

Rideal Symposium
London, March 2010

ORDERING AT HYDROPHILIC AND HYDROPHOBIC SURFACES

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Ian Wark Research Institute

Australian Research Council Special Research Centre
For Particle and Material Interfaces



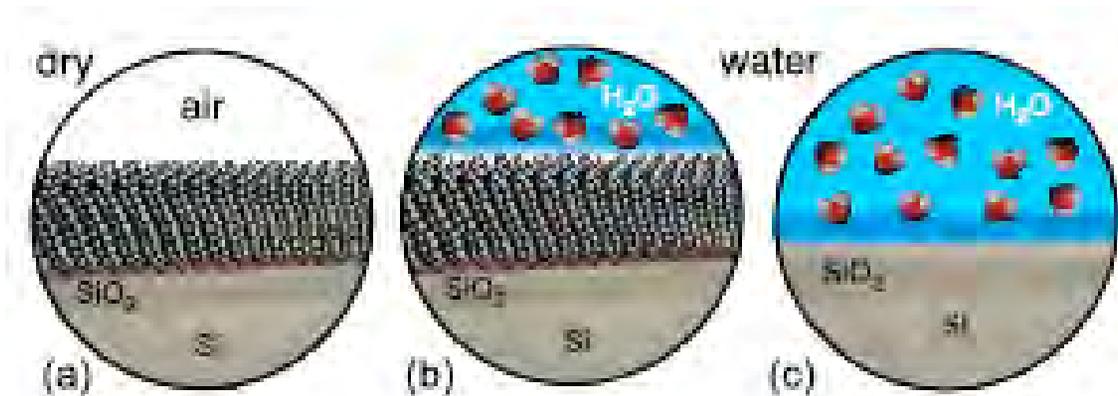
Essential Questions:

1. Is water structure altered at the smooth hydrophobic solid-water interface? For solid-ice?
2. What is the influence of dissolved gas?
3. When water advances over surfaces of different hydrophobicity, how is this connected to surface friction?
4. How does surface hydrophobicity influence flow through narrow channels and capillaries?

Why?

Water structure at interfaces can influence adsorption behaviour and boundary conditions when flow occurs.

Regarding structure, the systems we will study are:

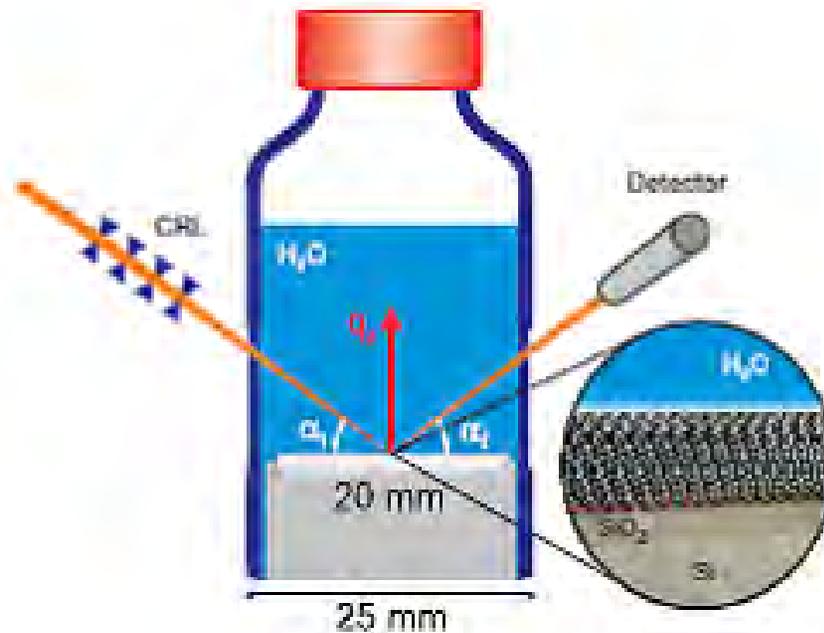


(a) Si-SiO₂-OTS-air

(b) Si-SiO₂-OTS-water

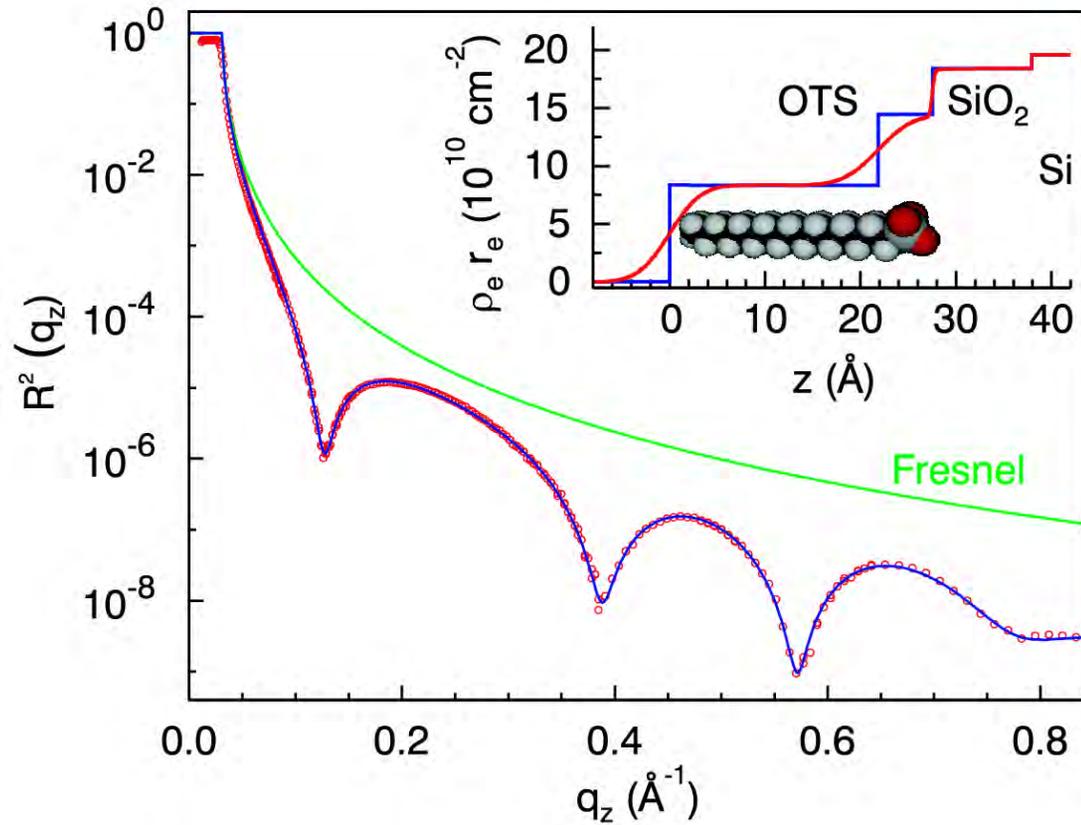
(c) Si-SiO₂-water.

