NOTTINGHAM
TRENT UNIVERSITY

Wetting and Adhesion: Topography and Surface Free Energy Considerations

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School of Science & Technology

32nd Annual Meeting of the Adhesion Society, Savannah, Georgia, USA

15th-18th February 2009

Overview

1. Structured Surfaces for Superhydrophobicity

- Hydrophobicity and Superhydropobicity
- Some of our Surfaces

2. Topography and Surface Free Energy

- Fakir’s Carpet, Skating and Impalement
- Surface Free Energy Derivations
- Local and not Global Parameters

3. Consequences for Adhesion?

- Liquid Marbles: Solid-on-Solid Contact
- Biofouling: Flow Enhanced Detachment
- Plastrons: Liquid-Vapor Interfaces for Flow
- Electrowetting: Overcoming Contact Angle Hysteresis

Structured Surfaces for Superhydrophobicity

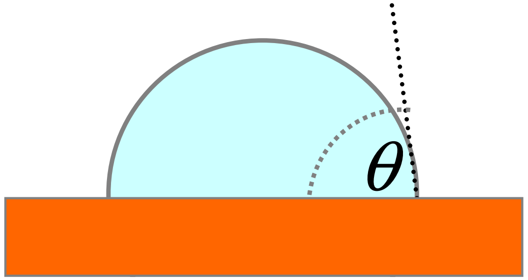
Hydrophobicity and Superhydrophobicity

Surface Chemistry

Terminal group determines whether surface is water hating

Hydrophobic terminal groups are Fluorine (CF_x) and Methyl (CH_3)

Contact Angles on Teflon

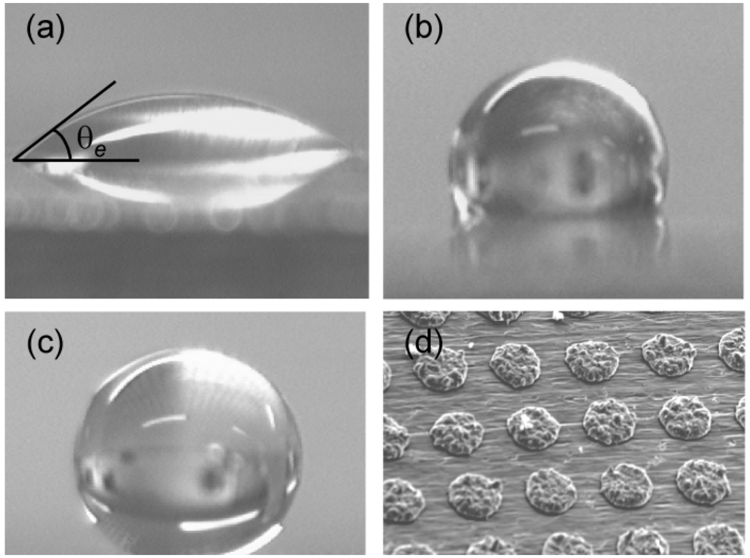


Characterize hydrophobicity

Water-on-Teflon gives ~ 115°

The best that *chemistry* can do

Enhancement by Topography



(a) is water-on-copper

(b) is water-on-fluorine coated copper

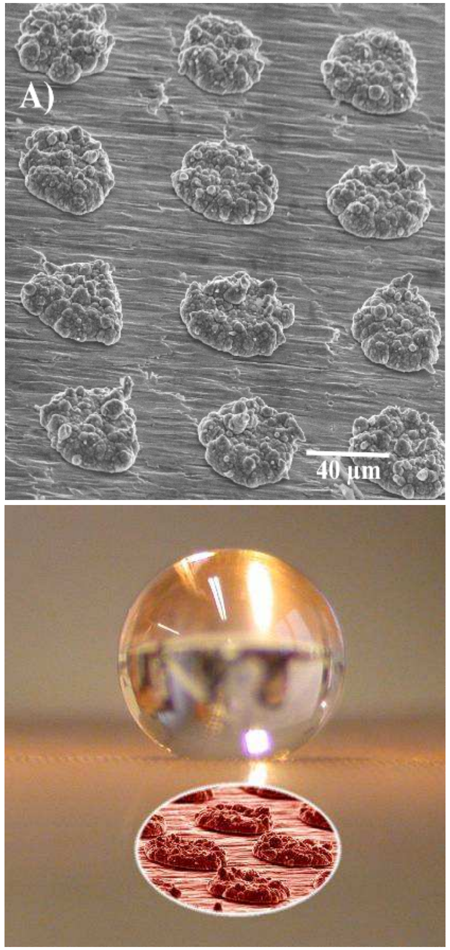
(c) is a super-hydrophobic surface

(d) “chocolate-chip-cookie” surface

Superhydrophobicity is when $\theta>150^o$
and a droplet easily rolls off the surface
(low contact angle hysteresis)

