Forces across thin liquid film

Effect of surface charge and hydrophobicity on wetting film stability

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For Particle and Material Interfaces

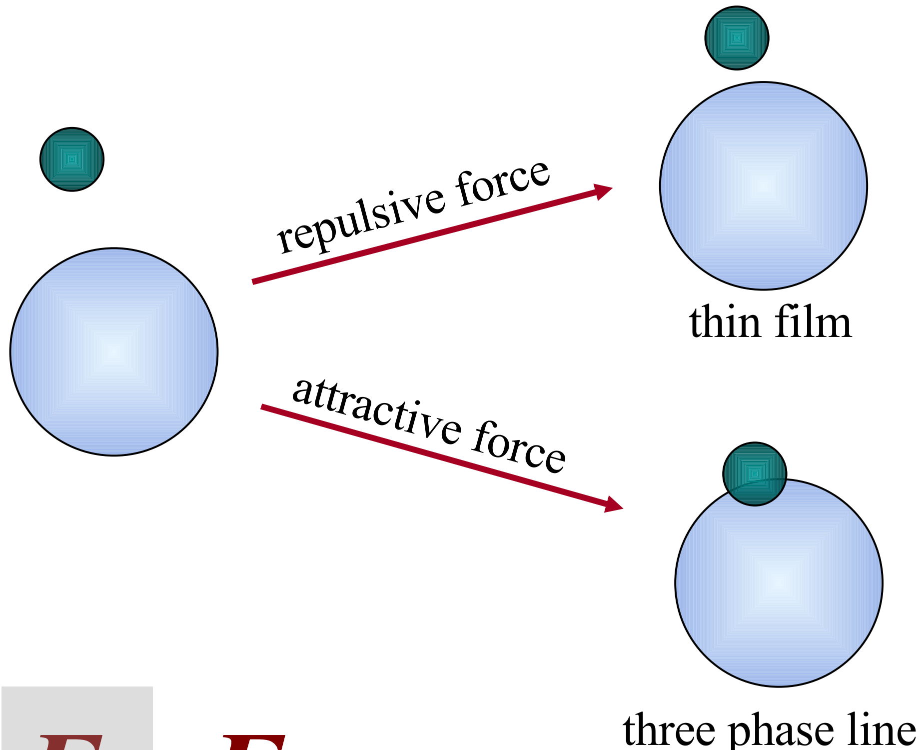
The Wark

Bubble-particle interactions

1. Collision

2. Attachment

3. Detachment



$$E_{coll} = E_c \cdot \boxed{E_a} \cdot E_d$$

attachment efficiency

When a particle approach a bubble close enough two kinds of interactions may occur:

CONTACT TIME (t_{cont})

1) Collision (impact) – bubble surface is strongly deformed and the particle is repelled unless attachment takes place during the first collision

2) Sliding – bubble surface is weakly deformed

Successful attachment involves three steps:

INDUCTION TIME (t_{ind})

1) Thinning of the intervening film between the bubble and the particle to the critical thickness - t_f

2) Rupture of the liquid film and formation "nuclei" of the TPC - t_r

3) Expansion of the TPC to form a stable aggregate - t_{TPC}

For attachment to occur $t_{cont} \geq t_{ind}$

Attachment – only when the thin liquid film between bubble and particle is not stable (i.e. attractive forces are dominant) and ruptures.

$$F_{TOT} = F_{el} + F_{vdW} + F_{st} + F_{H} + \dots$$

Factors affecting attachment:

- electrolyte concentration
- pH of the solution

→ affects F_{el}

- bubble size → affects ***deformation***
- particle size → affects ***film drainage***

