Immersed Superhydrophobicity, Reconfigurable Substrates and Shaped Liquid Surfaces

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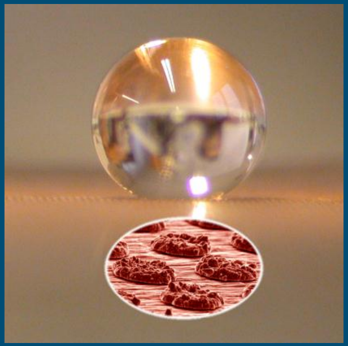
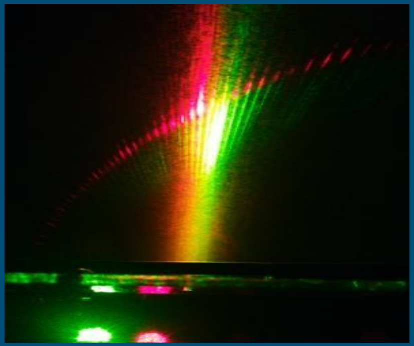




www.naturesraincoats.org

22nd February 2011

Overview

1. Concepts of Water Repellency
2. Effects of Topography
3. Amplification, Switching and Superspreading
4. Conformable Substrates
5. Immersed Superhydrophobic Surfaces
6. Dielectrowetting

1. Concepts of Water Repellency

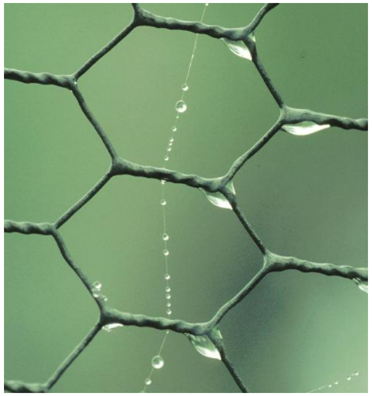
Surface Tension

Liquid Surface

Molecules at a surface have fewer neighbours

Liquid surface ("skin") behaves as if it is in a state of tension

For a free "blob", the smallest area is obtained with a sphere



http://www.brantacan.co.uk

Size Matters

Surface tension force ∝ length

e.g. Force~$R\gamma_{LV}$

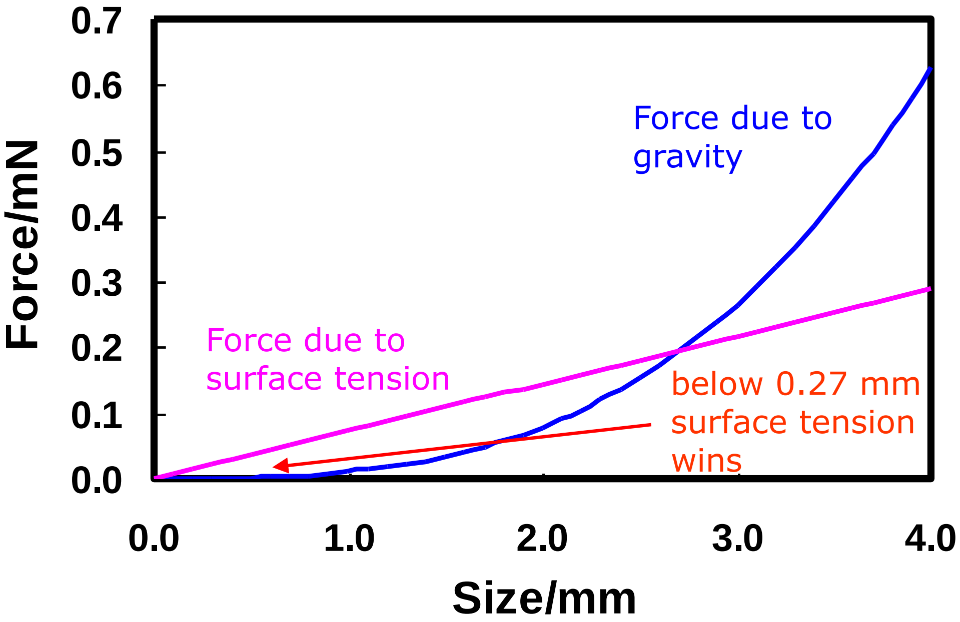
Gravity forces ∝ length^3

e.g. Force~$R^3\rho g$

Small size ⇒ surface tension wins

Small means<<capillary length

$\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2}$ ~ 2.73 mm (water)



Size Matters: Fiction or Fact?

The Movie – Antz (1998)

Copyright: DreamWorks Animation (1996)

Is it just imagination?

Or could it happen?

Hydrophobicity and Superhydrophobicity

Surface Chemistry

Terminal group determines whether surface is water-liking or water-fearing

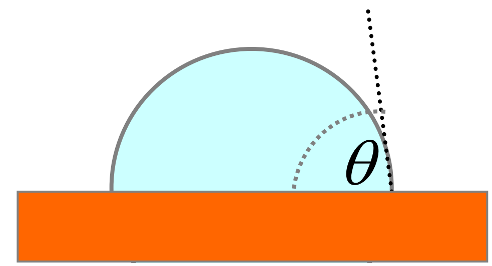
Hydrophobic terminal groups are Fluorine (CF_x) and Methyl (CH_3)

Contact Angles on Teflon

Characterize hydrophobicity

Water-on-Teflon gives ~ 115^o

The best that *chemistry* can do



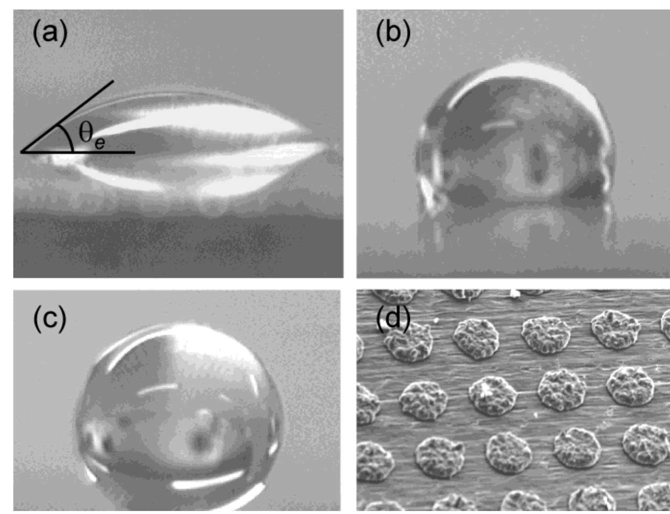
Enhancement by Topography

(a) is water-on-copper

(b) is water-on-fluorine coated copper

(c) is a super-hydrophobic surface

(d) "chocolate-chip-cookie" surface



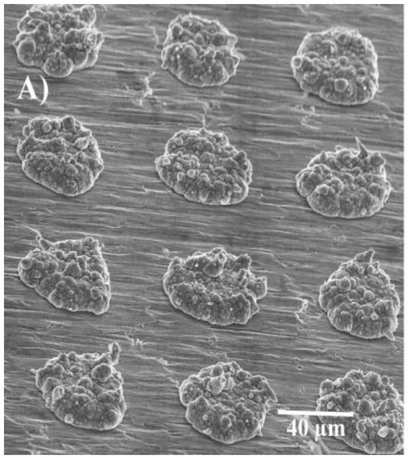
Superhydrophobicity is when $\theta > 150^o$ and a droplet easily rolls off the surface (low contact angle hysteresis)

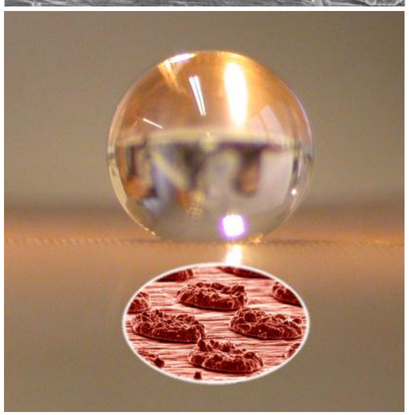
References Neinhuis,C., Barthlott, W. Ann. Bot., 79 (1997) 667-677; Planta 202 (1997) 1-8.
Onda, T. *et al.*, Langmuir 12 (1996) 2125-2127.