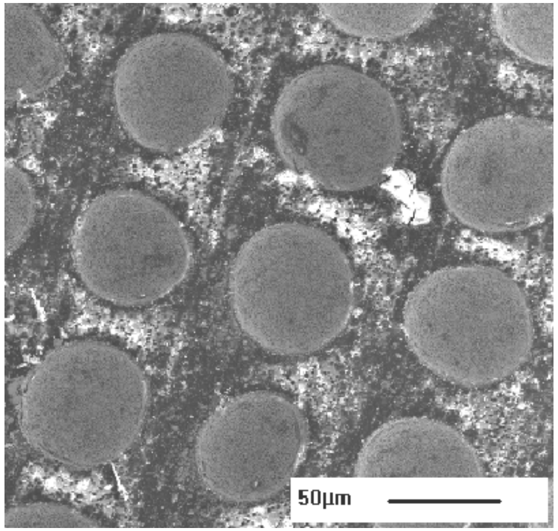
Superhydrophobicity – NTU Examples

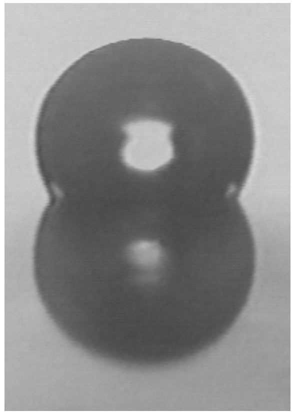
Deposited Metal



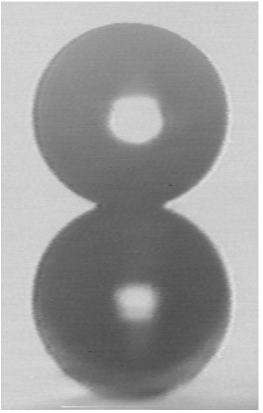
Patterned & hydrophobic

Etched Metal



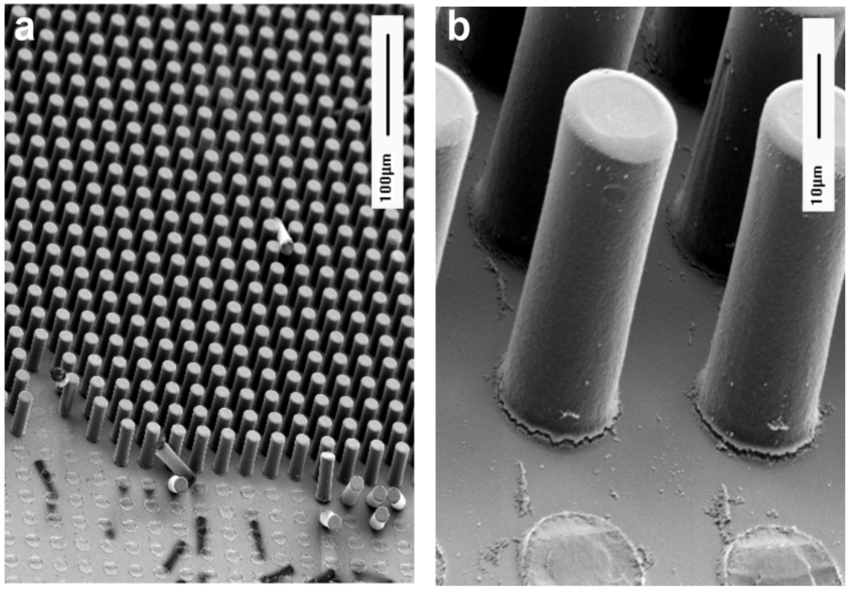


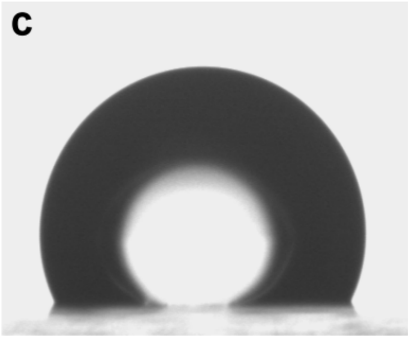
Flat & hydrophobic



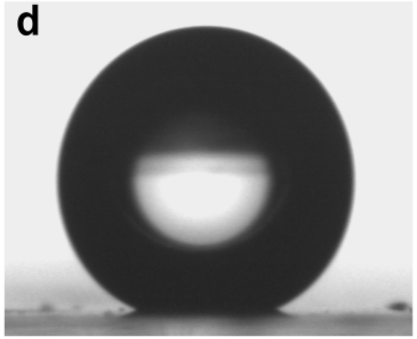
Patterned & hydrophobic

Polymer Microposts





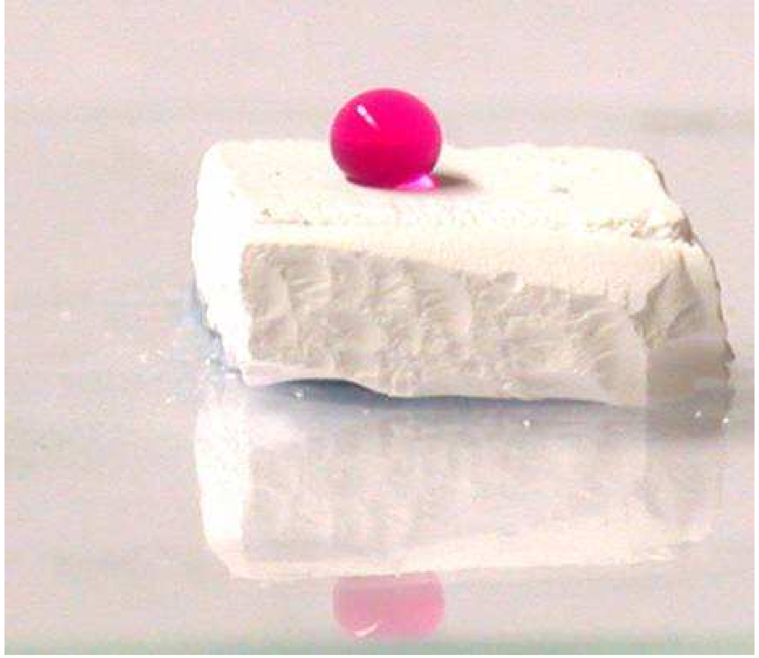
Flat & hydrophobic



Patterned & hydrophobic

<u>References</u> Shirtcliffe, N.J. *et al.*, Langmuir <u>21</u> (2005) 937-943; Adv. Maters. <u>16</u> (2004) 1929-1932; J. Micromech. Microeng. <u>14</u> (2004) 1384-1389.

Sol-Gel: Switching off Superhydrophobicity



Foam heated
(and cooled)
prior to droplet
deposition

Mechanisms for Switching

- Temperature history of substrate
- Surface tension changes in liquid (alcohol content, surfactant, …)
- Electrowetting

Switch could trigger a large change ⇒ Sensor based on hydrophobicity

Reference Shirtcliffe, N.J. *et al.*, Chem. Comm. (25) (2005) 3135-3137 (Nature News "*Quick change for super sponge*" On-line 20/7/05). Shirtcliffe, N.J., *et al.*, Maters. Chem. & Phys. 103 (2007) 112–117.

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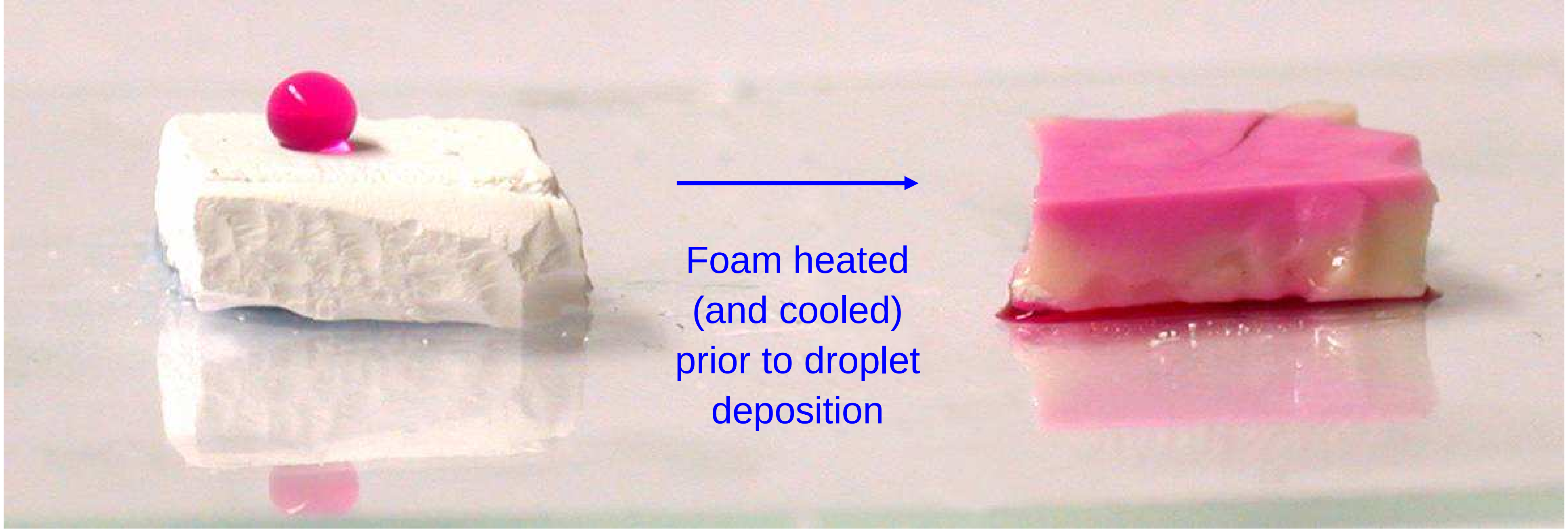
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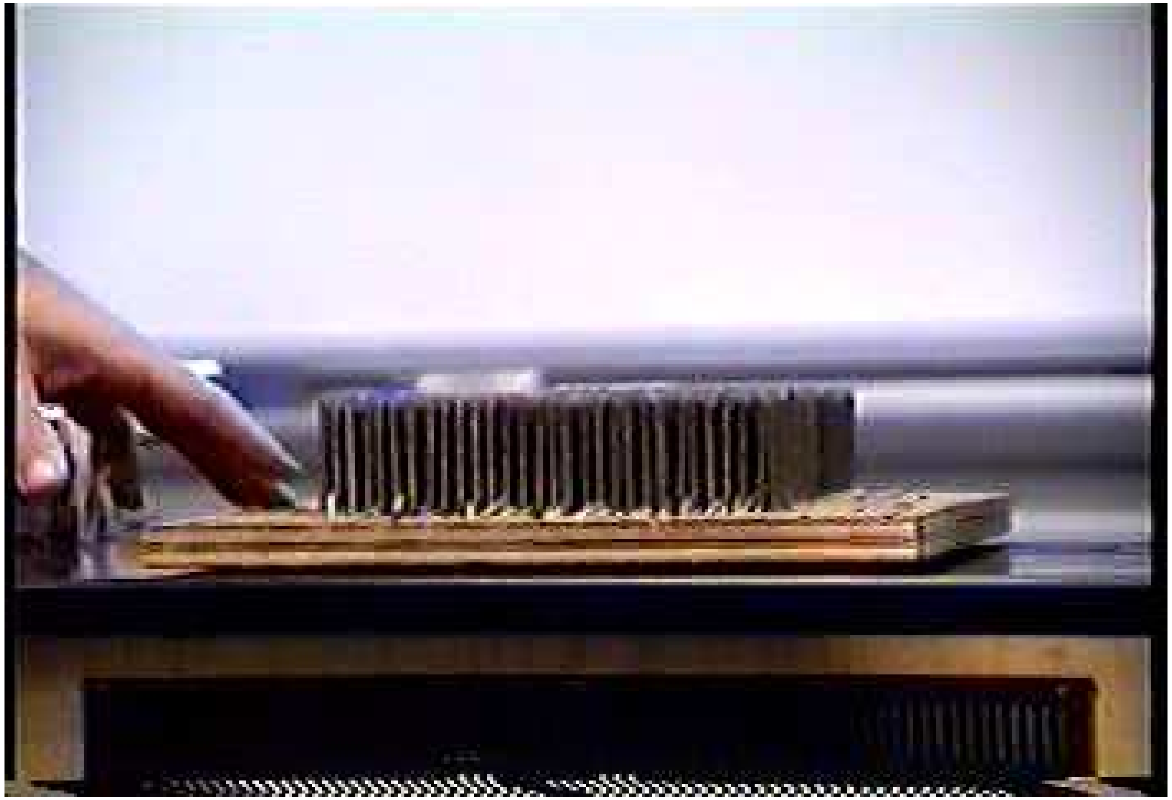
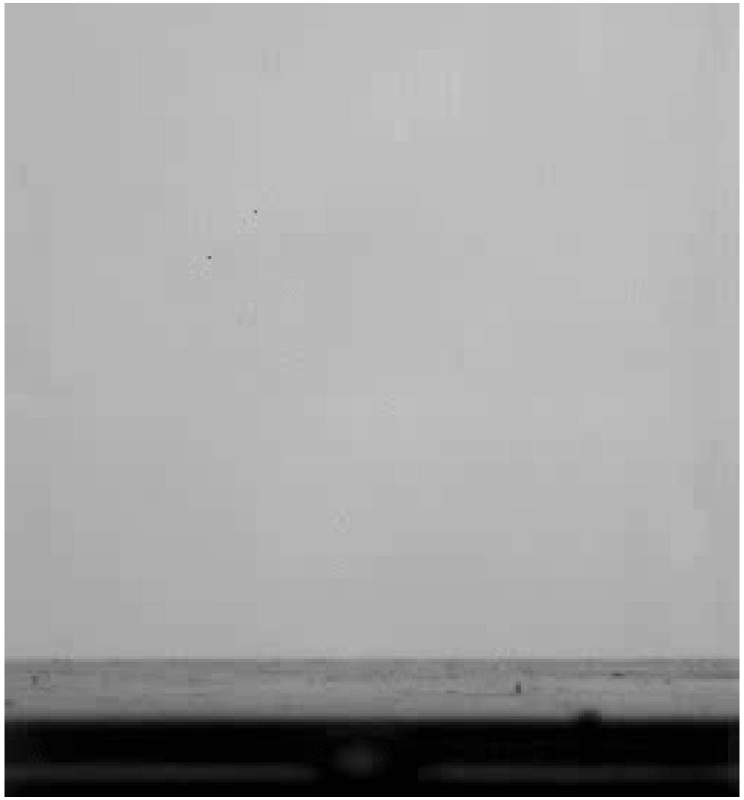
Fakir’s Carpet (and Bouncing Droplets)