- particle hydrophobicity
- particle shape and surface roughness

→ affects ***nanobubbles presence***

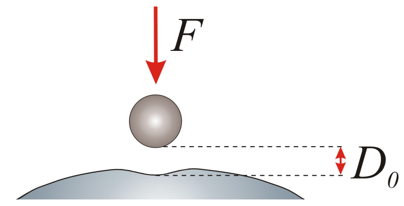
DLVO forces

non-DLVO forces

Methods

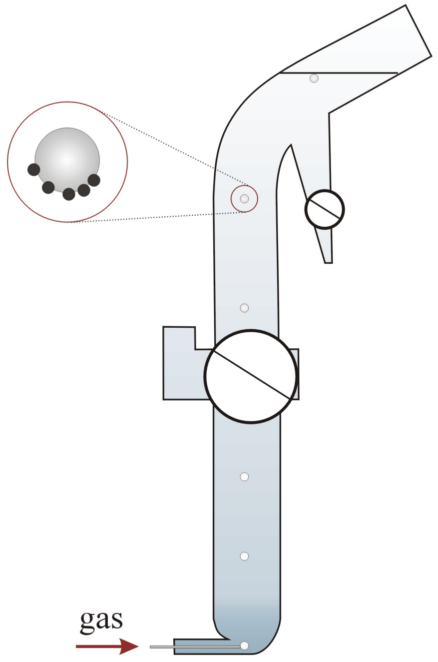
1. AFM – model system

restrained bubble – restrained particle

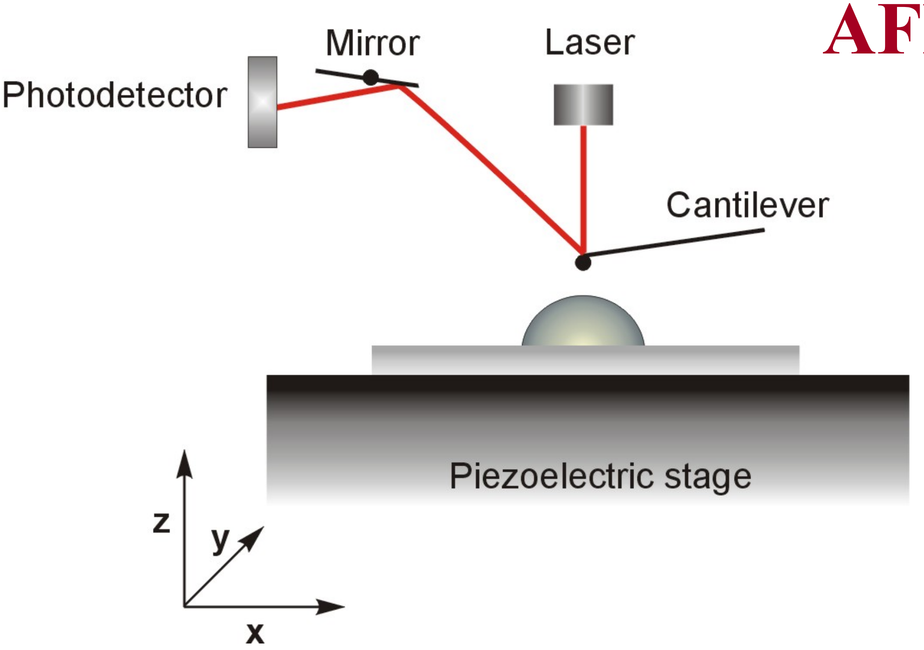


2. Single bubble flotation – diagnostic technique

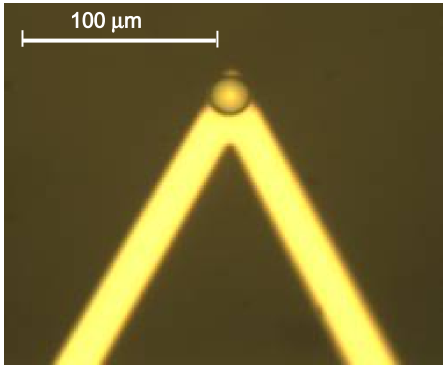
free bubble – free particles



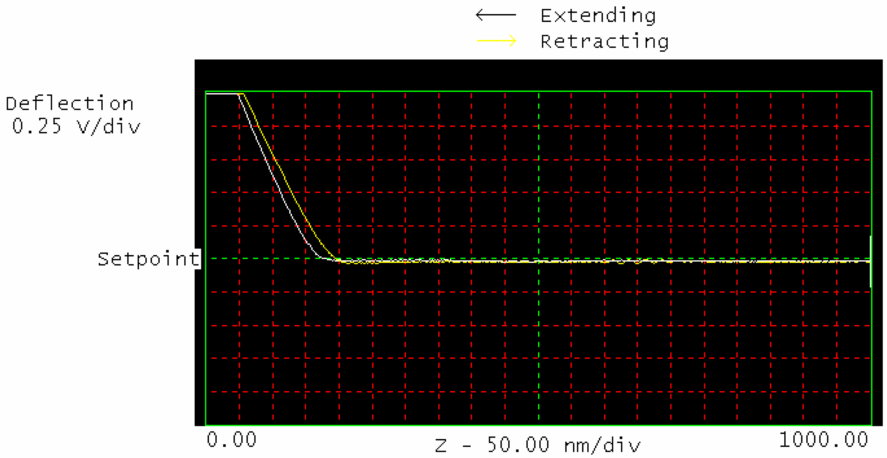
AFM



Mirror
Laser
Photodetector
Cantilever
Piezoelectric stage
z
y
x



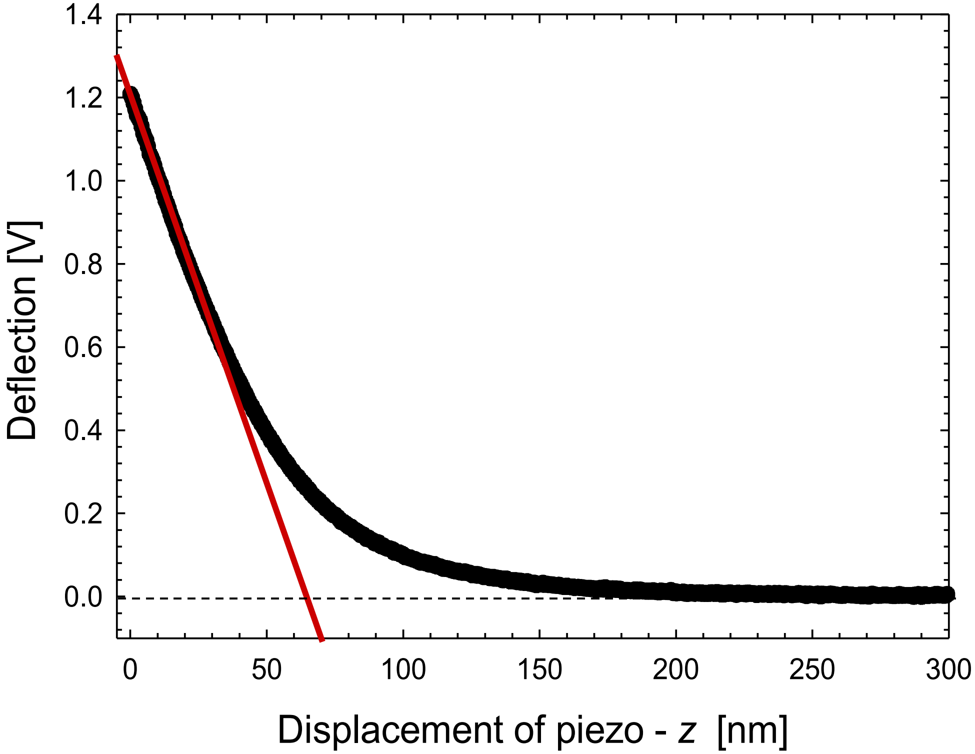
100 µm



Extending
Retracting
Deflection
0.25 V/div
Setpoint
0.00
Z - 50.00 nm/div
1000.00

$$F = K_c d$$

Linear compliance region - to convert deflection (V) into deflection (nm)



