquad a_3 = 12\pi\gamma a^4 H_2^2 \qquad H_2 \approx 45\text{nm}$$

# Forced irregular contact line

Park & Furst, *Soft Matter* 7, 7676–7682 (2011).

## PS doublets




H. R. Sheu, et al. J. Poly. Sci. A, 28:629–651, 1990.

Thanks: E. Dufresne and Jin-Gyu Park, Yale University

$$F(r) = -\frac{4a_3 k_B T}{r^5}$$

## Capillary attraction

Trap and release with optical tweezers