Acknowledgement: Wake Forest University



Courtesy: Prof. David Quéré, ESPCI

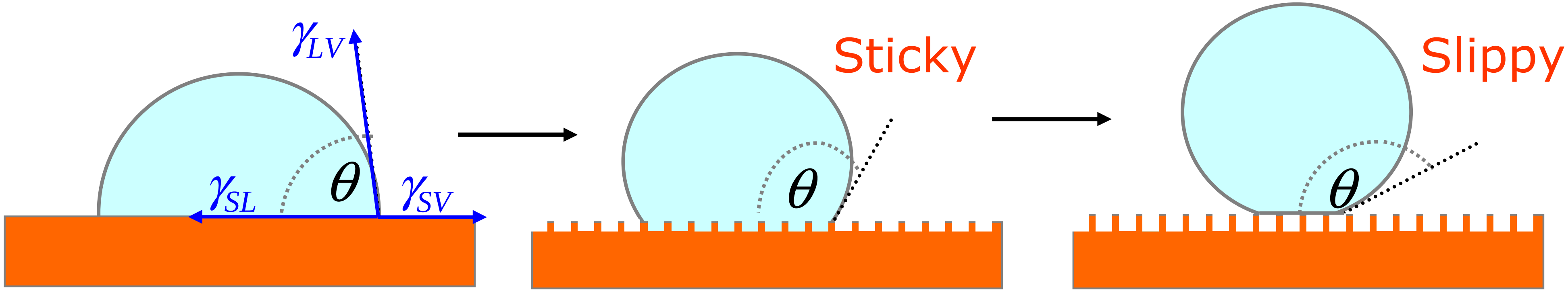
But …. liquid skin interacts with solid surfaces and “nails” do not need to be equally separated. A useful analogy, but it is not an exact view.

Topography and Surface Free Energy

Topography & Wetting

Droplets that Impale and those that Skate

What contact angle does a droplet adopt on a “rough” surface?



Young’s Law

Wenzel Eq.

Cassie-Baxter Eq

$\cos\theta_e=(\gamma_{SV}-\gamma_{SL})/\gamma_{LV}$

$\cos\theta_W(x)= r(x)\cos\theta_e$

$\cos\theta_{CB}(x)= f_s(x)\cos\theta_e-(1-f_s(x))$

Chemistry

Roughness

Chemistry

Topography

Force view:

$\gamma_{SL}+\gamma_{LV}\cos\theta_e=\gamma_{SV}$

$r(x)$= true area/planar projection at edge

Young’s Law θ_e

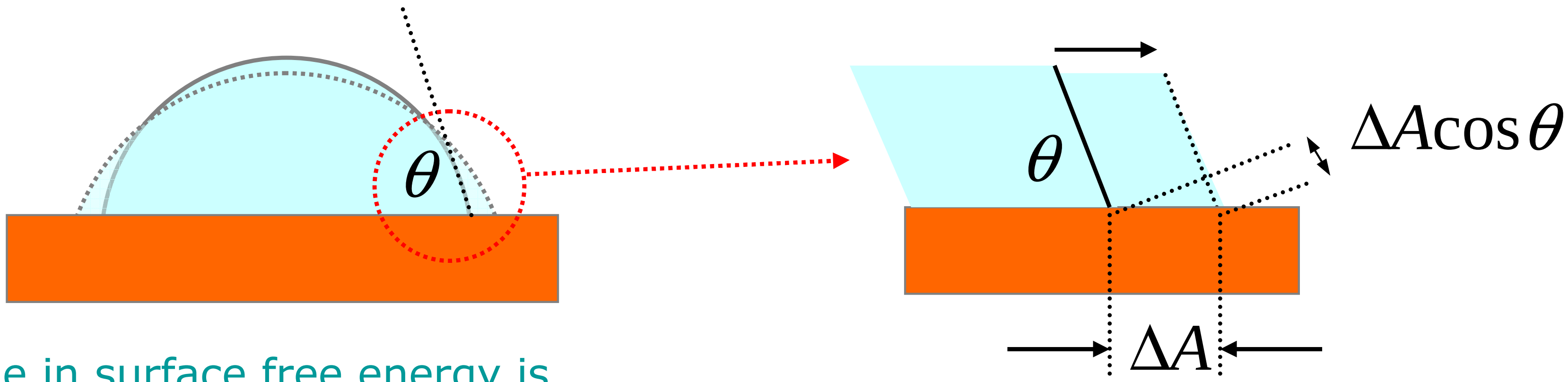
$f_s(x)$= solid surface fraction at edge

References Cassie, A. B. D.; Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. Wenzel, R. N. Ind. Eng. Chem. 28 (1936) 988-994; J. Phys. Colloid Chem. 53 (1949) 1466-1467. McHale, G., Langmuir 23 (2007) 8200-8205.

Minimum Surface Free Energy

Young’s Law – The Chemistry

What contact angle does a droplet adopt on a flat surface?