2. Effects of Topography

Superhydrophobicity – NTU Examples

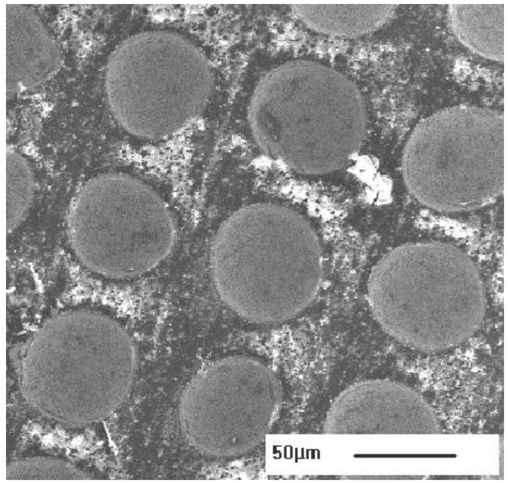
Deposited Metal

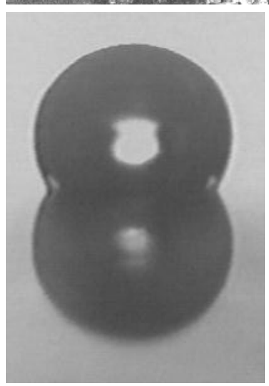




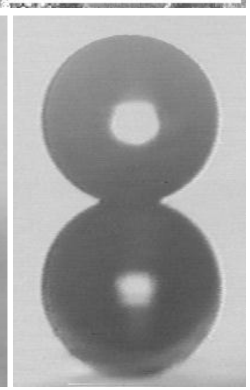
Patterned & hydrophobic

Etched Metal



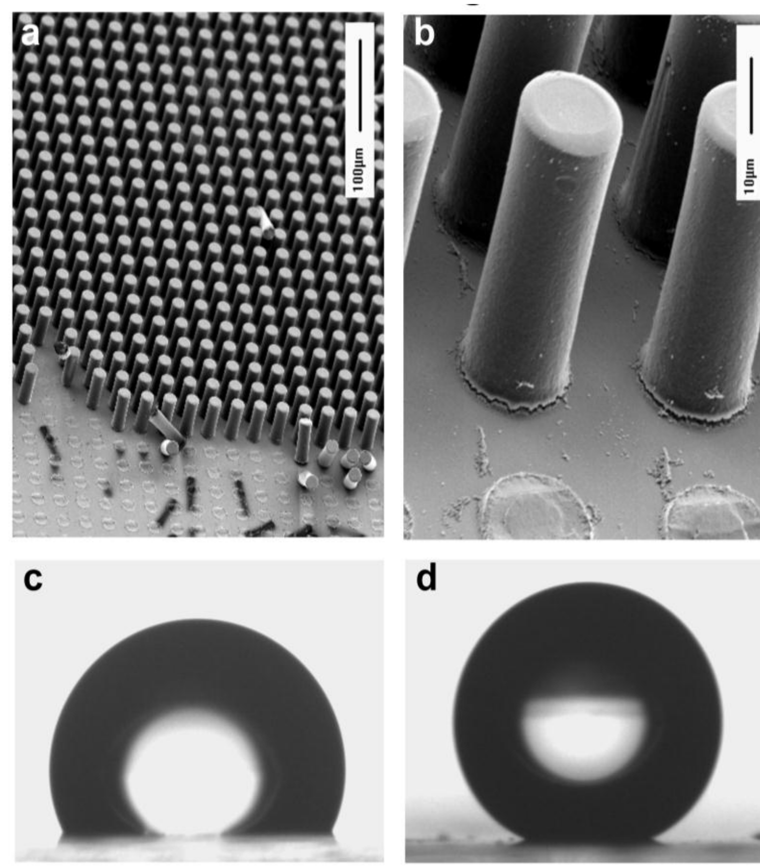


Flat & hydrophobic



Patterned & hydrophobic

Polymer Microposts

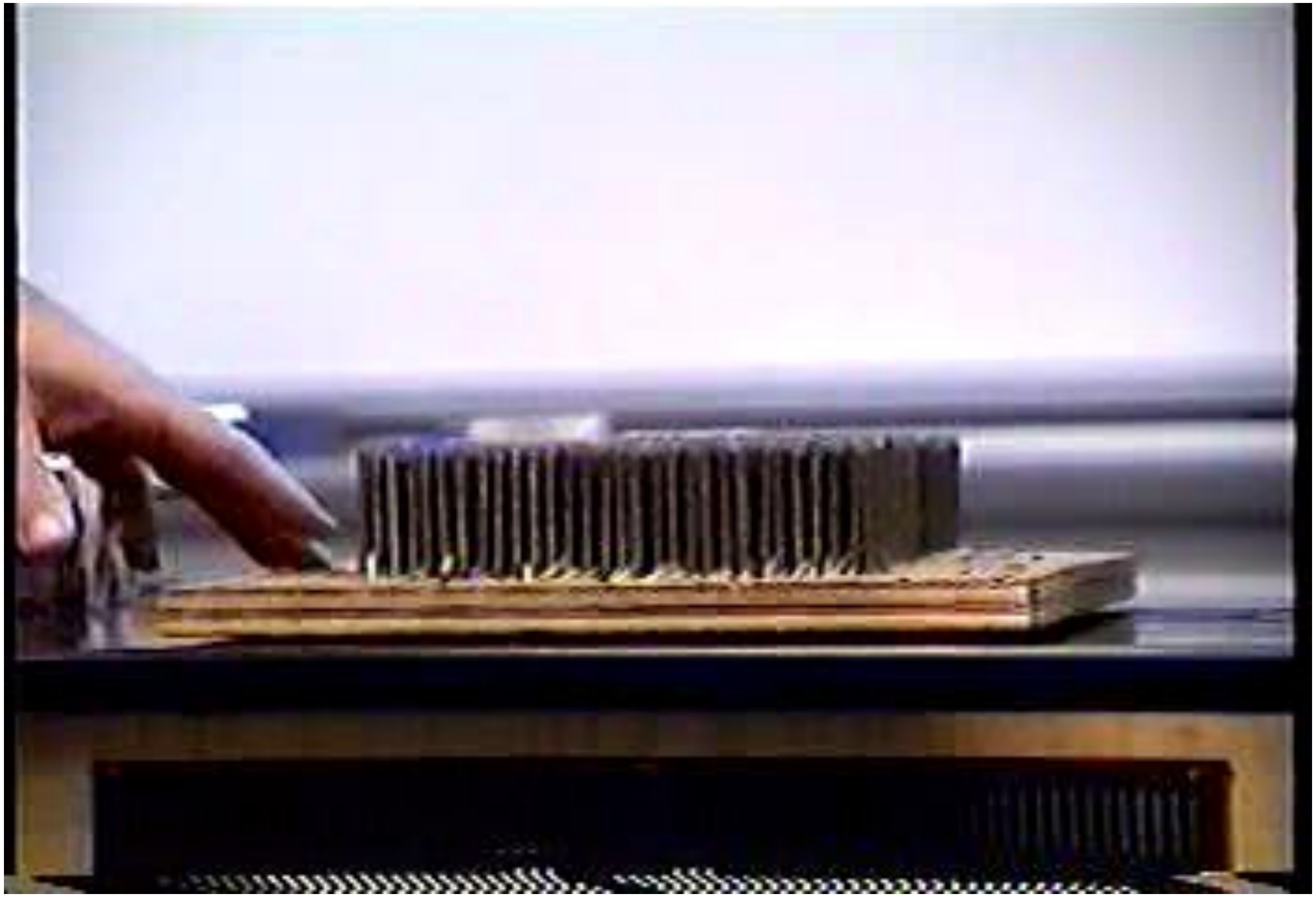


Flat & hydrophobic

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.

Fakir's Carpet



Acknowledgement: Wake Forest University

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.

Bed of Nails

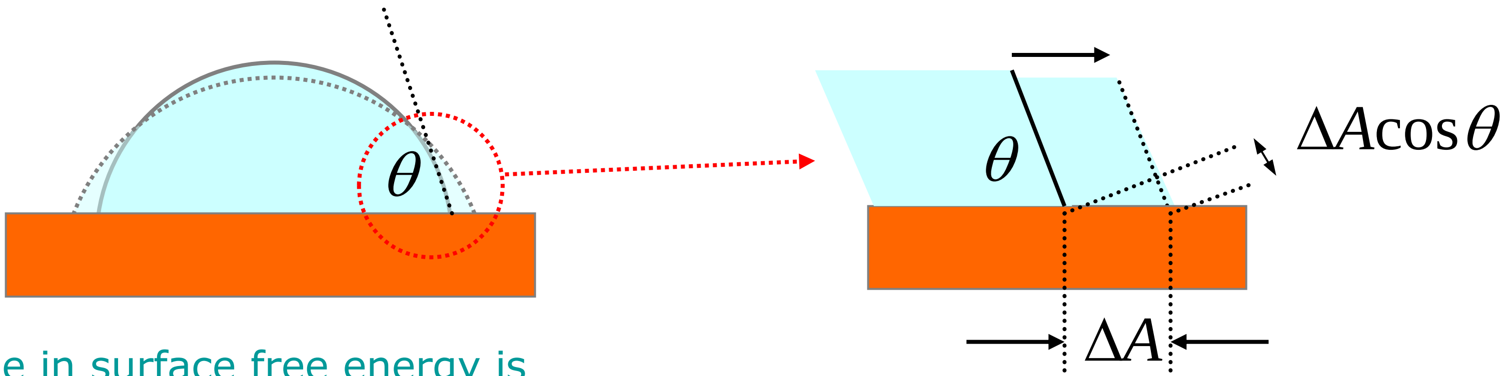
Roman consul Marcus Atilius Regulus is tortured to death by Carthaginians in about 255 BC. The illustration was painted in about 1415 in Paris.