X-Ray reflectivity

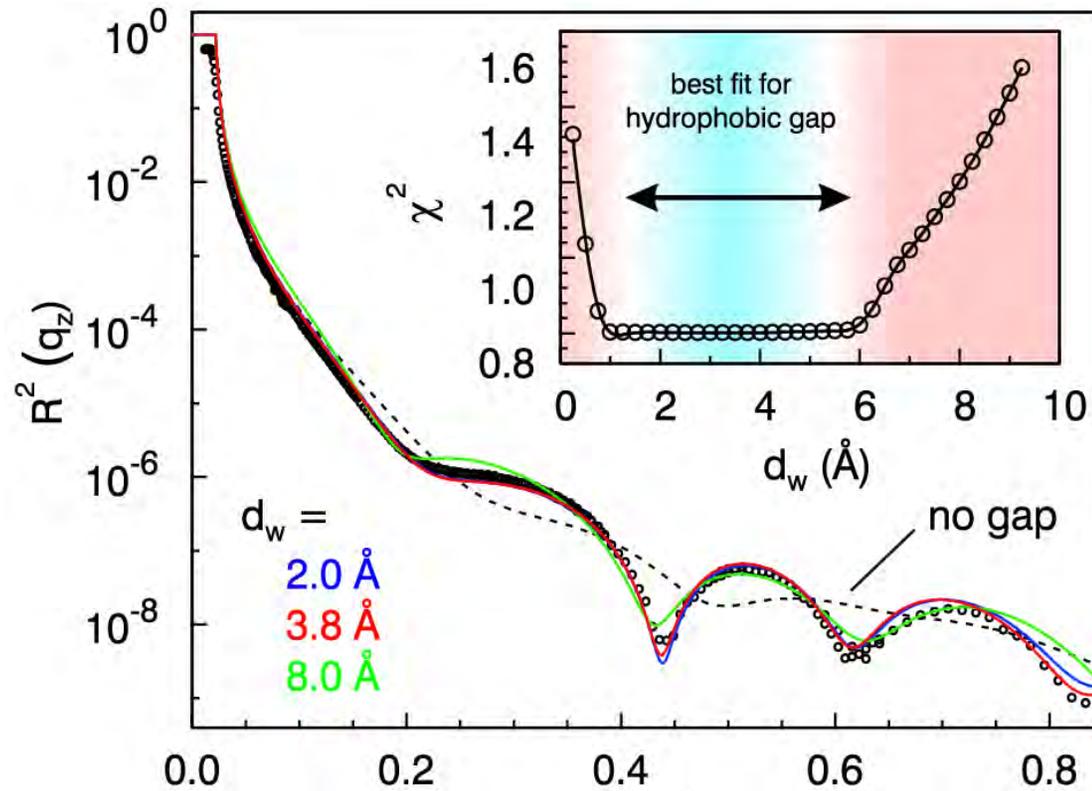


- (i) Proc National Ac. Sci., 103, 18401 (2006).
- (ii) J.Chem.Phys. 128, 244705 (2008)