Change in surface free energy is

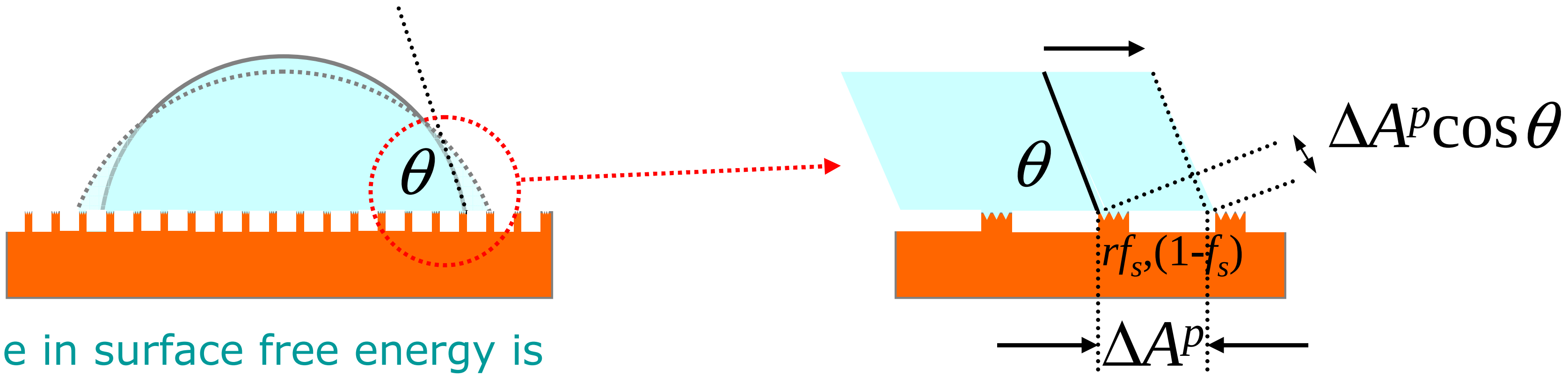
solid-liquid energy per unit area × gain of substrate area	-	solid-vapor energy per unit area × loss of substrate area	+	liquid-vapor energy per unit area × gain of liquid-vapor area

$$\Delta F(x)=(\gamma_{SL}-\gamma_{SV})\,\Delta A(x)+\gamma_{LV}\,\Delta A(x)\cos\theta$$

Equilibrium is when $\Delta F(x)=0$ $\Rightarrow$ $\boxed{\cos\theta_e=(\gamma_{SV}-\gamma_{SL})/\gamma_{LV}}$ Young’s Law

Same result as from resolving forces at contact line

Top-Filled Dual Length Scale Surfaces



Change in surface free energy is

$$\Delta F = (\gamma_{SL} - \gamma_{SV})\, rf_s \Delta A^p + \gamma_{LV}\,(1-f_s)\,\Delta A^p + \gamma_{LV}\,\Delta A^p \cos\theta$$

Equilibrium is when $\Delta F = 0$ $\Rightarrow$ $\cos\theta_{CB} = rf_s(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} - (1-f_s)$

$$\boxed{\cos\theta_{Obs}(x) = f_s(x) r(x) \cos\theta_e - (1 - f_s(x))}$$

Topography $\Rightarrow$ $f_s(x) = \Delta A_{SL}{}^P / (\Delta A_{SL}{}^P + \Delta A_{LV}{}^P)$ = solid surface fraction from planar projections

$r(x) = \Delta A_{SL} / \Delta A_{SL}{}^P$ = local roughness of “tops” of features

Transformation via Wenzel law and then by Cassie-Baxter equation

$$\theta_e \rightarrow \theta_W(\theta_e) \rightarrow \theta_{CB}(\theta_W)$$

References Shirtcliffe, N.J. *et al.*, Adv. Maters. 16 (2004) 1929-1932; Bachmann, J.; McHale, G. accepted for publication Eur. J. Soil Sci. (2009).

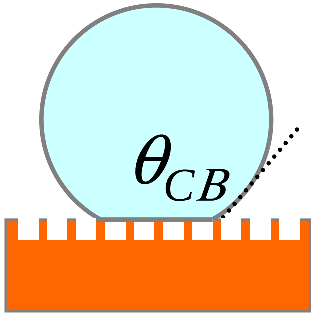
Local and not Global Parameters

Cassie-Baxter

Define surface fractions: $f_i(x)=\Delta A_i(x)/(\Delta A_1(x)+\Delta A_2(x))$

$$\cos\theta_c(x) = f_1(x)\cos\theta_1 + f_2(x)\cos\theta_2$$

for a simple post-type superhydrophobic surface ⇒

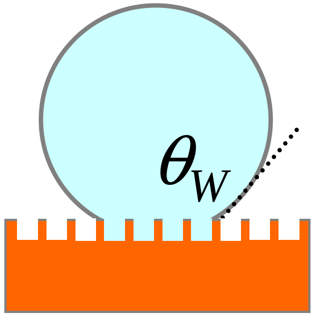


$$\boxed{\cos\theta_{CB}(x) = f_s(x)\cos\theta_e - (1 - f_s(x))}$$

where $f_s(x)$ is the solid surface fraction and the x indicates values at the three-phase contact line ($\theta_e = \theta_e(x)$ is also local to the three-phase contact line)

Wenzel

Define roughness: $r(x)=\Delta A_{wetted}(x)/\Delta A_{projected}(x)$



$$\boxed{\cos\theta_W = r(x)\cos\theta_e}$$

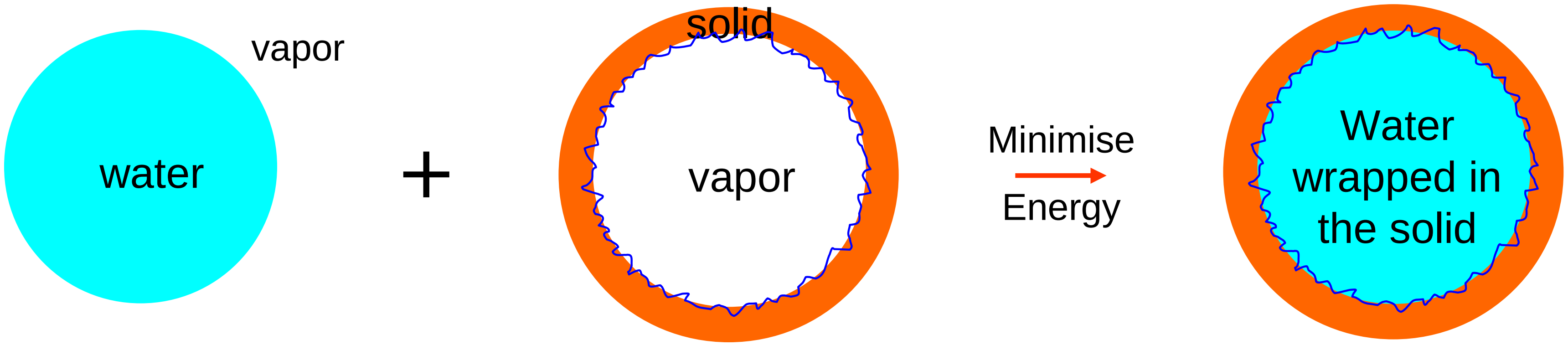
Adhesion?

Converting to a Solid-Solid Contact

Aren’t all Solids with θ_e<180° Hydrophilic?

1. Assume energy in deforming solid is zero
2. Assume solid is smooth
3. Under these conditions surface free energy always favors solid wrapping up a droplet providing the Young’s law contact angle is less than 180°

Hydrophobic Solid Shell (of thickness ε) and Water


vapor

water

+

solid

vapor

Minimise

Energy

Water wrapped in the solid

$$4\pi R^2\gamma_{LV} \quad + \quad r\,4\pi R^2\gamma_{SV} + 4\pi(R+\varepsilon)^2\gamma_{SV} \quad > \quad r\,4\pi R^2\gamma_{SL} + 4\pi(R+\varepsilon)^2\gamma_{SV}$$

gives $\Delta F/4\pi R^2 = r\,\gamma_{SL} - \gamma_{LV} - r\,\gamma_{SV}$ Use Young’s Law $\Rightarrow$ $= -(1+r\cos\theta_e)<0 \Rightarrow \theta_e$ $\theta_e<90^\circ$ $r\to\infty$

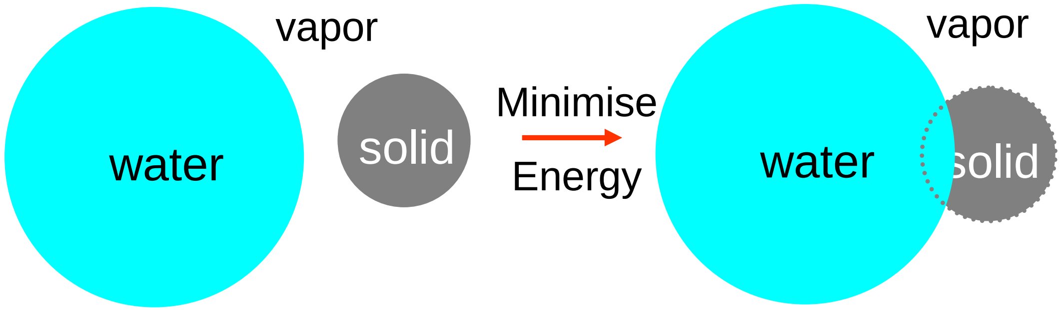
All smooth (r=1) solids with Young’s law θ_e<180° , incl. Teflon, are absolutely hydrophilic, although those with θ_e >90° have a tendency to hydrophobicity (in a Wenzel sense)