Acknowledgement: Physics, UCLA

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 $\Delta F(x) = 0$ $\Rightarrow$ $\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$ Young's Law

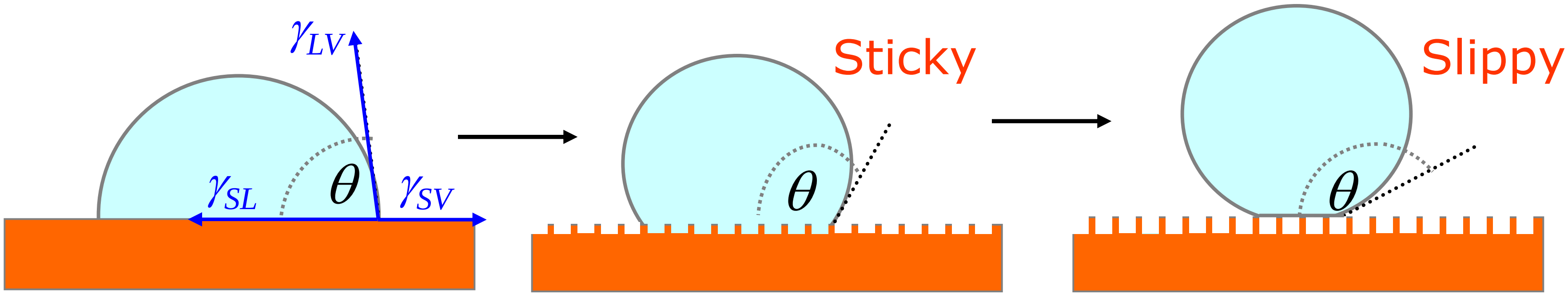
Same result as from resolving forces at contact line

References Shirtcliffe, N.J., *et al.*, An Introduction to Superhydrophobicity, Adv. In Coll. Interf. Sci. 161 (2010) 124-138.

Topography Modifies Energy Argument

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

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

Young’s Law θ_e

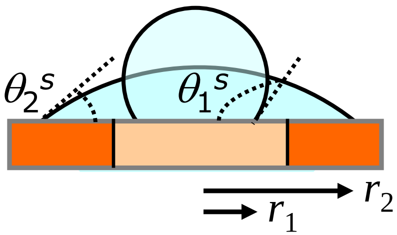
$f_s(x)$= solid surface fraction at edge

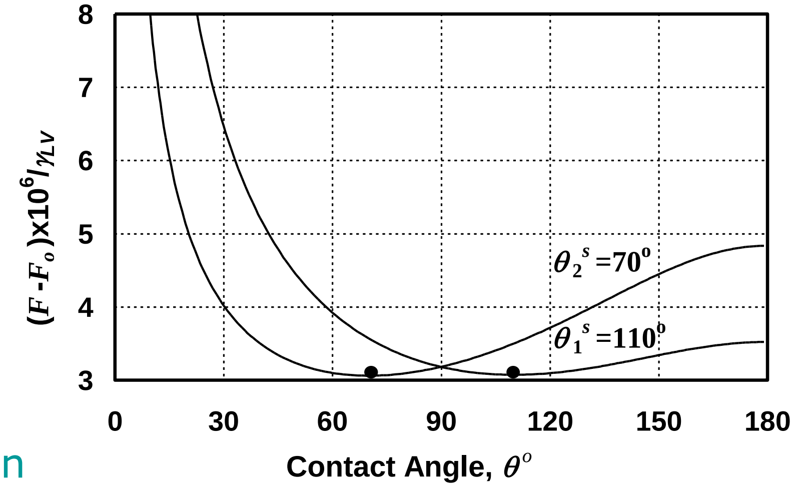
References Cassie, A. B. D., Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. Wenzel, R. N. Ind. Eng. Chem. 28 (1936) 988-994; J. Phys. Colloid Chem. 53 (1949) 1466-1467. McHale, G., Langmuir 23 (2007) 8200-8205.

Importance of the Three-Phase Contact Line

Isolated Defect Surface

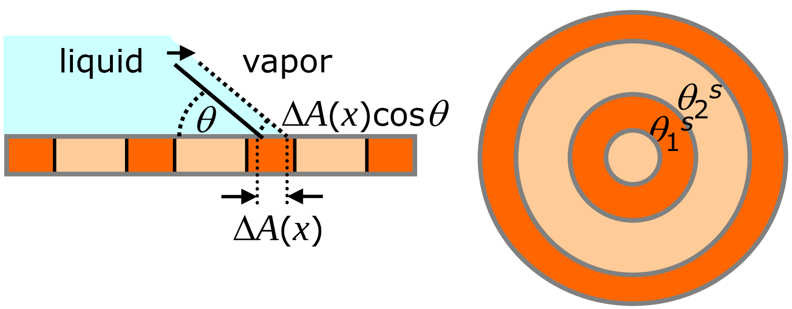
Surface has $\theta_1^s=110^o$, $\theta_2^s=70^o$



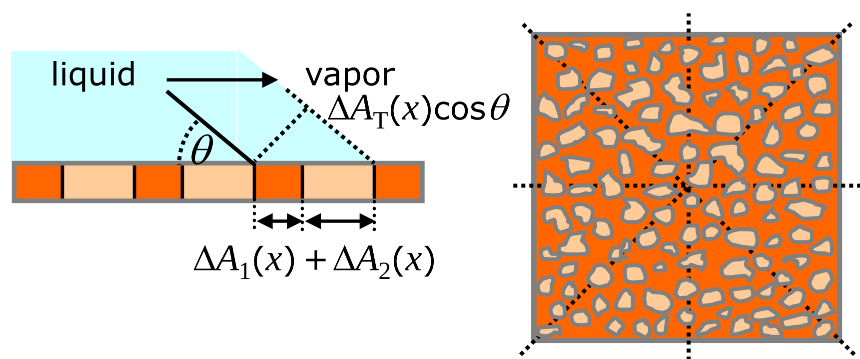


Two droplet configurations exist with min in their local surface free energy corresponding to the same droplet volume

Radial Symmetry



Random Surface



References Gao, L.C., McCarthy, T.J. Langmuir 23 (2007) 3762-3765. McHale, G. Langmuir 23 (2007) 8200-8205.

Local (not Global) Differential Parameters

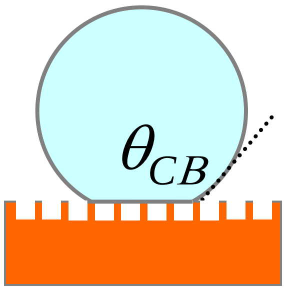
Cassie-Baxter

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 $\Rightarrow$

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

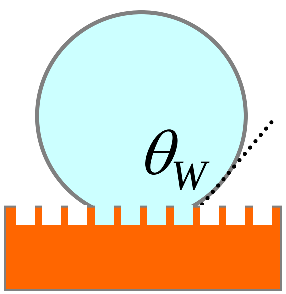


where $f_s(x)$ is the solid surface fraction and the x indicates values at the three-phase contact line ($\theta_e = \theta_e(x)$ is also local to the three-phase contact line)