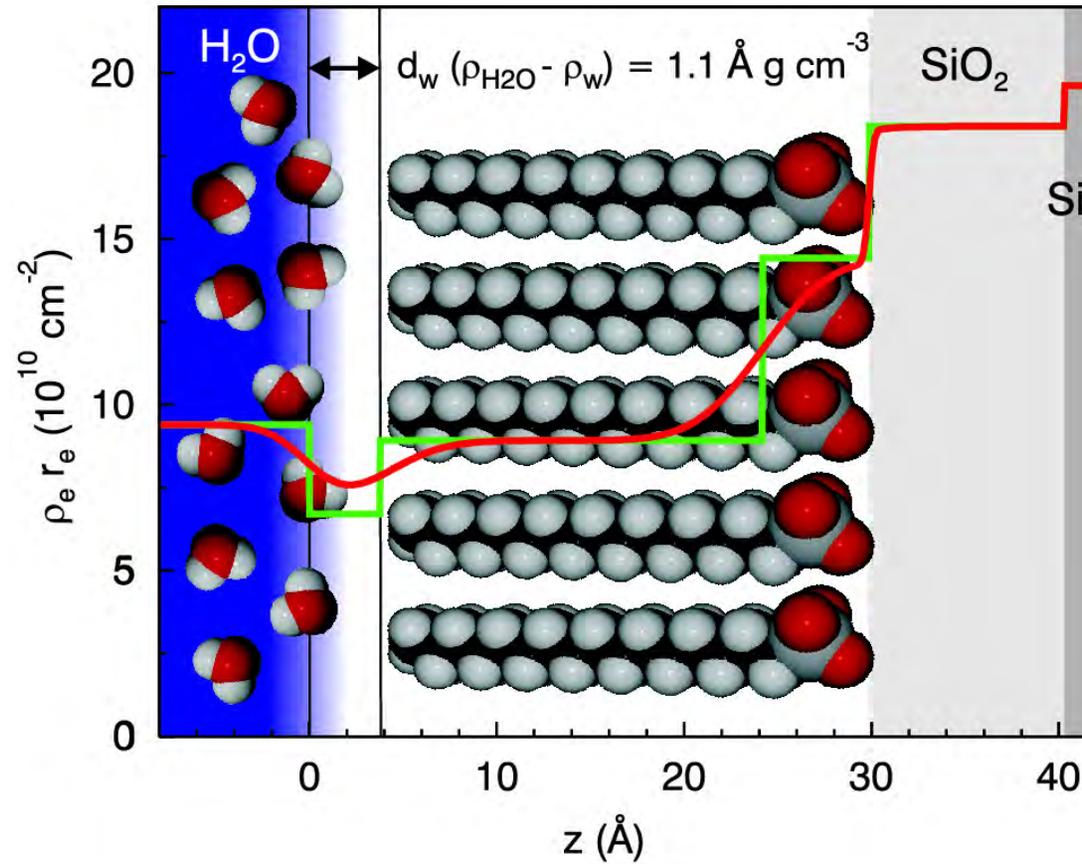
In absence of water



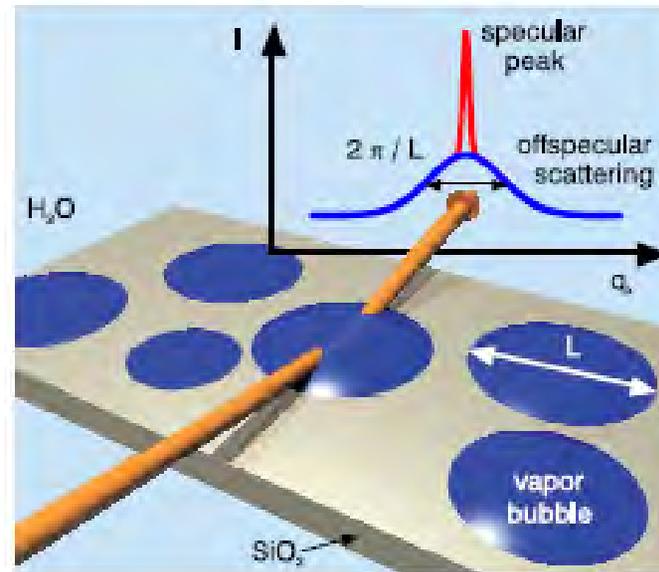
In presence of water:



Depletion region of 1-2 water layers exists:

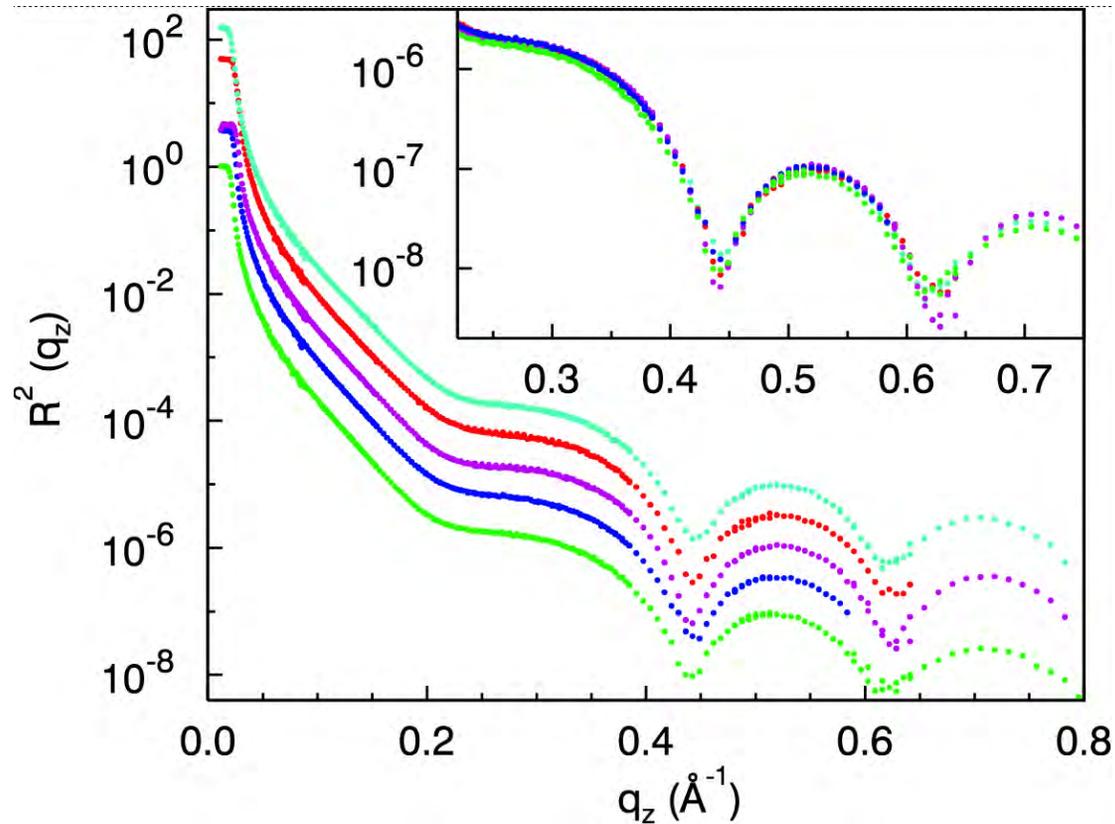


What would happen if surface nanobubbles were present?