Slope of the curve < 1 for the bubble-particle system

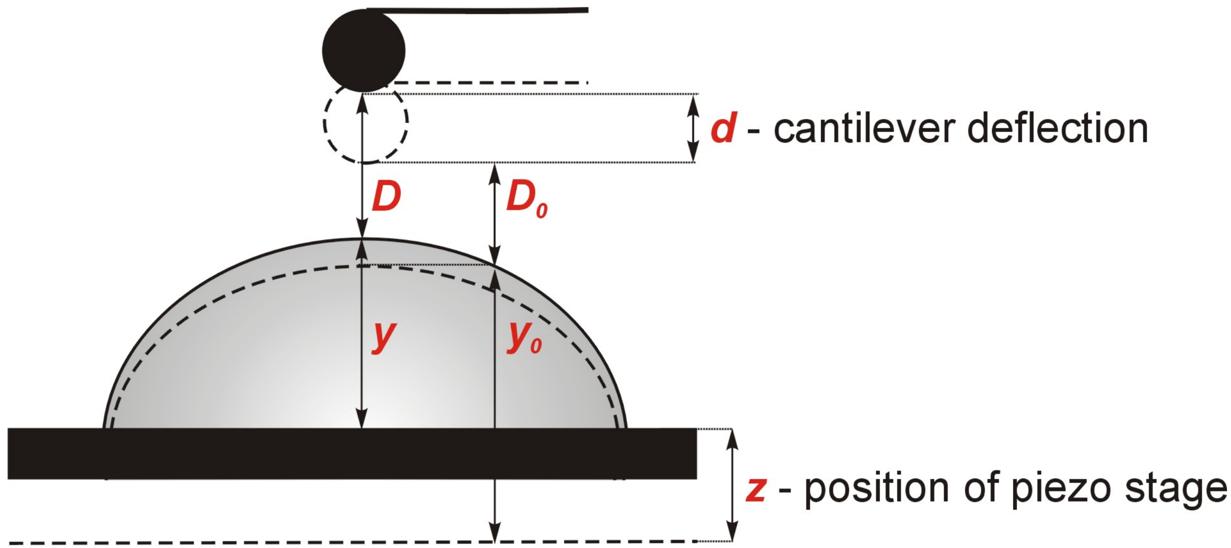
Difficult to get actual separation due to the bubble deformation

springs/capacitances model*

Force vs "normalized" separation

Slope of the curve = 1 for rigid bodies
EASY!!!

* *W.A. Ducker, Z.H. Xu, J.N. Israelachvili (1994) Langmuir **10**, 3279*



D_0 - initial separation distance
D - actual separation distance
y_0 - initaial highs of the bubble
y - actual high of the bubble

The distance balance gives:

$$D + y + z = D_0 + y_0 + d$$

Picture out of scale

$$F = K_c d$$

$$F = K_b (y_0 - y)$$

$$y_0 - y = d \, \frac{K_c}{K_b}$$

$$\mathbf{D + y + z = D_0 + y_0 + d}$$

$$D = d(1+K_c/K_b) - z$$

$$D_c = d_c(1+K_c/K_b) - z_c + D_0$$ ← Subscript “c” for linear compliance regime