Wenzel

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

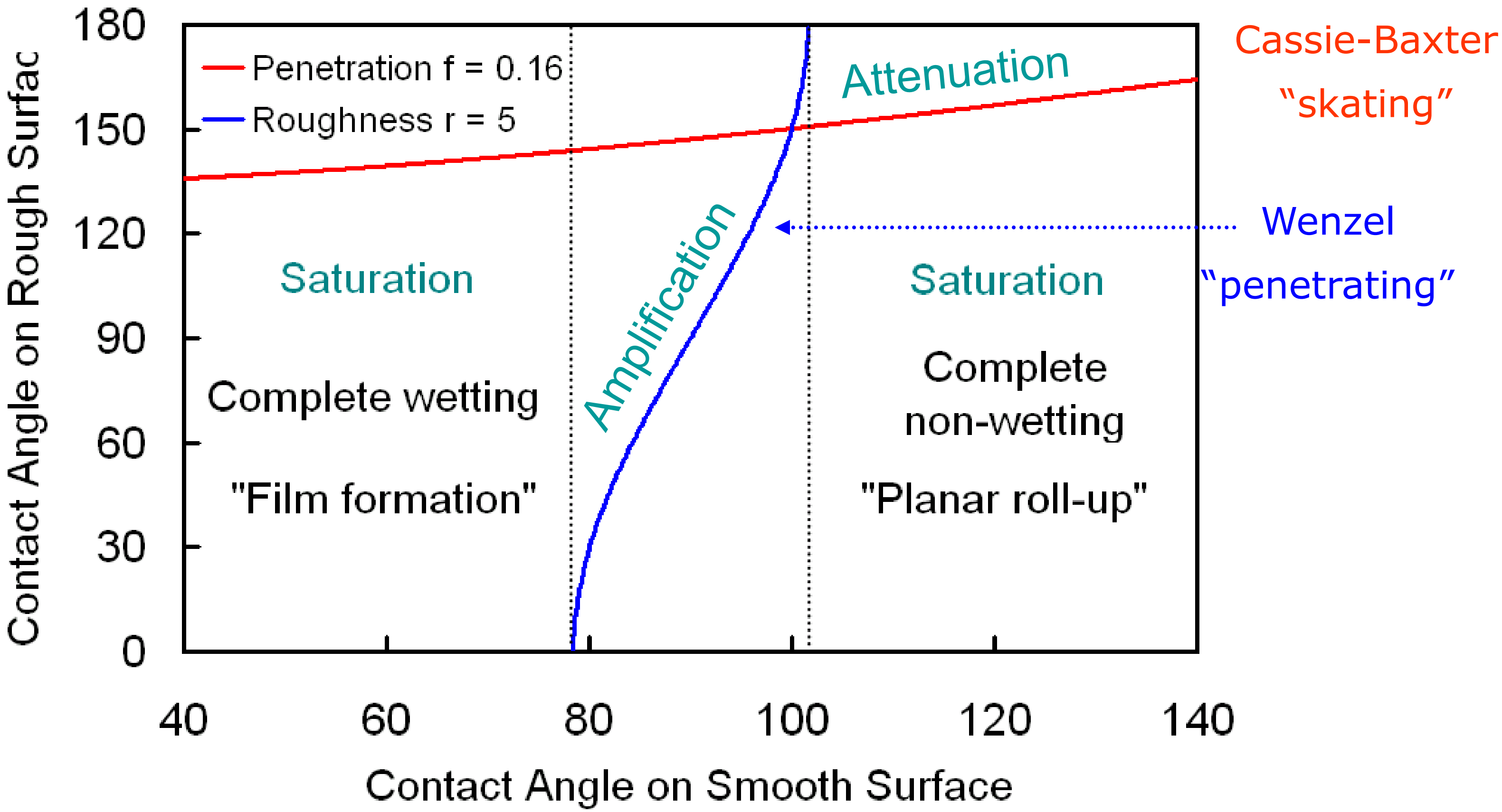
$$\boxed{\cos\theta_W = r(x)\cos\theta_e}$$



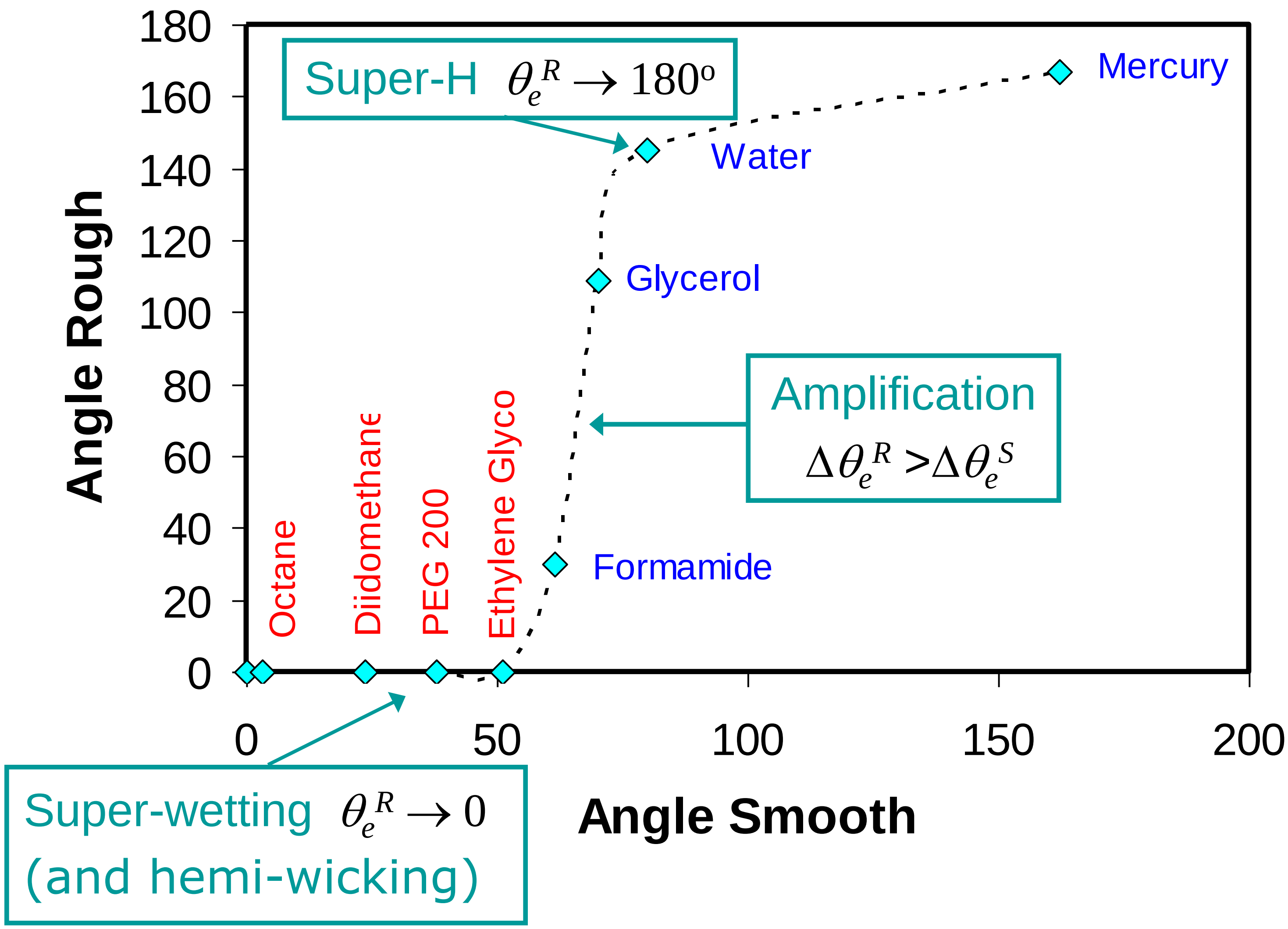
Reference McHale, G. Langmuir 23 (2007) 8200-8205.

3. Amplification, Switching and Superspreading

Amplification, Attenuation, Saturation

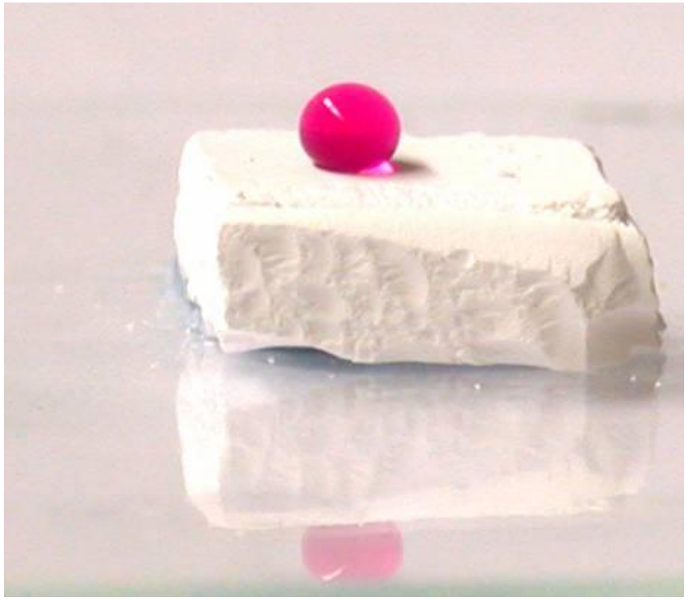


Liquids on a Superhydrophobic Surface



References McHale, G. *et al.*, Analyst 129 (2004) 284-287; Langmuir 20 (2004) 10146-10149.