Sketch of the scattering in forward direction from an interface
Covered by randomly spaced bubbles

Different gases have no effect – no detectable effects at smooth hydrophobic surface



Curves simply shifted for clarity

The situation changes when surfaces are heterogeneous, with distinct hydrophobic patches and modest physical heterogeneity.

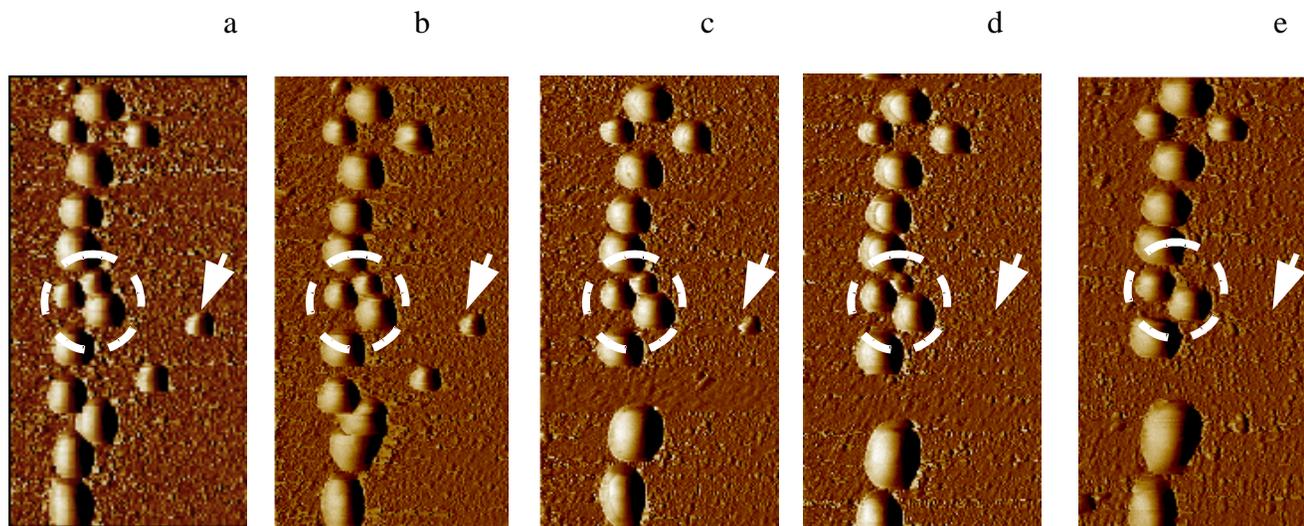


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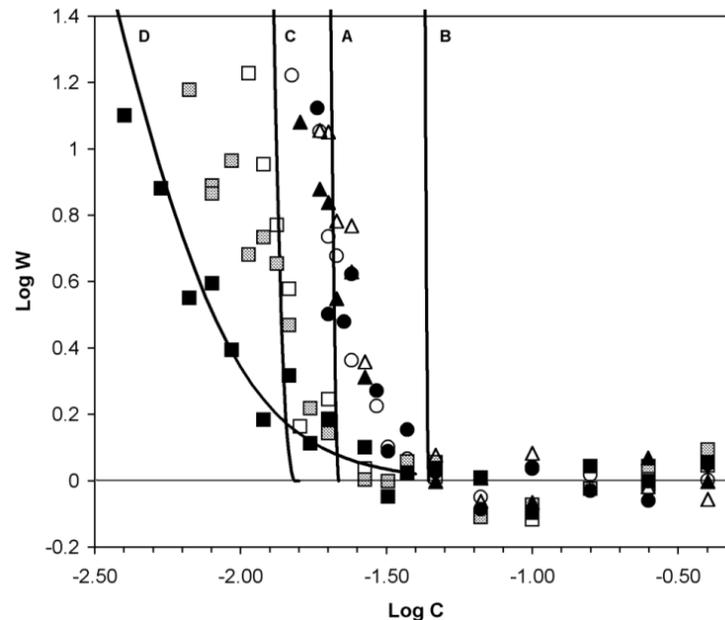
Bubble Coalescence Images:



TMAFM bubble coalescence images: (a) made at 20 hours after CO₂ saturated water was injected into the fluid cell. (b), (c), (d) and (e) made at time intervals of 20 minutes after (a). Scan Area: 10 μm × 5 μm, Height= 300nm. Phase images

Journal of Physical Chemistry B., 107, 25, 6139-6147 (2003).