$$D_c = (d-d_c)(1+K_c/K_b) - (z-z_c) + D_c$$ ← D_c << than z and z_c

$$D_c = (d-d_c)(1+K_c/K_b) - (z-z_c)$$

$$d_c = z_c \times \text{slope - intercept}$$

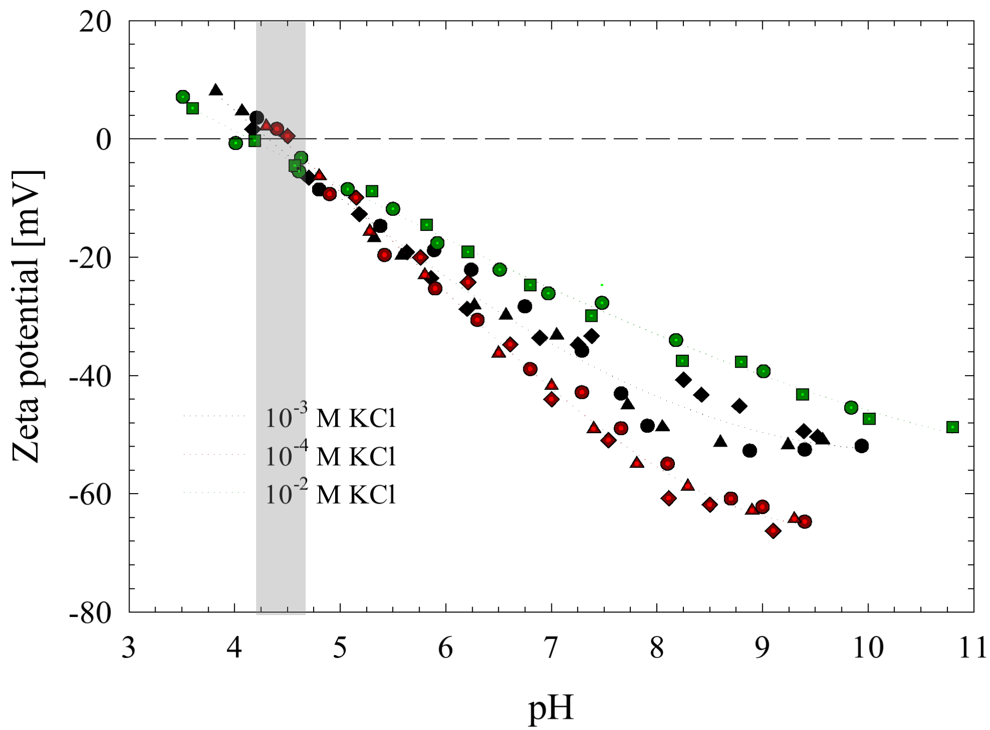
$$D_0 = D_c + \text{intercept/slope}$$

$$D = -z + ((d+\text{intercept})/\text{slope}) + Dc \sim -z + (d+\text{intercept})/\text{slope}$$

Materials

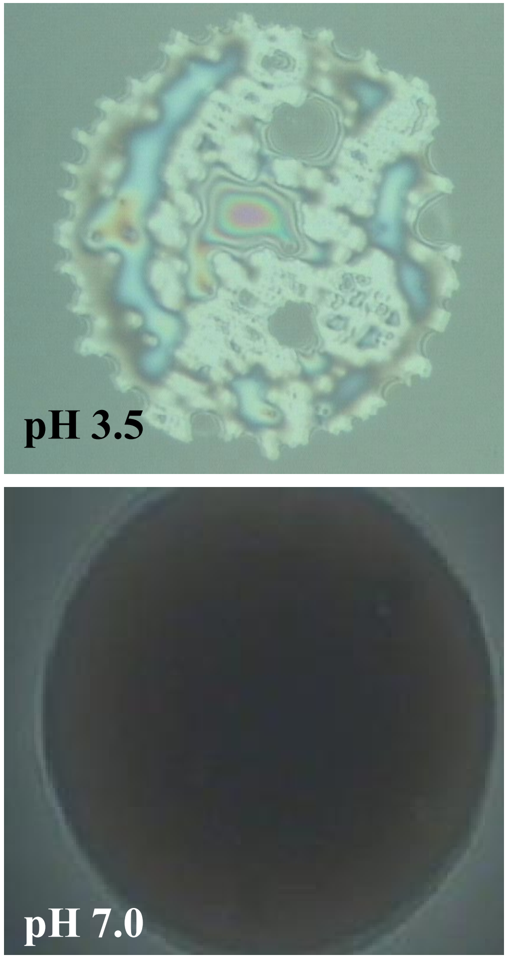
Titania

- small hydrophilic particles and smooth, flat surfaces
- isoelectric point at pH 4.3-4.8 – variation of surface potential
- can be easily hydrophobized in order to change wettability