Liquid Marbles

Loose Surfaces

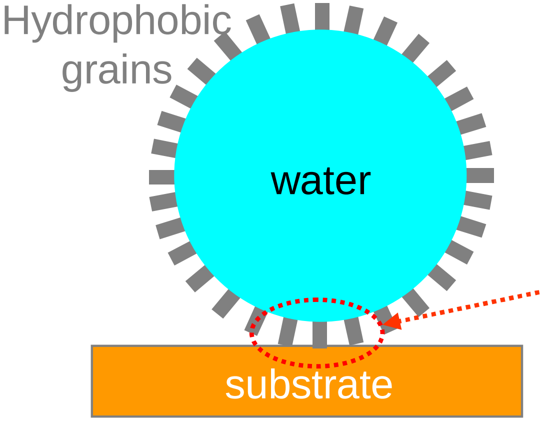
1. Grains are not fixed, but can be lifted by the liquid
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble

Hydrophobic Grains and Water



$$\Delta F = -\pi R_g^2 \gamma_{LV}(1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment



Similar to pillars, but solid conformable to liquid

Reference Aussillous, P.; Quéré, D. Nature 411 (2001) 924-927.; McHale, G. *et al*., Langmuir 23 (2007) 918-924; Newton M. I. *et al*., J. Phys. D. Appl. Phys. 40 (2007) 20-24.

Adhesion?

Biofouling: Protein Adsorption and Flow Enhanced Detachment

Biofouling and Superhydrophobic Channels

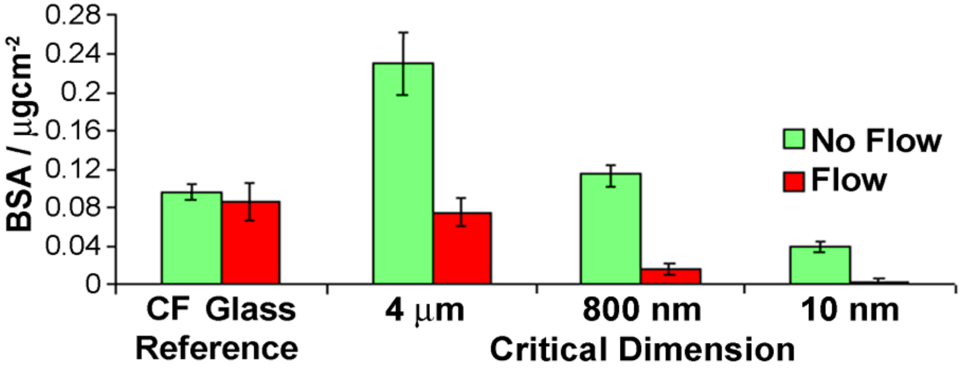
Superhydrophobic Surfaces Used

1. Glass slides
2. Sputter coated 200 nm Cu on 5 nm Ti on slides
3. Large grained (4 μm particles, 20 μm pores) superhydrophobic sol-gel on slides
4. Small grained (800 nm particles, 4 μm pores) superhydrophobic sol-gel on slides
5. CuO nanoneedles (10 nm) on Cu sheet

Proteins on Superhydrophobic Surfaces

1. Substrates incubated in BSA protein (15 nm in size) in phosphate buffer
2. Flow cell 1500μm x 650μm x 65mm using buffer solution
3. Fluorimetric assay to quantify protein removal

Fluorinated nanoscale superhydrophobic surfaces showed almost complete removal of protein under shear flow



Reference Koc, Y.; de Mello, A.J., McHale, G.; Newton, M.I.; Roach, P.; Shirtcliffe, N.J. Lab on a Chip 81 (2008) 582-586.

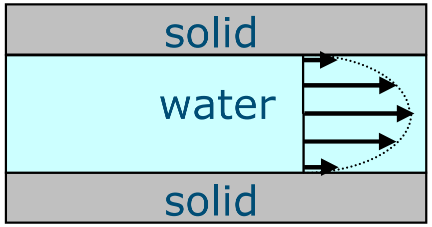
Adhesion?

Flow: Enhancement using Superhydrophobic Tubes

Flow in Pipes with Superhydrophobic Walls

Concept

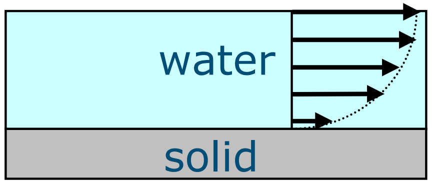
Closed-channel



Two walls cause
frictional drag

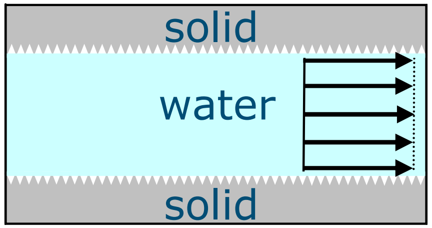
Open-channel

Low frictional drag to air



High frictional drag to solid

Super-channel



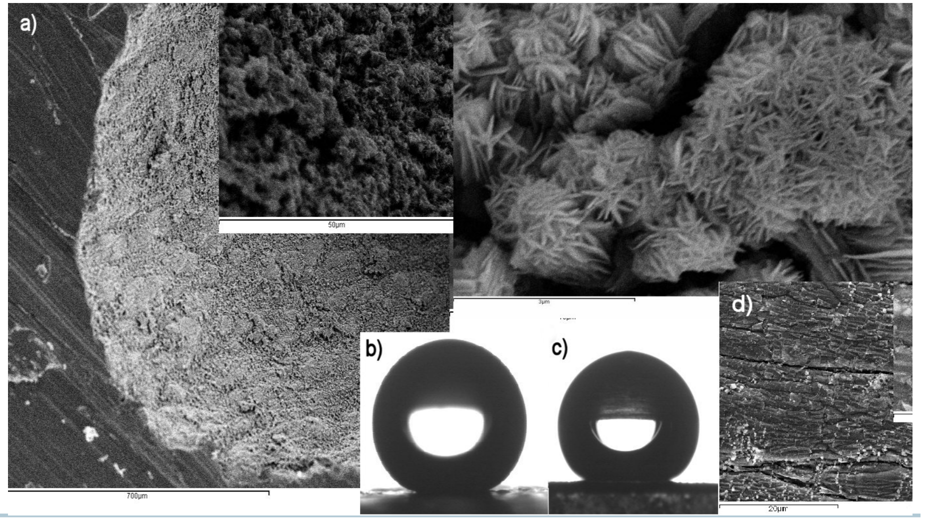
Walls appear as
cushions of air

Experiment

Forced flow through small-bore Cu tubes

Electron microscope images of hydrophobic nano-ribbon (1μm x 100nm x 6nm) decorated internal copper surfaces of tubes (0.876 mm radii).

Side-profile optical images of droplets of b) water, and c) glycerol on surface shown in a) the original surface is shown in d)