Sol-Gel: Switching off Superhydrophobicity



Foam heated (and cooled) prior to droplet deposition

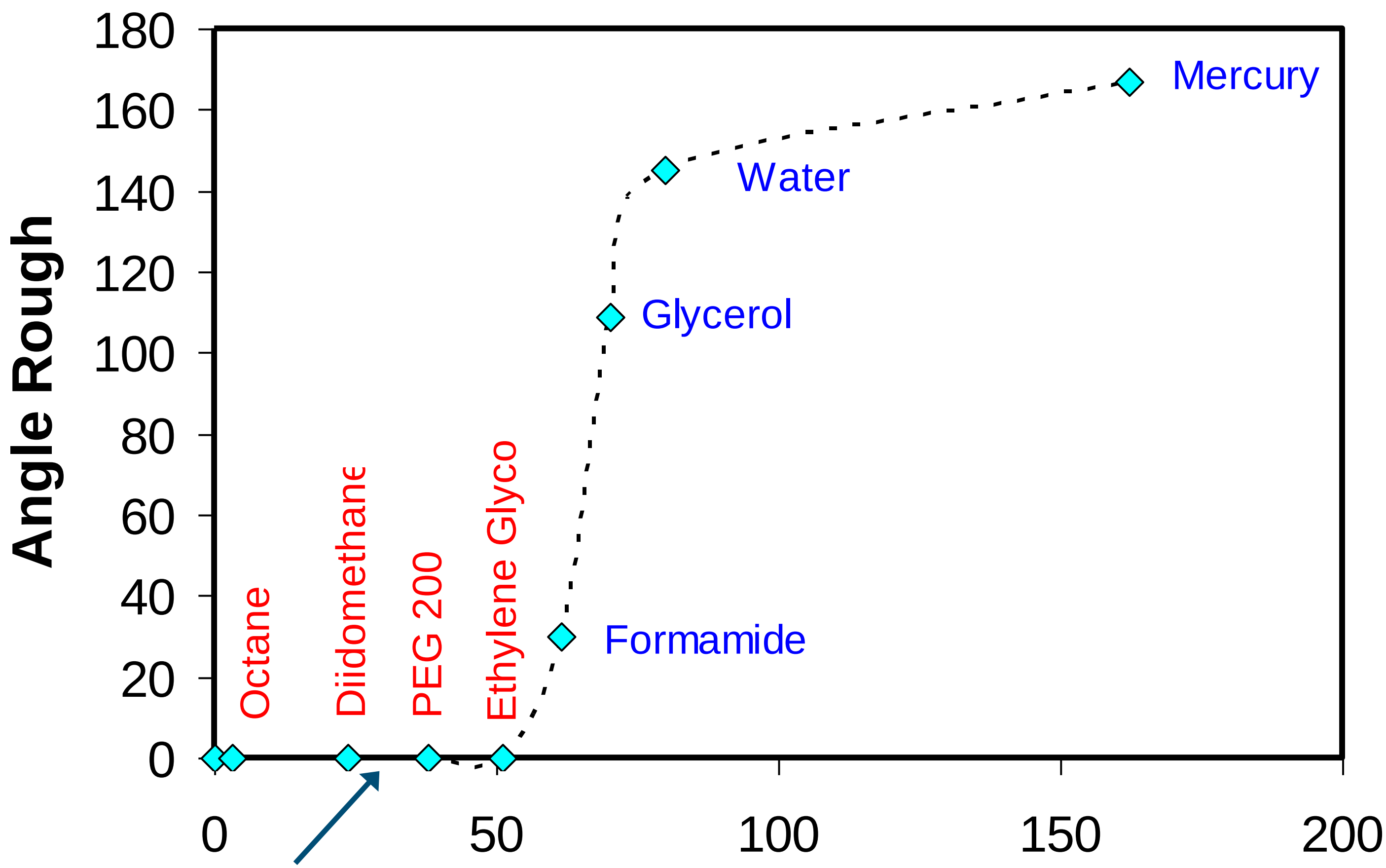
Mechanisms for Switching

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

Switch could trigger a large change ⇒ Sensor based on hydrophobicity

References 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. Mohammadi, R., Wassink, J., Amirfazli, A. Langmuir 20 (2004) 9657.

Super-spreading



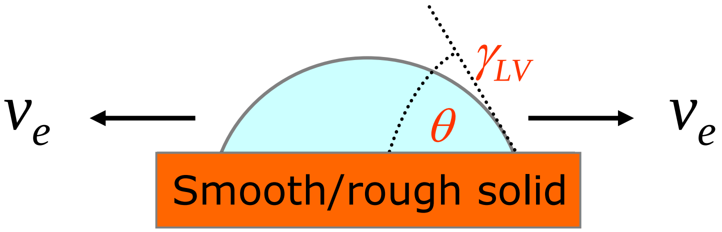
Different spread states are approached at different rates

References McHale, G. *et al.*, Analyst 129 (2004) 284-287; Phys. Rev. Lett. 93 (2004) art. 036102.

Driving Forces for Spreading

Drop spreads radially until contact angle reaches equlibrium

Horizontally projected force $\gamma_{LV}\cos\theta$



Smooth Surface

Driving force ~ $\gamma_{LV}(\cos\theta_e^s - \cos\theta)$

Cubic drop edge speed

$$\Rightarrow v_E \propto \theta\,\gamma_{LV}(\theta^2 - \theta_e^{s2})$$

Wenzel Rough Surface

Driving force ~ $\gamma_{LV}(r\cos\theta_e^s - \cos\theta)$

Linear droplet edge speed

$$\Rightarrow v_E \propto \theta\,\gamma_{LV}((r-1)+((\theta^2 - r\theta_e^{s2})/2)$$

Prediction : Weak roughness (or surface texture) modifies edge speed:

$v_E \propto \theta(\theta^2 - \theta_e^{s2})$ changes towards $v_E \propto \theta$

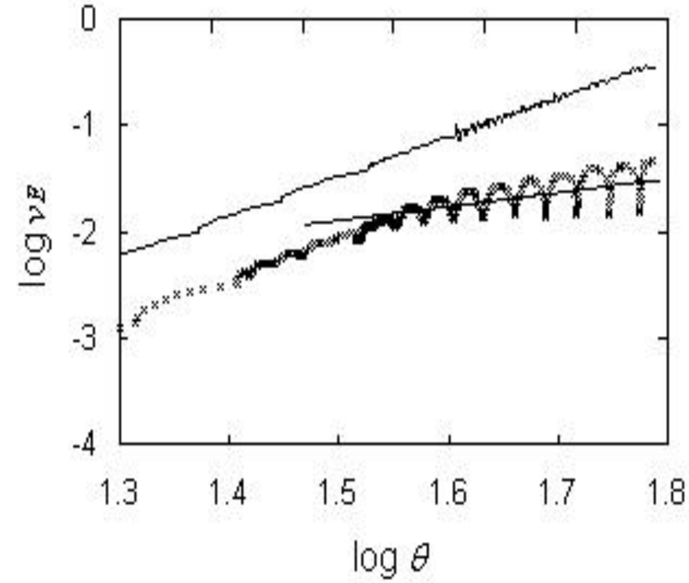
Reference McHale, G.; Newton, M.I. Colloids & Surfaces, A206 (2002) 193-201.

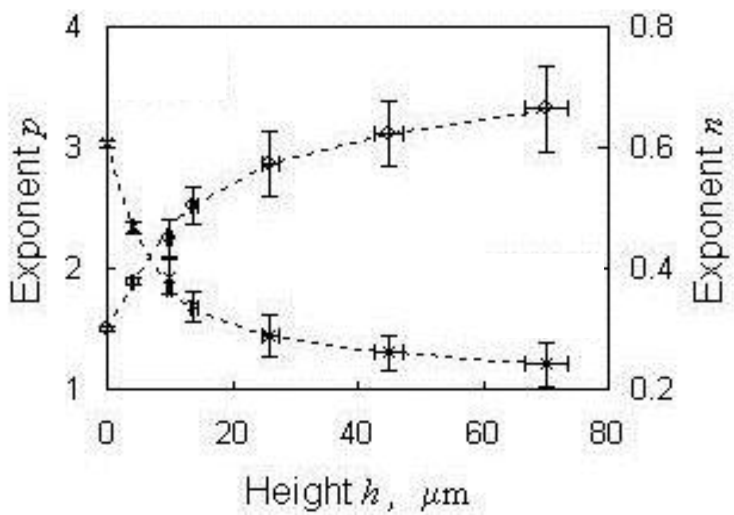
Superspreading of PDMS on Pillars

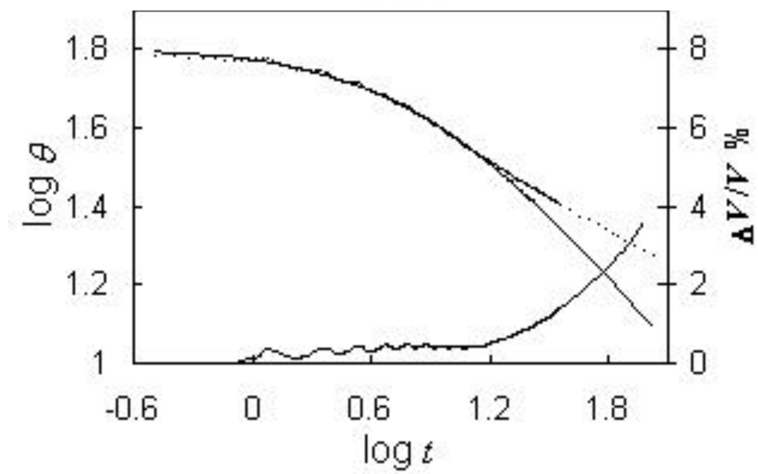
Tanner's Law exponents *p* and *n*

(cubic to linear transition)