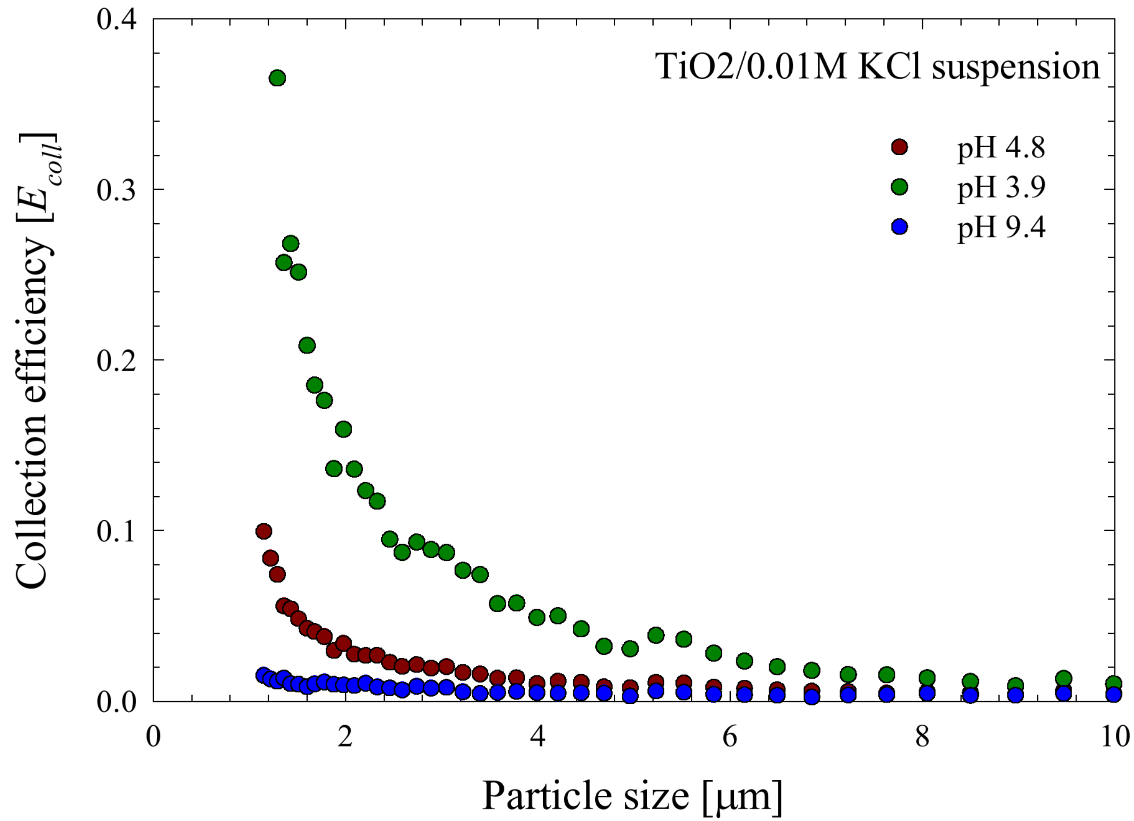


Zeta potential of TiO_2 suspension (Zetasizer Nano , Malvern).

$$E_{coll} = \frac{N_{pf(i)}}{PNC \cdot \pi \cdot h_s \left(d_p + d_b\right)^2 / 4}$$