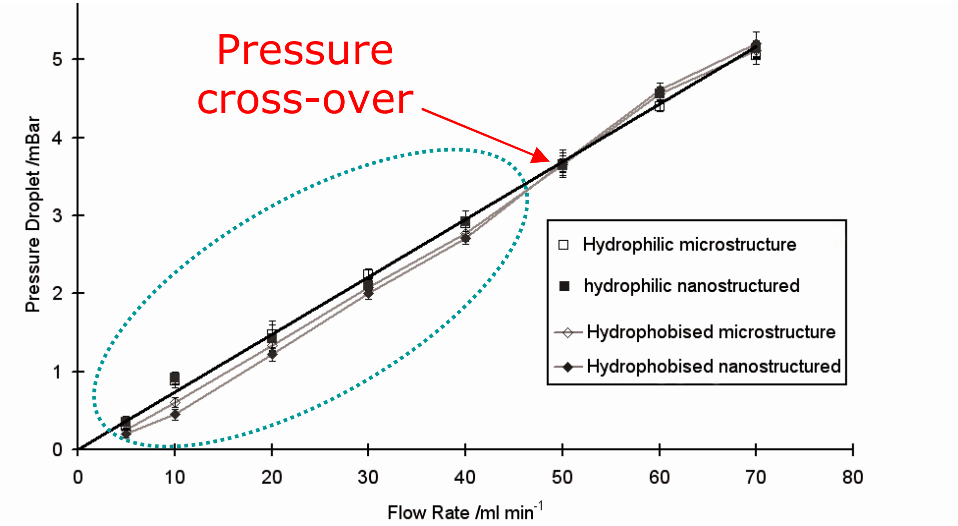


Flow in Pipes with Superhydrophobic Walls

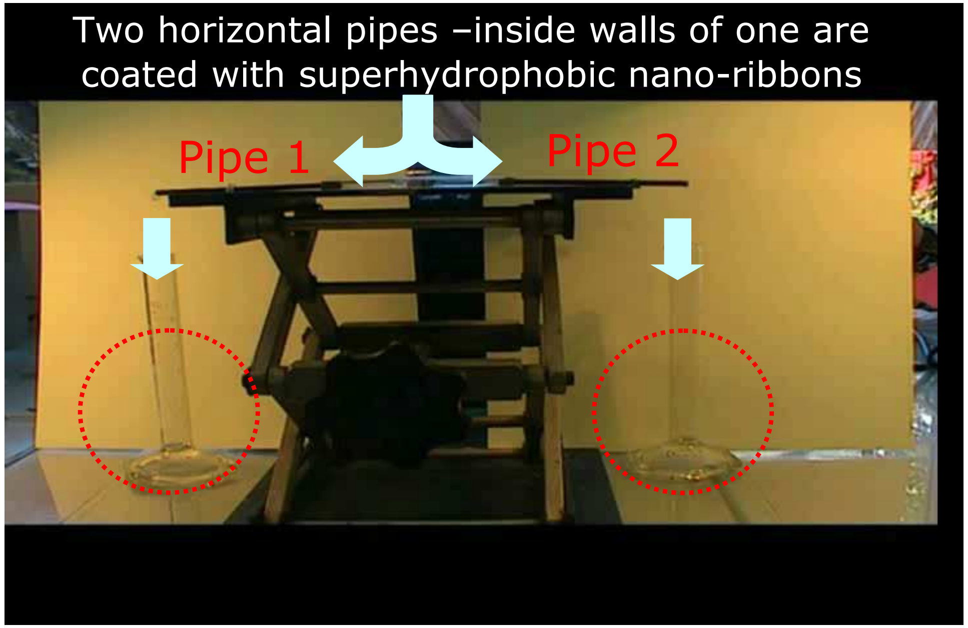
Quantitative Experiment

1. 4 parallel tubes with 4 surface finishes
2. Cu, hydrophobic Cu, nanoribbon Cu, hydrophobic nanoribbon Cu
3. Peristaltic pump to force flow in all 4
4. Measure pressure drop across each

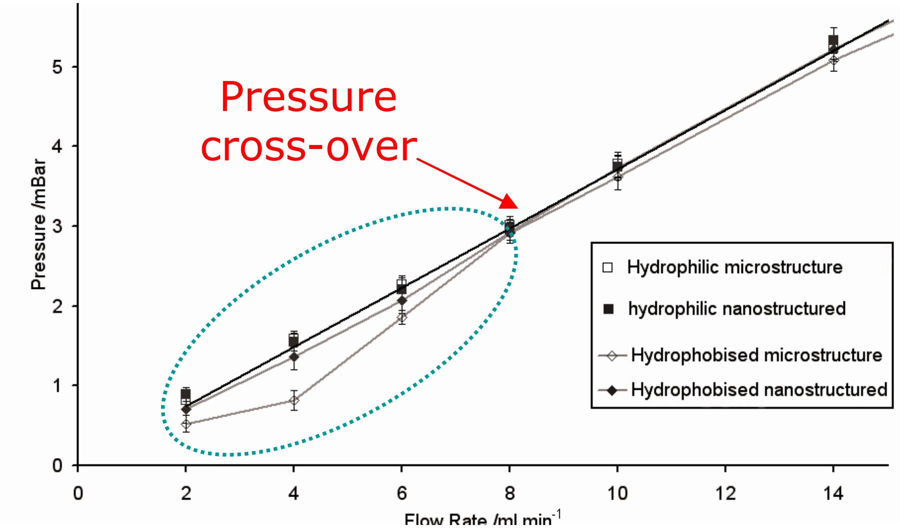
Water



Supporting Visualization Experiment


Two horizontal pipes –inside walls of one are coated with superhydrophobic nano-ribbons

50% Water - 50% Glycerol



Adhesion?

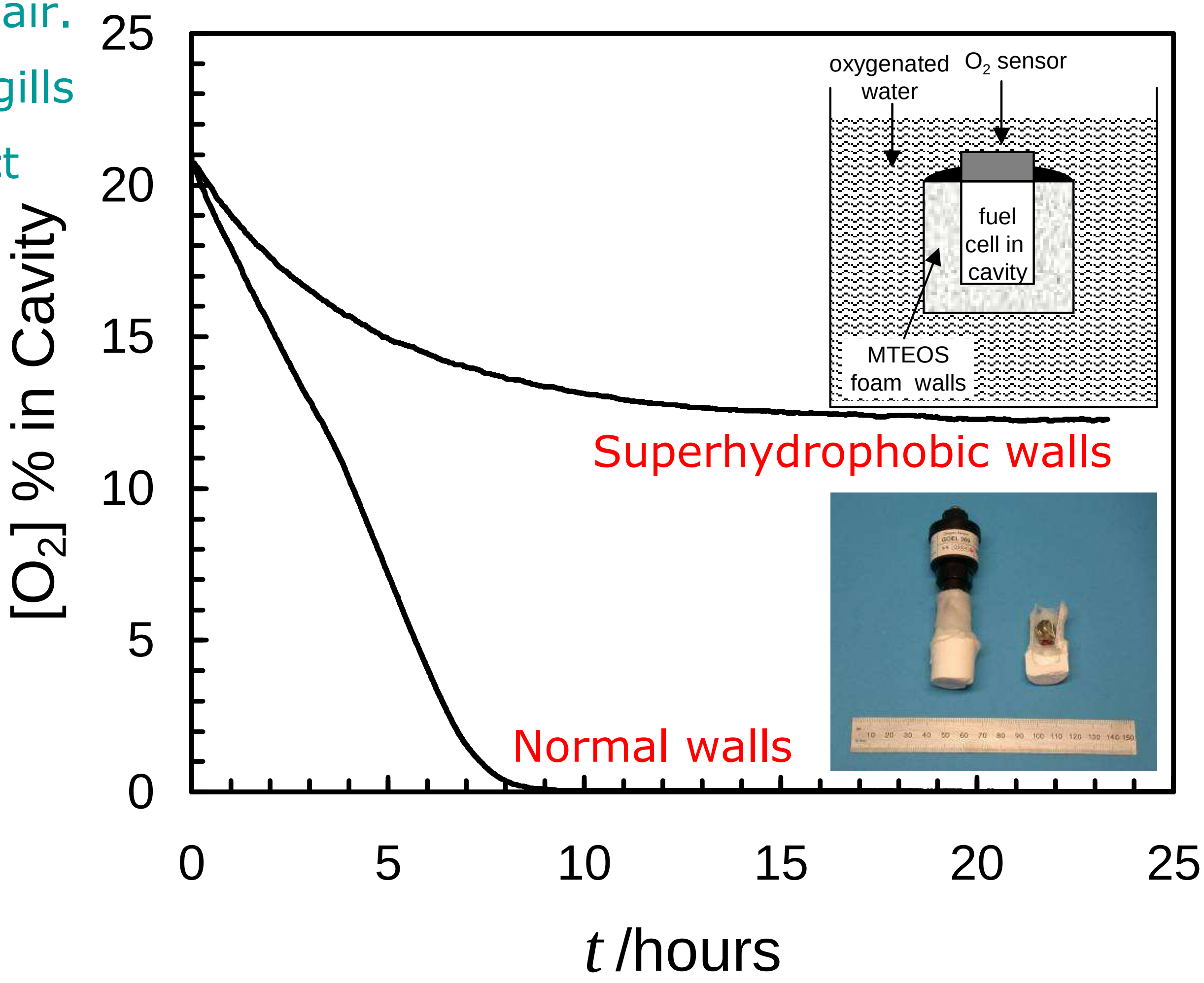
Plastrons: Replacing Liquid-Solid with Liquid-Vapor Boundaries

Plastrons in Biology

Superhydrophobic surfaces have a silvery sheen when immersed – due to surface retained layer of air. Plastrons for breathing without gills have been known about in insect physiology for since the 1940's.