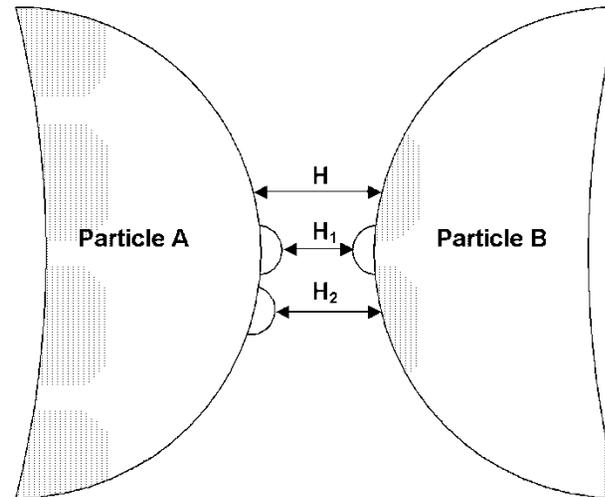
What is the influence of dissolved gas on colloid stability?



J.Phys.Chem.B., 107, No. 13, 2986-2994
(2003).

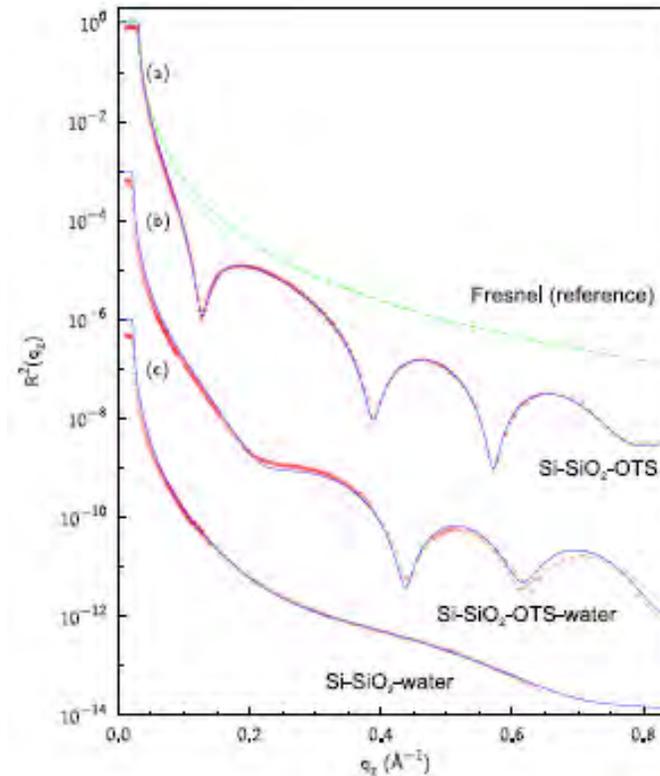
Stability ratio versus KCl concentration for Geltech silica spheres at pH 4.2 with a clean hydrophilic surface under normal conditions (○), clean hydrophilic surface / dissolved CO₂ concentration 10⁻² M (●), methylated hydrophobic surface / normal conditions, methylated hydrophobic surface / dissolved CO₂ concentration 10⁻² M (■) and methylated hydrophobic surface / degassed (□), dehydroxylated surface / normal conditions (△), dehydroxylated surface / dissolved CO₂ concentration 10⁻² M (▲). Solid lines, A, B, C and D indicate calculated stability curves.

What forces are dominant?



Scale diagram representing two 1 μm diameter particles with 100 nm diameter surface bubbles demonstrating the three separate interactions that can occur. In terms of the van der Waals forces these are; strongly attractive bubble-water-bubble interactions occurring over distance H , strongly repulsive silica-water-bubble interactions occurring over distance H_1 and attractive silica-water-silica interactions occurring over distance H_2 .

Let's consider all 3 systems:



Comparison of the experimentally recorded x-ray reflectivity patterns (circles) from the different samples. The measurements are shifted by three orders of magnitude for clarity.

The Fresnel reflectivity from an ideal silicon substrate is shown for the dry OTS-covered substrate (top). The x-ray reflectivities from all interfaces are perfectly reproduced by refinement of a slab model. (a) Dry silicon wafer covered with a self-assembled OTS-layer. (b) Silicon wafer covered with a native SiO₂-layer and immersed in degassed water. (c) Native silicon wafer covered with a self-assembled OTS-layer immersed in degassed water.

In summary:

1. There is clear evidence for a depletion region of 1-2 water layers at a smooth hydrophobic surface.
2. SiO_2 – water and ice are inconclusive.
3. Surface heterogeneity facilitates nanobubble formation.
4. Note that NMR (especially relaxation time) data indicate that water in nano-capillaries and pores behaves differently (structured?) from the bulk.

How do surface hydrophobicity and hydrophilicity influence liquid flow over surfaces?