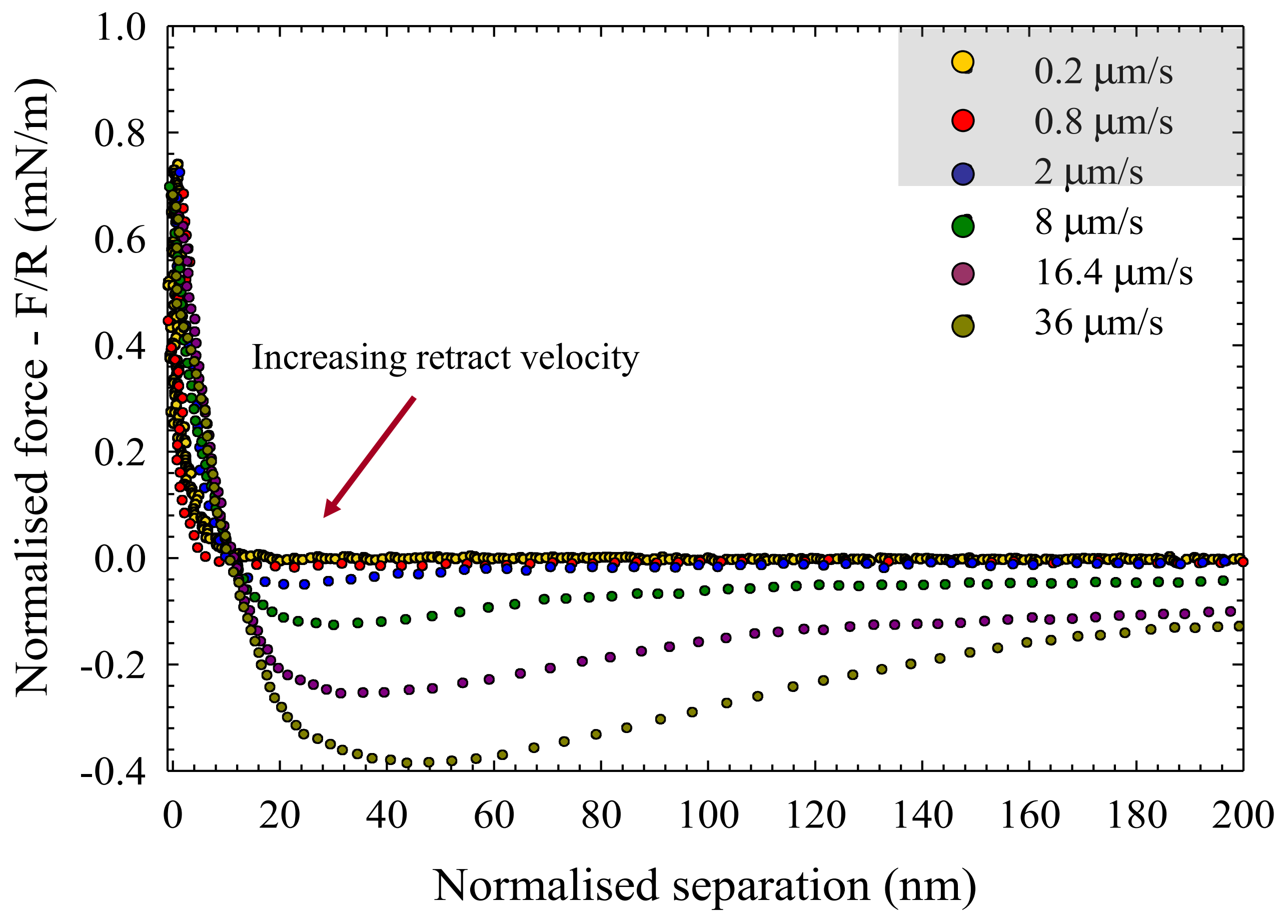


Aqueous wetting films ($I = 10^{-2}$ M) on titania, G. Hanly, PhD thesis



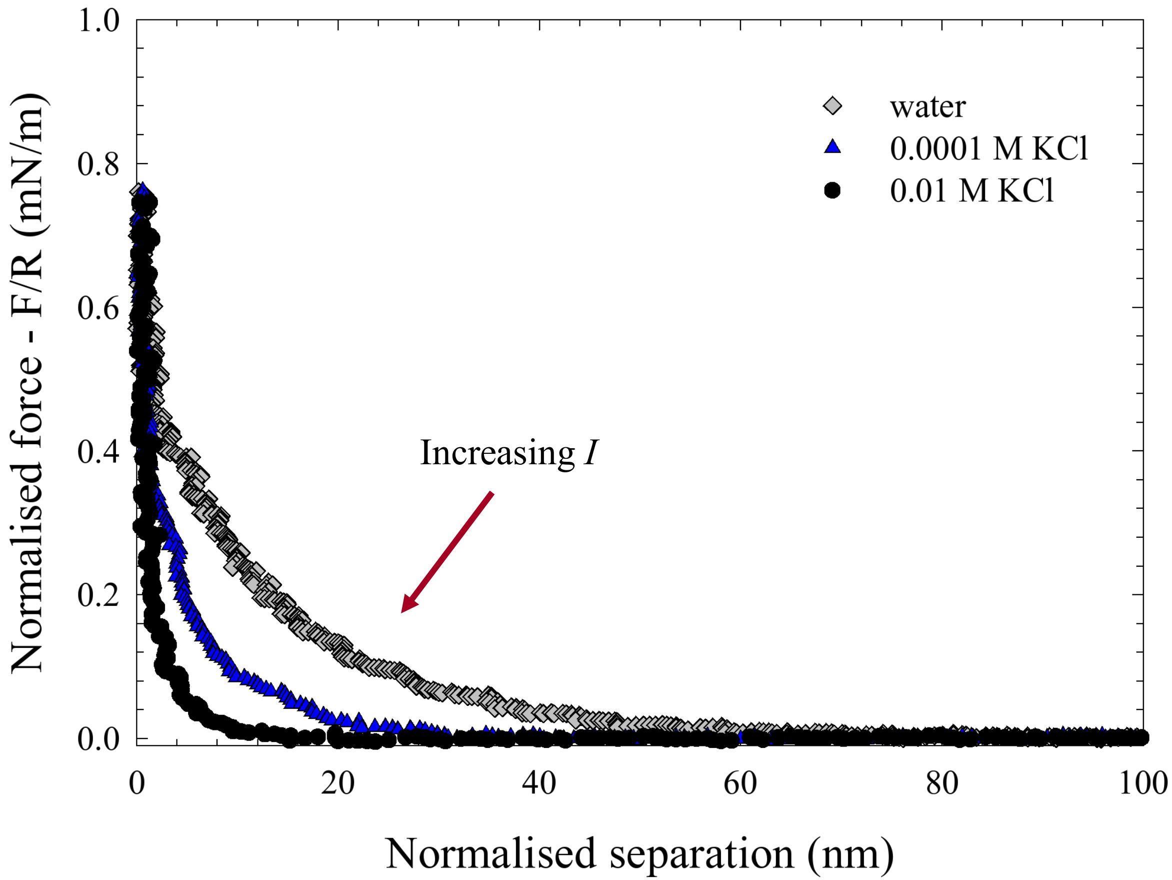
Single bubble flotation for hydrophobic TiO_2 ($\theta = 56°$) - preliminary data

Effect of retract velocity



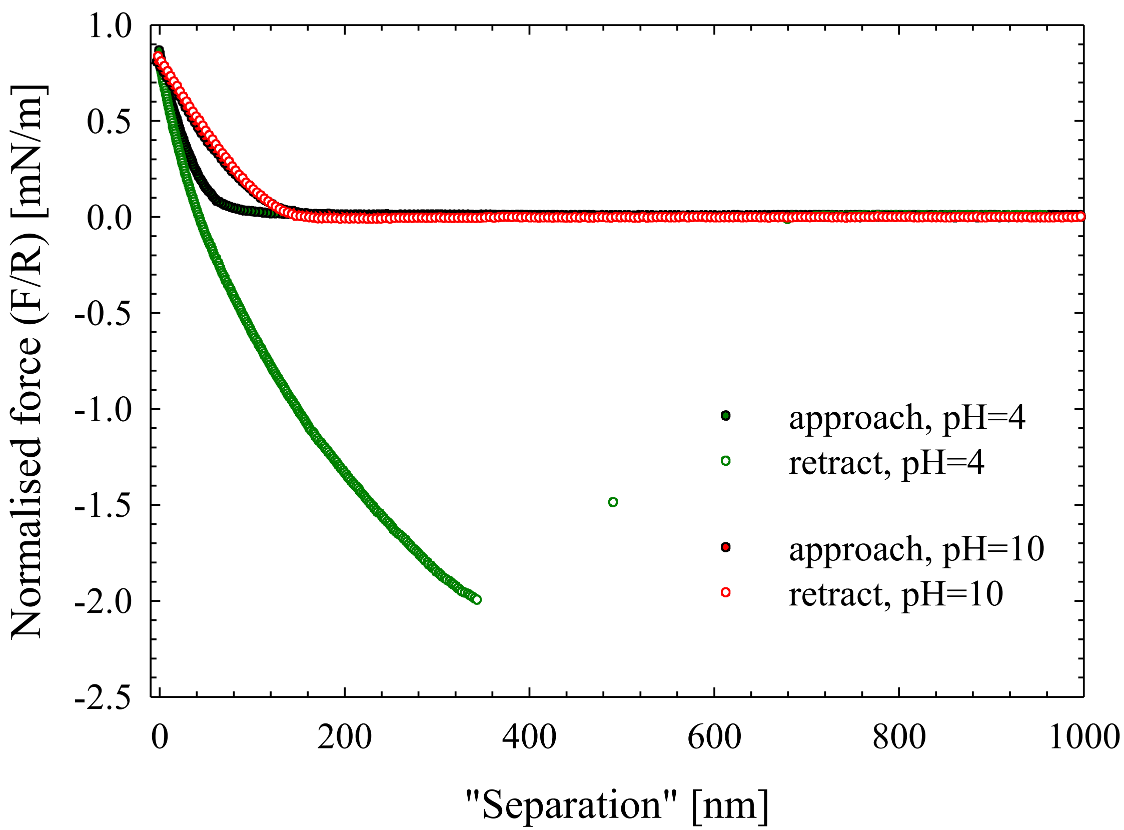
TiO_2 probe (20µm) against the air bubble (300-350 µm), at constant ionic strength (in 10^{-2}M KCl) and constant pH=5.8 - retract curves