Water ("Diving Bell") Spider –
but not bubble respiration

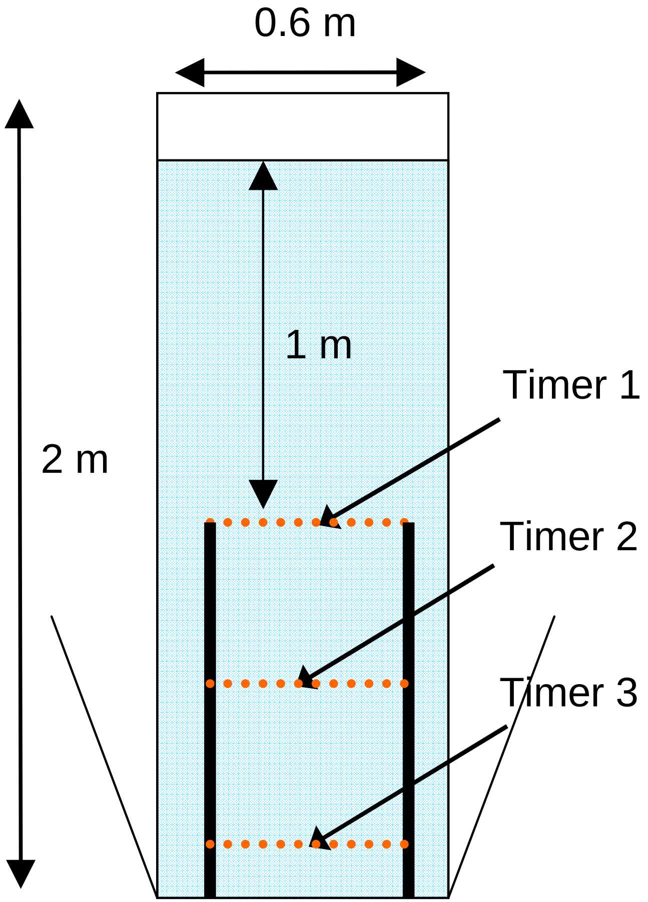
The Movie – Microcosmos



References Thorpe, W. H.; Crisp, D. J., J. Exp. Biol. 24 (1947) 227. Shirtcliffe, N.J.; McHale, G., *et al*., Appl. Phys. Lett. 89 (2006) art. 104106.

Terminal Velocity

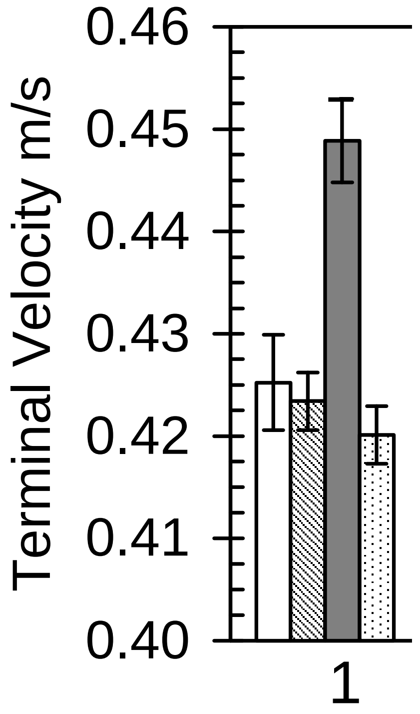
In the presence of a fluid, a falling object eventually reaches a terminal velocity. Textbooks tell us that in water the terminal velocity does not depend on the surface chemistry …. But is that true?




Dr Carl Evans

Terminal Velocity Results

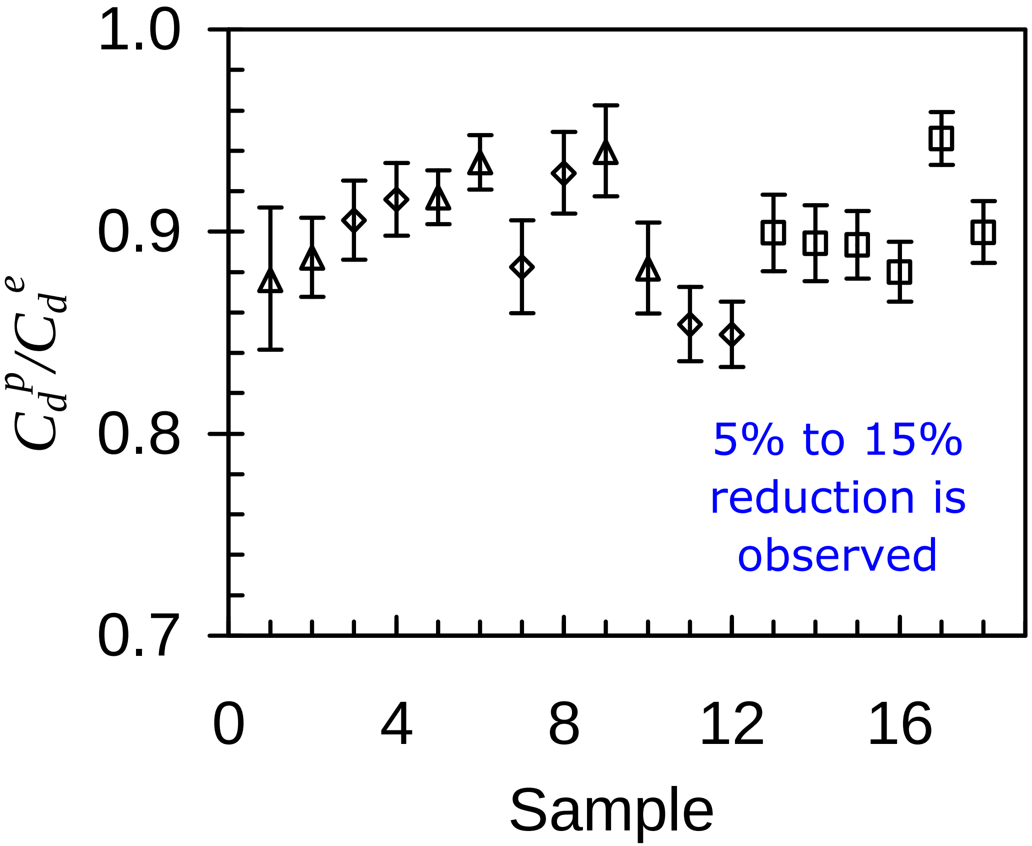
Results for 1-inch Diameter Sphere



Sequence of Four Bars

1. Blank surface
2. Sieved sand surface
3. (Super) Hydrophobic sand
4. Hydrophobic sand with ethanol pre-treatment to prevent plastron

Reduction in Drag Coefficient



5% to 15% reduction is observed

Superhydrophobicity alone is not enough. Also need a plastron to persist to achieve drag reduction

Reference McHale, G. *et al*., Appl. Phys. Lett. 94 (2009) art. 064104.

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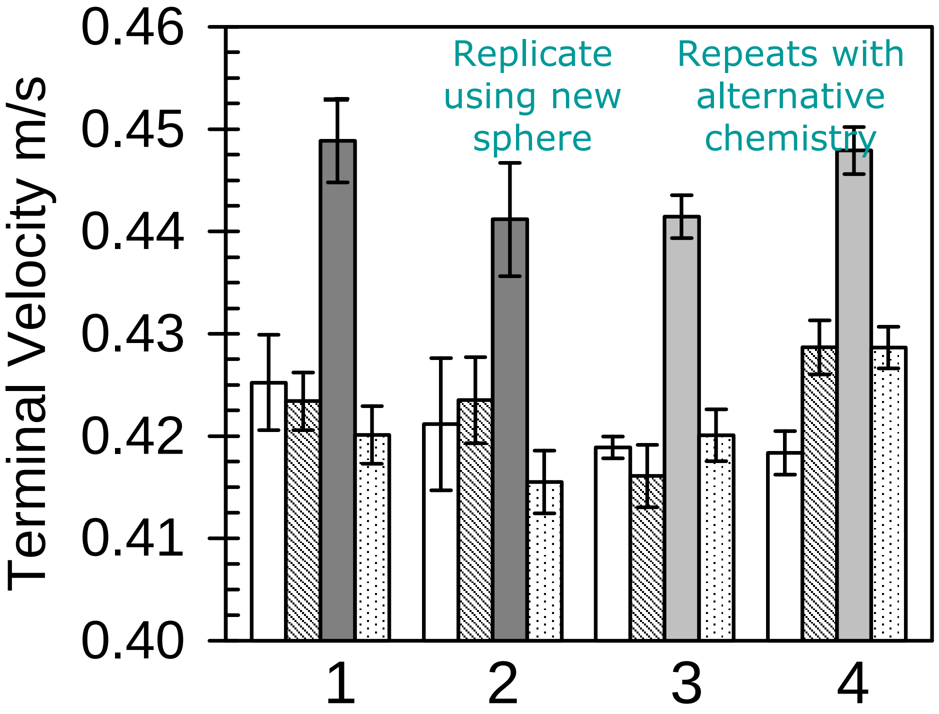