$$v_E \propto v^* \theta^p \qquad \theta \propto \left(\frac{V^{1/3}}{v^*}\right)^n \frac{1}{(t+t_o)^n}$$







References McHale□, G. *et al*., Phys. Rev. Lett. 93 (2004) art. 036102; Nature Materials. 6 (2007) 661-664.

4. Conformable Substrates

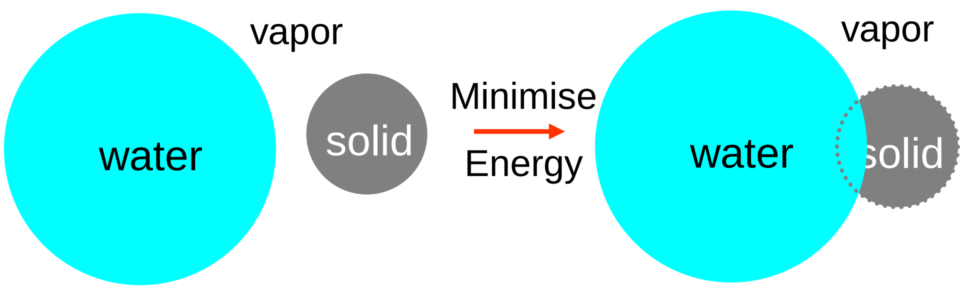
Liquid Marbles and Capillary Origami

Liquid Marbles – Assembling a Conformal Skin

Loose Surfaces

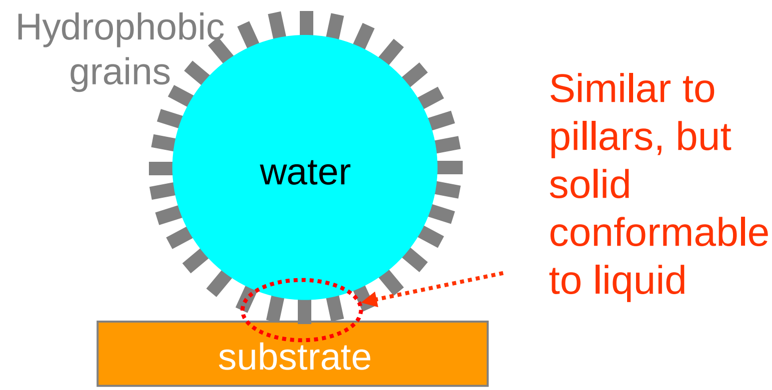
1. Grains are not fixed, but can be lifted by the liquid
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble

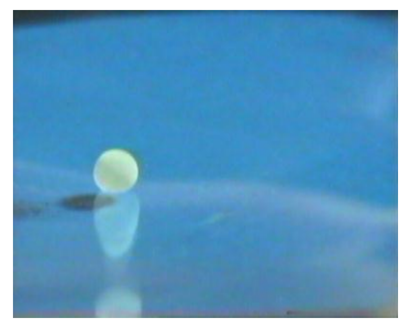
Hydrophobic Grains and Water



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

Energy is always reduced on grain attachment assuming grain is smooth ($r=1$)

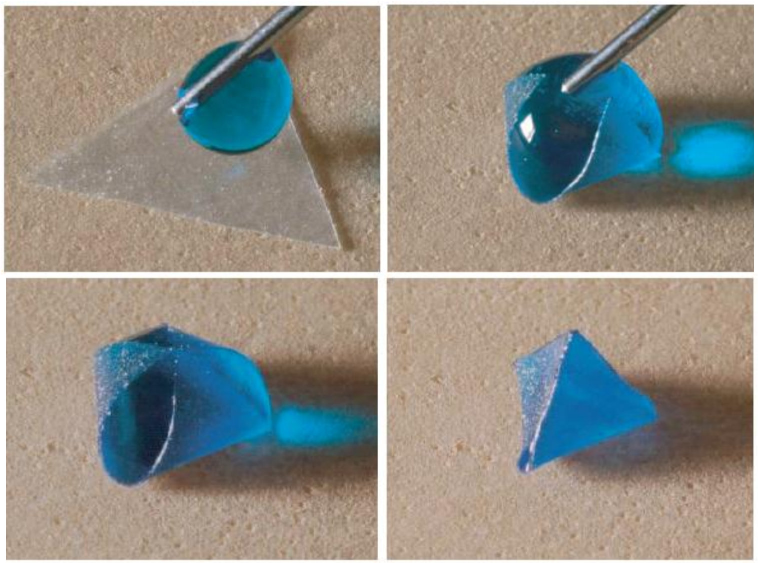




References Aussillous, P.; Quéré, D. Proc. Roy. Soc. A462 (2006) 973-999; Nature 411 (2001) 924-927. McHale, G., *et al*. 23 Langmuir (2007) 918-924. Newton, M.I., *et al*. J. Phys. D40 (2007) 20-24. McHale, G.; Newton, M.I., Soft Matter, accepted (2011).

Capillary Origami and "Hydrophilic" Teflon

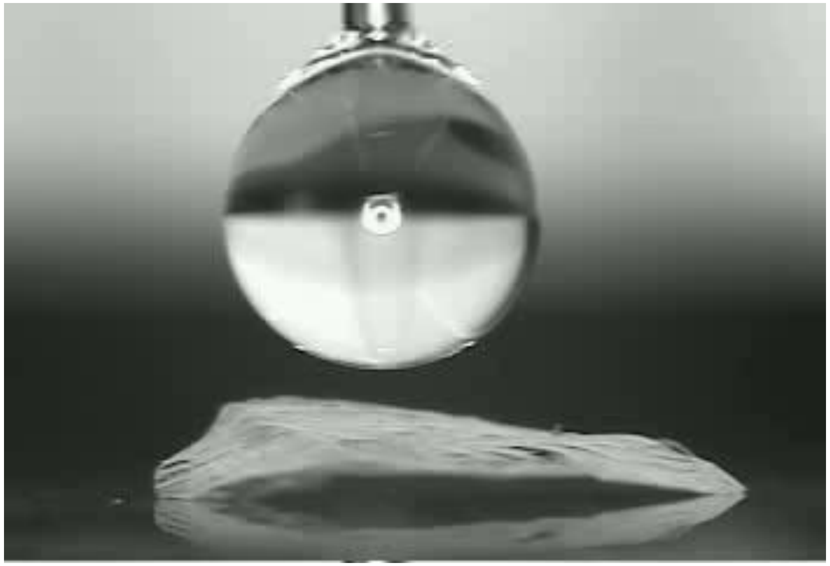
Py *et al's "Capillary Origami"*



Water droplet contacting triangular sheet of PDMS

Acknowledgement: Py *et al.* Eur. Phys. J.