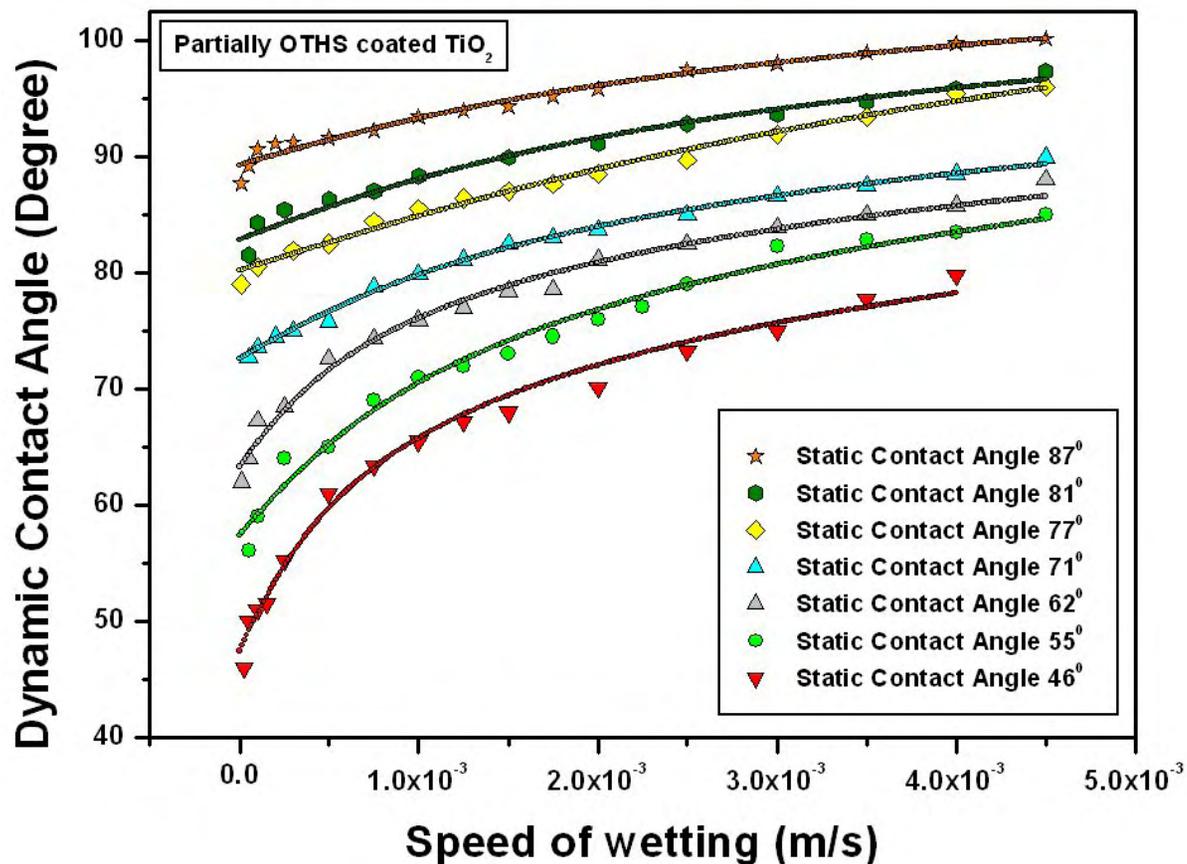
Let us consider two systems where the substrates are:

[a] titania, surface modified with OTHS,

and

[b] gold, surface modified with thiols.

Dynamic Contact Angle as Function of Hydrophobicity
OTHS/TiO₂ system, wetting with water/glycerol mixture.