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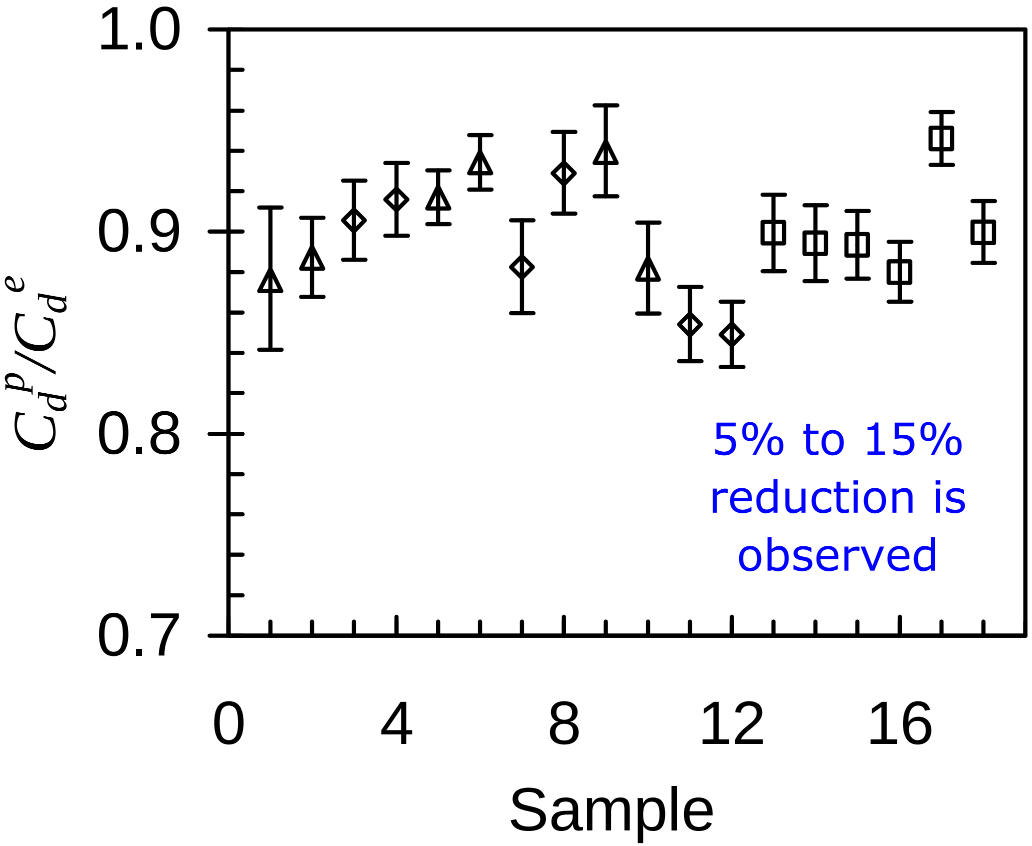

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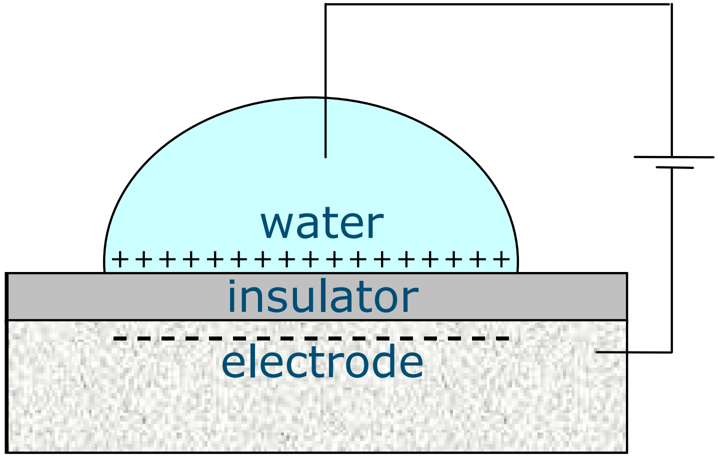
Adhesion?

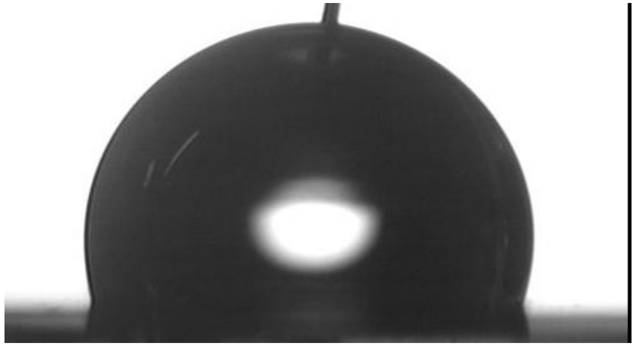
Electrowetting: Promoting Droplet Sliding

Electrowetting-on-Dielectric

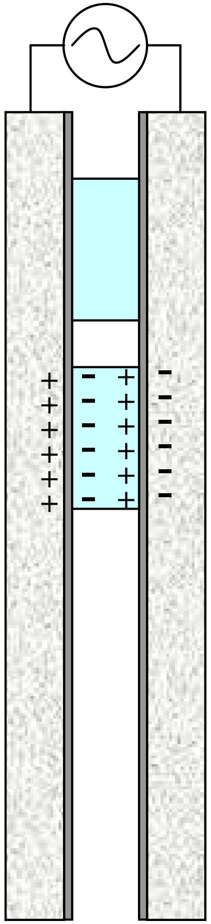
Use a droplet of water as an electrode – charge up water-solid interface

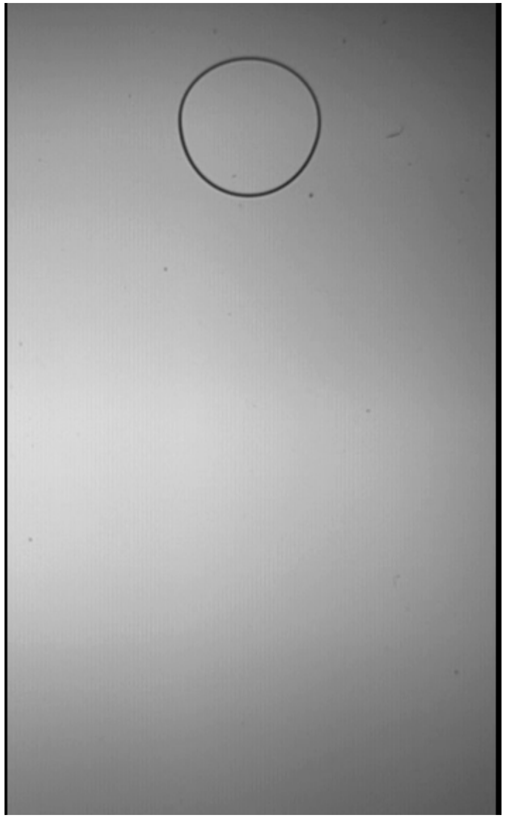
Electrowetting in Air





Electrowetting: Overcoming Hysteresis





Courtesy: Prof. Frieder Mugele (Univ. Twente)

Conclusions

1. Superhydrophobic Surfaces
   - Allow interplay between topography and surface chemistry to be explored
   - Uses of local variations in roughness and Cassie fraction still to be explored
2. Adhesion and Wetting
   - Droplets can be encapsulated to create free rolling solid-on-solid contact
   - Superhydrophobic surfaces may still foul, but flow can induce detachment
   - Plastrons can create boundary layers of air and reduce drag
   - Surface energy can be capacitively modulated to overcome hysteresis

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The End

Acknowledgements

Dr Mike Newton, Dr Neil Shirtcliffe, Prof. Carole Perry, Prof. Brian Pyatt, Dr Stefan Doerr (Swansea), Dr Stuart Brewer (Dstl), Dr Carl Evans, Dr Yong Zhang, Dr Dale Herbertson, Mr Steve Elliott

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