Effect of ionic strength



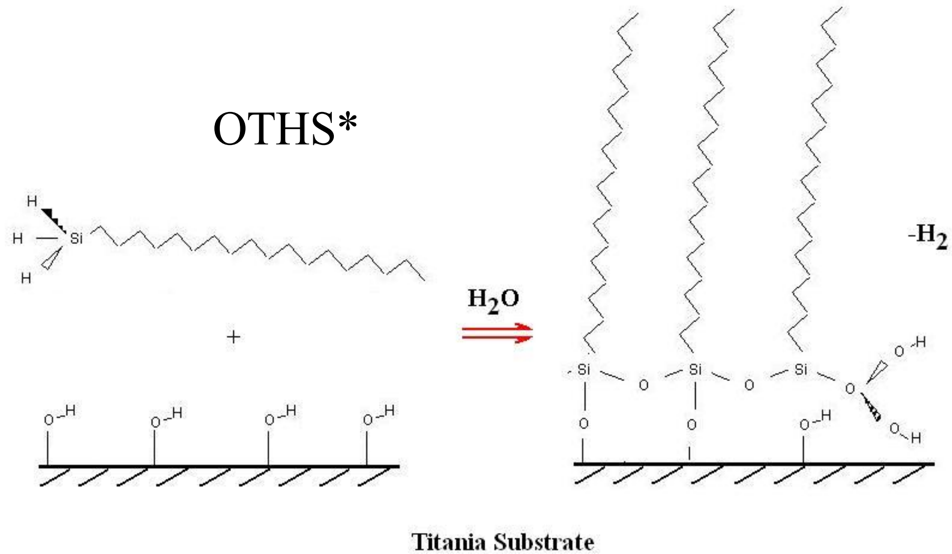
TiO_2 probe (20µm) against the air bubble (350 µm),
at constant pH =5.8, scanner velocity 0.5 µm/s - retract curves

Effect of pH



TiO_2 probe (20mm) against the air bubble (350 mm), at constant ionic strength (in 10^{-4}M KCl), scanner velocity 0.5 mm/s - retract curves