McCarthy's Experiment



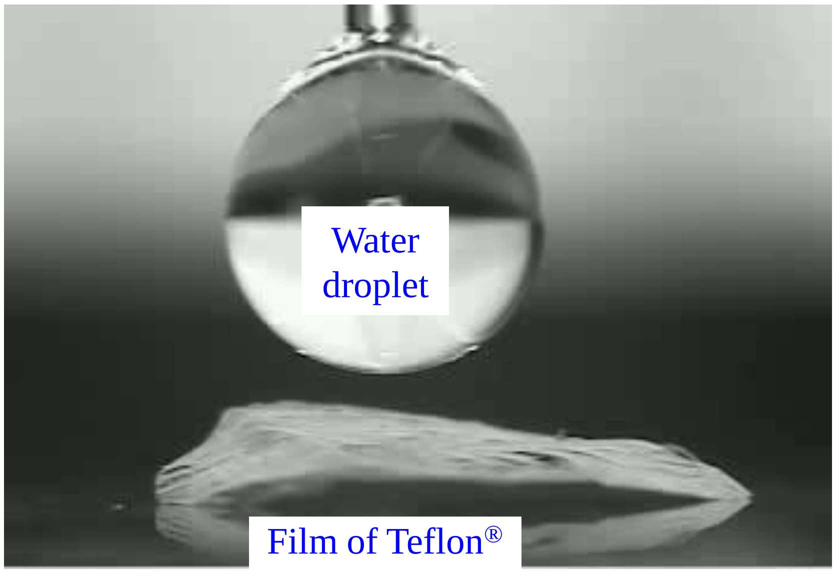
Water droplet contacting a 3.7 μm film of Teflon® AF2400

Courtesy: Prof. Tom McCarthy (UMass Amherst)

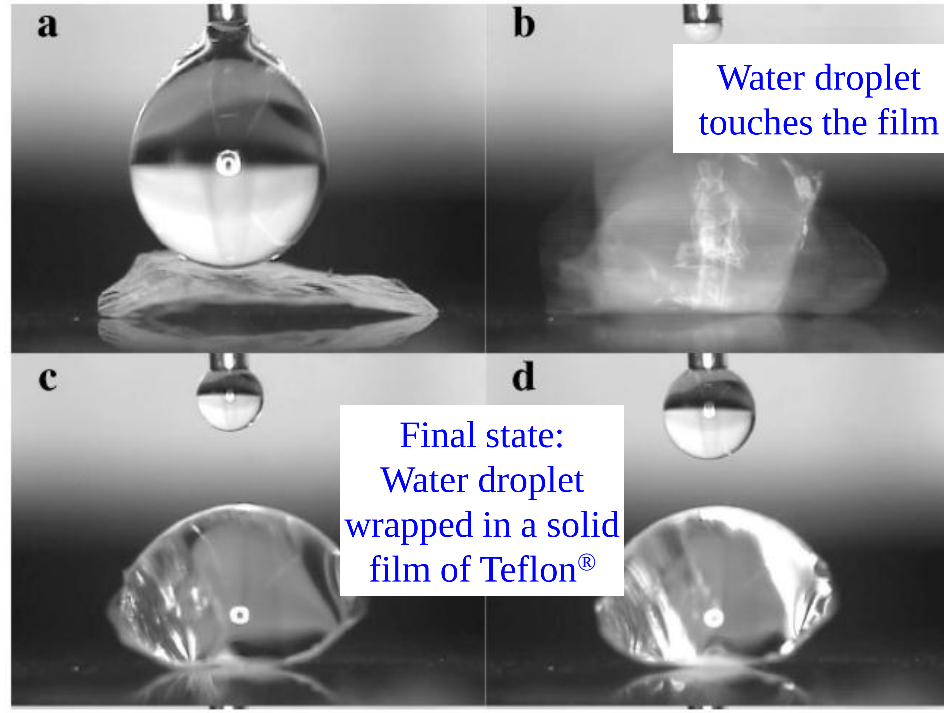
1. We all know Teflon® is a hydrophobic solid and gives a non-stick surface …..
2. Consider a thin film of Teflon contacted by a droplet of water
3. What happens?

References Gao, L.; McCarthy, T.J. Langmuir 24 (2008) 9183-9188. Py, C. *et al.*, Phys. Lett.. 98 (2007) art. 156103. Py, C. *et al.*, Eur. Phys. J. Special Topics, 166 (2009) 67-71. McHale, G. *et al.*, Beilstein Journal, accepted (2011).

Droplet Wrapping Video



Stills from Video



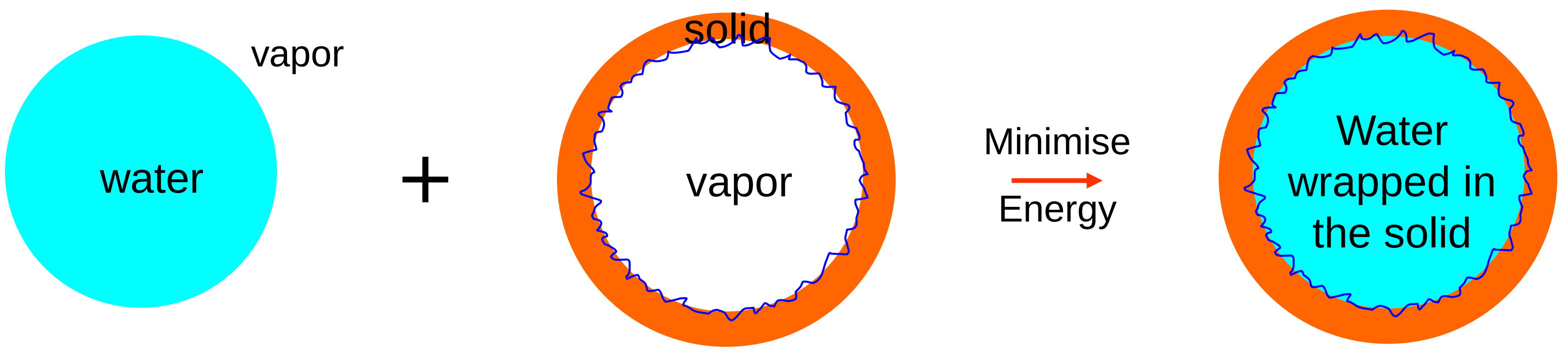
Courtesy: Prof. Tom McCarthy (UMass, Amherst)

If a droplet wraps itself up in Teflon® ... is this consistent with Teflon® being hydrophobic?

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

1. Assume energy in deforming/bending solid is zero
2. Assume solid is smooth and droplet is small
3. Under these conditions surface free energy always favors solid wrapping up a droplet providing the Young's law contact angle is greater than zero

<u>Hydrophobic Solid Shell (of thickness ε) and Water</u>



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

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

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)

<u>References</u> McHale, G. Langmuir <u>25</u> (2009) 7185-7187. McHale, G. *et al*., Beilstein J., Accepted (2011).

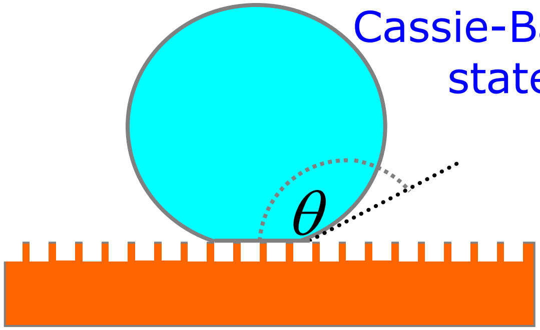
5. Immersed Superhydrophobic Surfaces

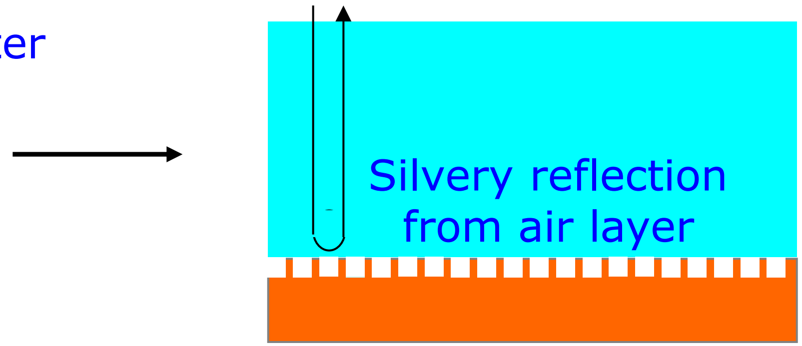
Superhydrophobicity and Plastrons

Immersed Superhydrophobic Surfaces

Provided design of features correct, penetration of water can be resisted

A silvery sheen can be seen when immersed – due to surface retained layer of air.