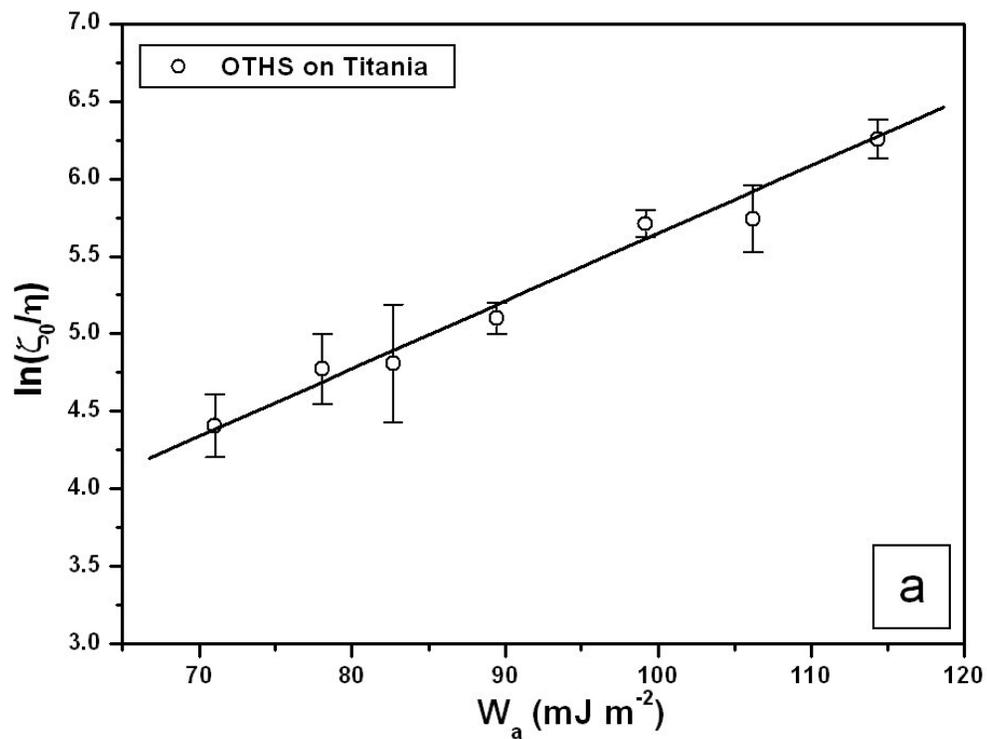


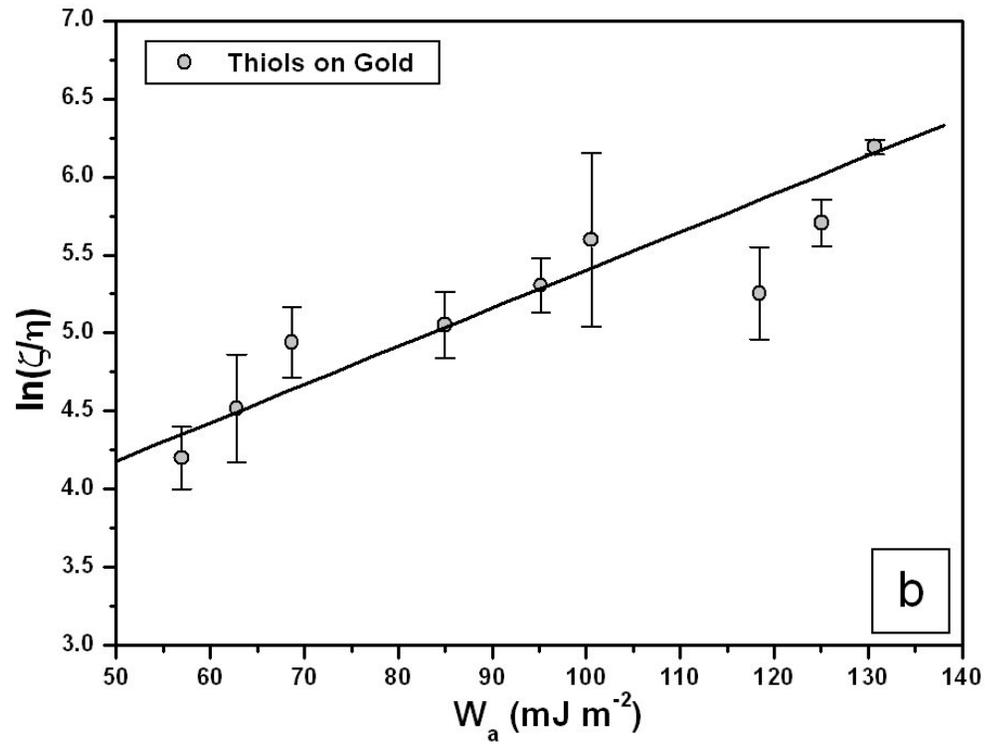
Langmuir, 24, 13007 (2008)

The velocity dependence of dynamic contact angle can be described by the Molecular-Kinetic Theory. The friction coefficient, ζ^0 and work of adhesion, $W_{ad} = \gamma (1 + \cos\theta)$ are linked by:

$$\zeta^0 = \frac{\eta v_L}{\lambda^3} \exp\left(-\frac{\lambda^2 \gamma (1 + \cos\theta)}{k_B T}\right)$$

Contact-line friction should therefore increase with both liquid viscosity and with the work of adhesion. The MKT theory has been shown to describe a good range of experimental data very well with a strong connection between K_0 and work of adhesion. For a surface where the wettability may be varied in the presence of a single liquid, a plot of $\ln(\zeta_0/\eta)$ versus $\gamma(1 + \cos\theta^0)$ should give a straight line of positive slope, from which v_L can be obtained giving a unique insight into the unit volume which is displaced in the MKT theory.





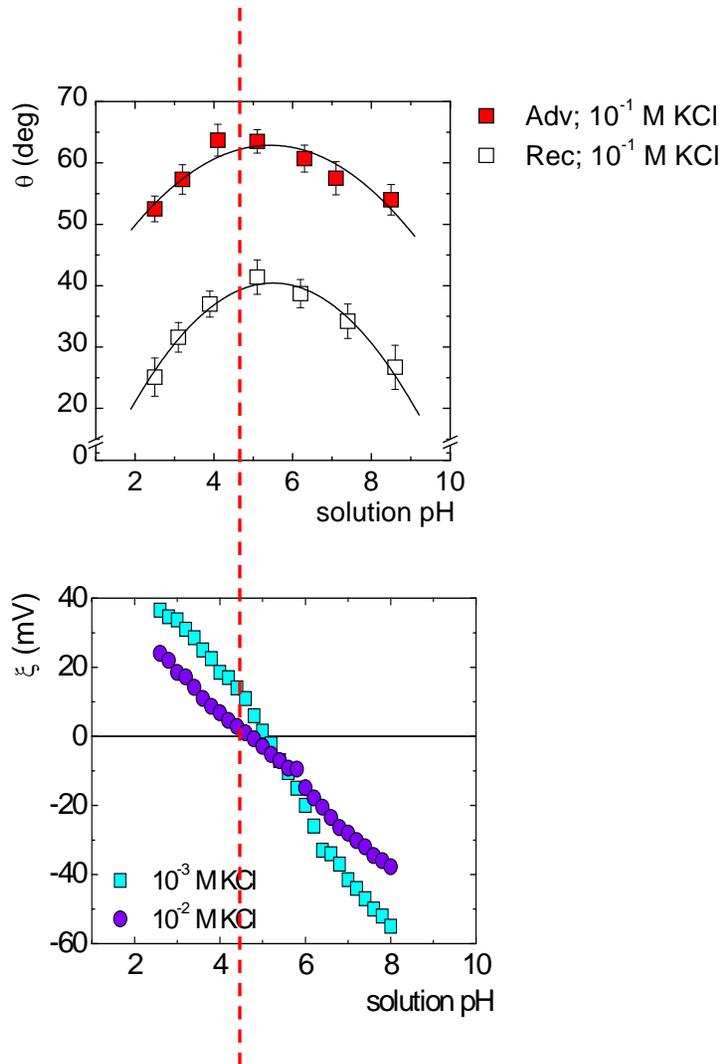
Molecular parameters derived from the results:

Solid Surface	λ^a [nm]	λ^b [nm]	V_L^b [nm ³]
Thiol on Gold	0.8 - 1.1	0.32 ± 0.02	0.60 ± 0.20
OTHS on Titania	0.8 - 1.4	0.42 ± 0.01	0.27 ± 0.09

- a. Using a statistical Bootstrap procedure
- b. From the linear fits in the figures and simple equation.