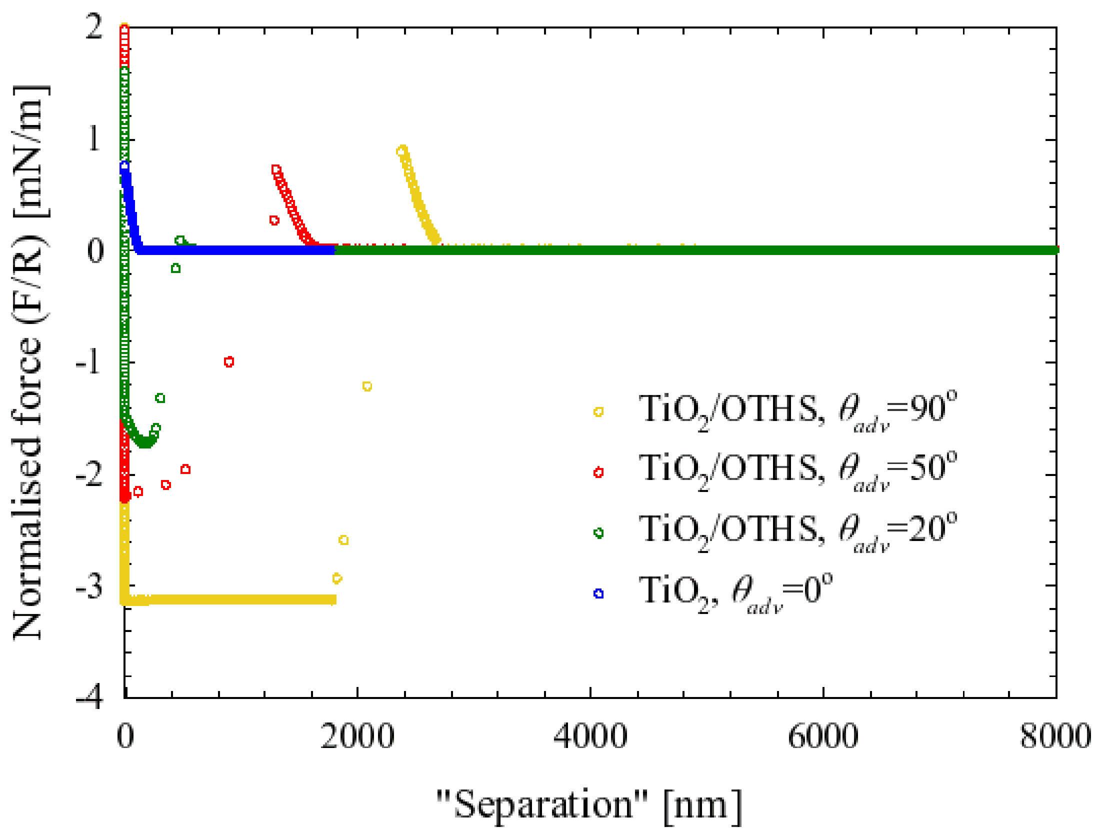
Surface modification



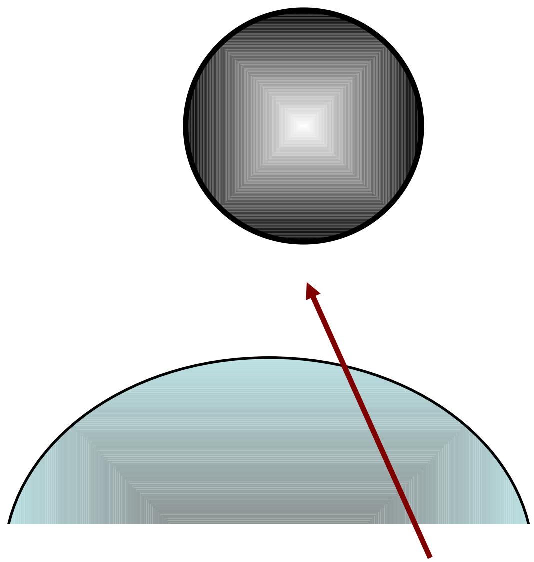
OTHS concentration
Exposure time → Different hydrophobicity

OTHS* - Octadecyltrihydrosilane consists of an eighteen carbon long hydrocarbon chain attached to a silicon hydride head group

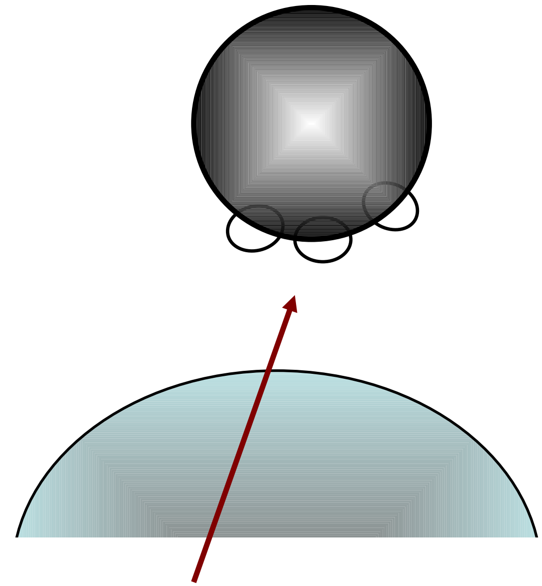
Effect of surface hydrophobicity



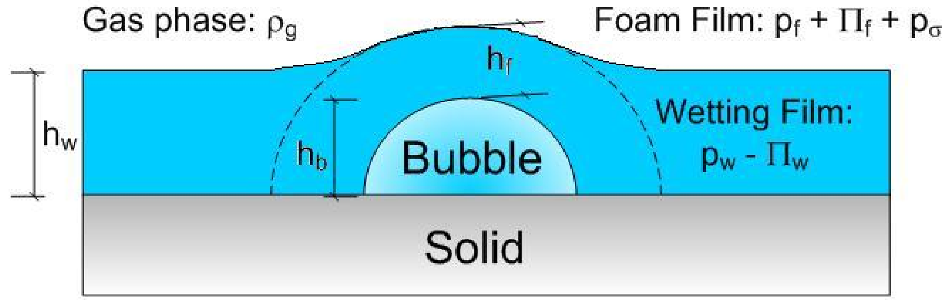
Effect of TiO_2 surface hydrophobicity on particle-bubble interaction in MilliQ water (ph=5.8) - approach curves



Wetting film



Foam film



adapted from Stockelhuber, K.W., Radoev, B., Schulze, H.J., Wenger, A., *Rupture of Wetting Films Caused by Nanobubbles*. Langmuir, 2004. **20**(1): p. 164-168.

Conclusions

Electrostatic interactions play a significant role in bubble-particle attachment and can be manipulated by altering the ionic strength and pH of the solution

When both solid/liquid and liquid/vapour interfaces are negatively charged - electrostatic repulsion dominates → stable wetting film

When the two film surfaces have opposite charges (for example below i.e.p.) the electrostatic attraction dominates → attachment is enhanced

Conclusions

Surface hydrophobicity facilitates thin liquid film rupture.
The greater surface hydrophobicity – the less stable film.

The more hydrophobic surface – the higher probability of the nanobubbles formation at the solid/liquid interface

Thank you for your attention