Static contact angle

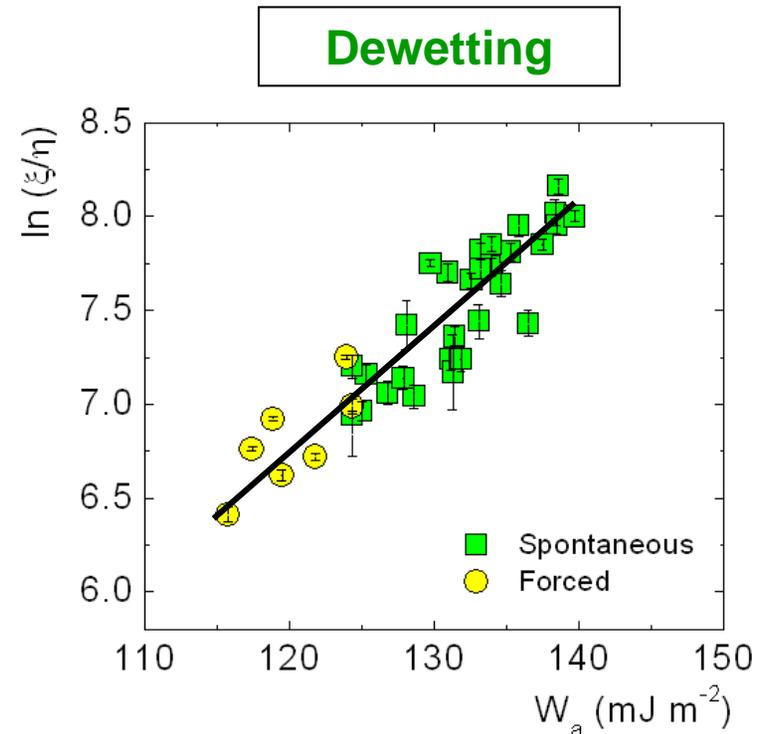
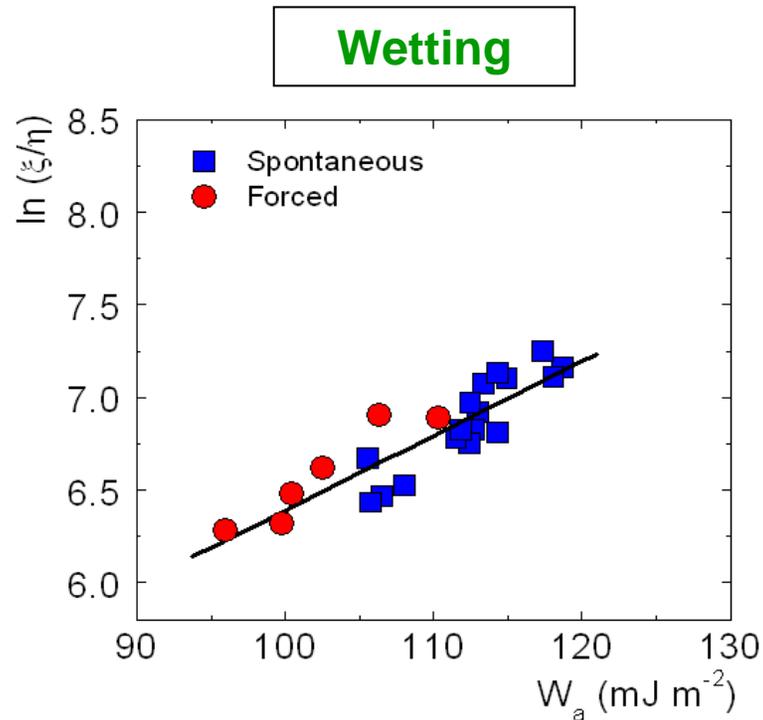
What is the influence of surface charge?
TiO₂ plate – OTHS, $\theta_{\alpha} \sim 60^{\circ}$



- θ_{max} at \sim pH 5 (pH_{pzc})
- Consistent with streaming potential result
- Substantial decreases in CA (15 -20°) when the solution pH is moved away is from pH_{pzc}
- Similar trend after adding glycerol

Relationship between ζ and W_a (modified simply by changing pH, I)

Recall $\ln\left(\frac{\zeta}{\eta}\right) = \frac{\lambda^2}{k_B T} W_a - \ln\left(\frac{\lambda^3}{v_L}\right)$



It is possible that spontaneous and forced spreading share the same underlying wetting mechanisms

Consider flow through nano and microchannels.

Hagen-Poiseuille gives

$$V = \frac{\Delta P \cdot \pi d^4}{128 \mu l}$$

Slip changes the effective diameter (i.e. $d + L_s$). L_s is the slip length.
The flow rate can increase.

VIP for nanochannels and capillaries: optimize slip by “structuring” the interior walls.

Lucas-Washburn

$$h(t) = \left[\frac{\gamma_{LV} (R + L_s)^2 \cos \theta}{2R\eta} \right] \sqrt{t}$$

R = capillary radius, L_s = slip length.

Phys.Rev.Letters, 99, 054501-1 (2007).

How are slip and surface friction connected?

$$L_s = \text{slip length} = M_D \left(\frac{\lambda^3}{n\nu_L} \right) \exp \left[\frac{-\lambda^2 \gamma (1 + \cos \theta)}{k_B T} \right]$$

$$\zeta^0 = \text{friction coefficient} = \left(\frac{n\nu_L}{\lambda^3} \right) \exp \left[\frac{+\lambda^2 \gamma (1 + \cos \theta)}{k_B T} \right]$$

If $\theta = 180^\circ$

$L_s \sim \text{few nm}$

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