Plastron Respiration

Insect physiologists have studied immersed S/H surfaces since 1940's

Silvery sheen from air layer indicates an air-water interface, e.g diving spider - acts as a gas exchange membrane to extract oxygen from water and remove carbon dioxide from insect

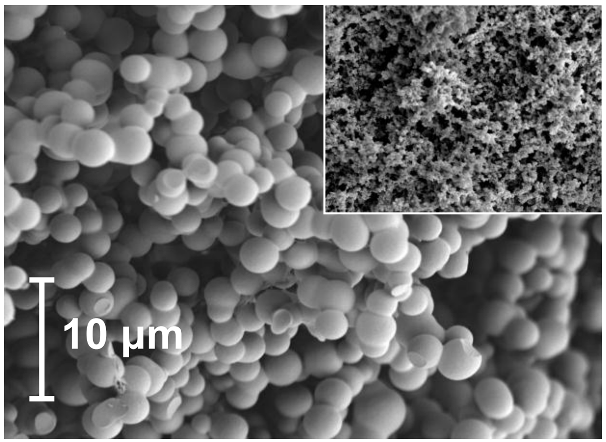
Microcosmos ©Allied Films Ltd (1996)

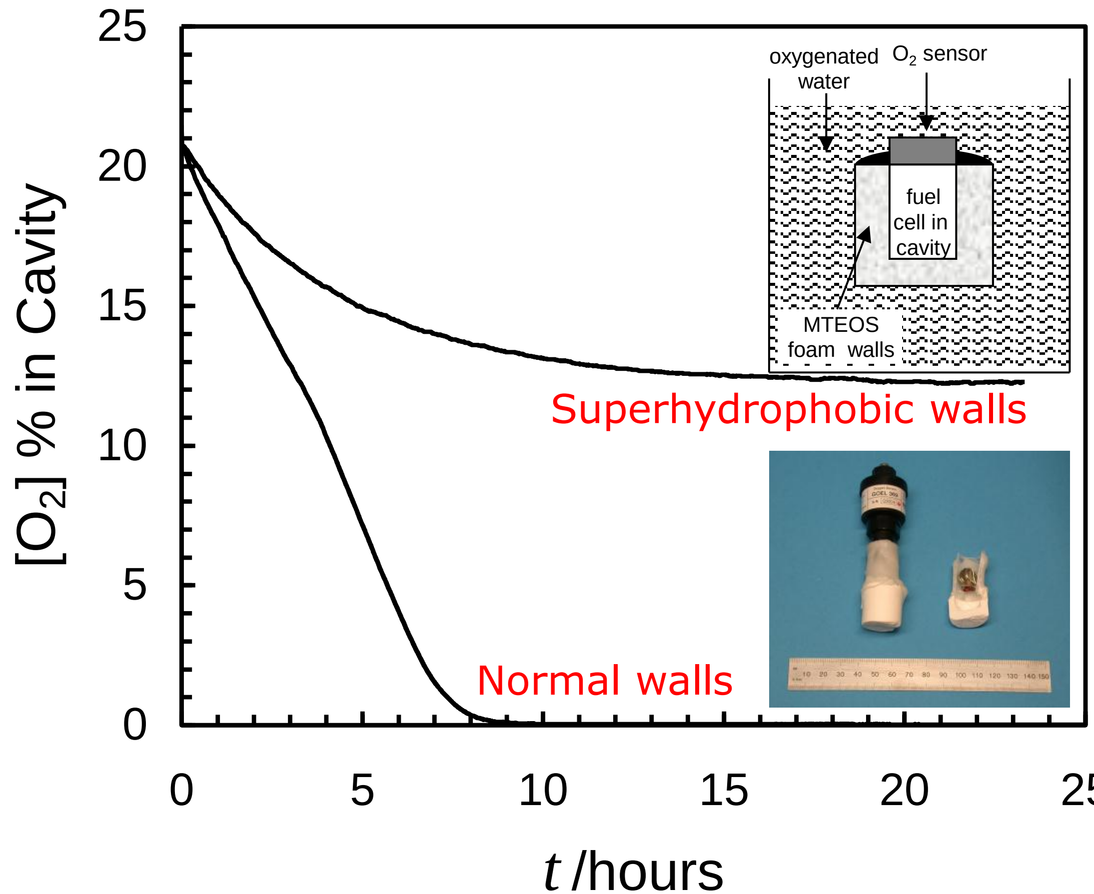
References McHale, G., *et al*., Appl. Phys. Lett. 89 (2006) art. 104106. Thorpe, W. H.; Crisp, D. J., J. Exp. Biol. 24 (1947) 227. McHale, G., *et al*., Soft Matter 6 (2010) 714-719.

Plastron/Underwater Respiration Biomimic

Intrinsically superhydrophobic MTEOS organo-silica sol-gel foam surfaces

Structure controllable from nano- to macro-porous





References Shirtcliffe *et al.*, Langmuir 19 (2003) 5626-5631; Appl. Phys. Lett. 89 (2006) art. 104106.
Flynn, M.R.; Bush, J.W.M., J. Fluid Mech. 608 (2008) 275–296.

Superhydrophobicity: Plastron Respiration

Similar to super gas exchange membranes

Edward Cussler

Underwater Breathing:

BBC Radio 4 Broadcast

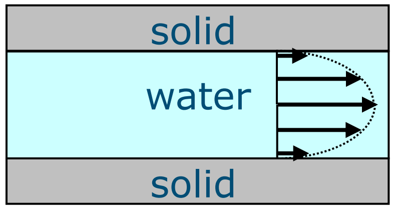
Edward Cussler, Professor of Chemical Engineering (University of Minnesota)

Speaking 9th February 2006

Flow in Pipes with Superhydrophobic Walls

Concept

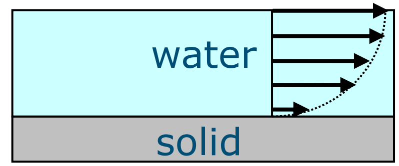
Closed-channel



Two walls cause frictional drag

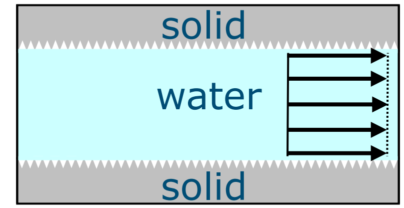
Open-channel

Low frictional drag to air



High frictional drag to solid

Super-channel



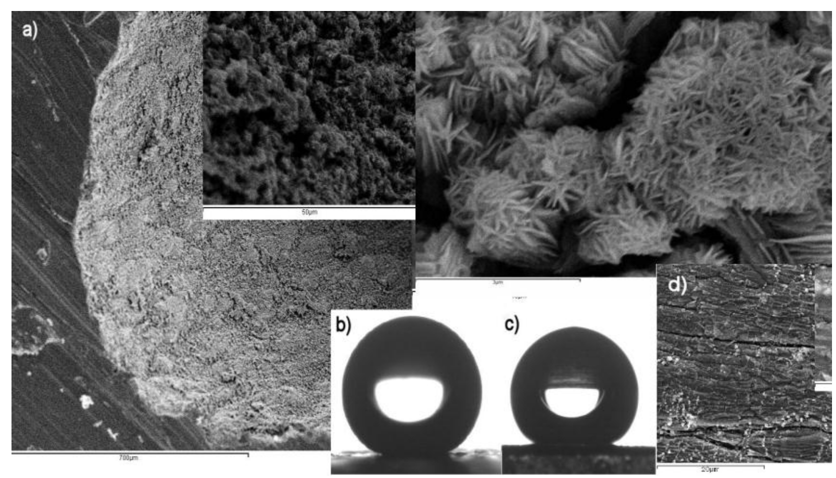
Walls appear as cushions of air

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)

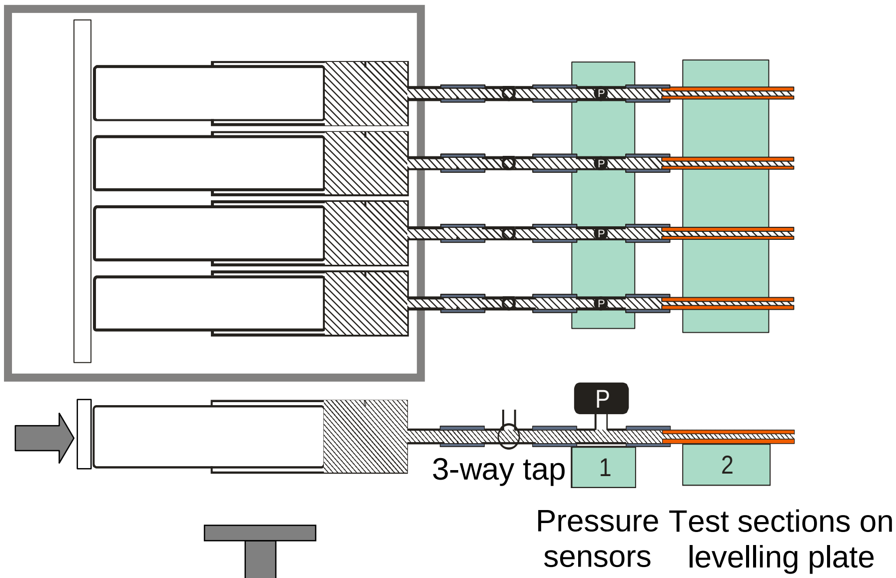


Reference Shirtcliffe, N.J., *et al*.. ACS Appl. Maters. Interf., 1 (2009) 1316-1323.

Flow Experiments

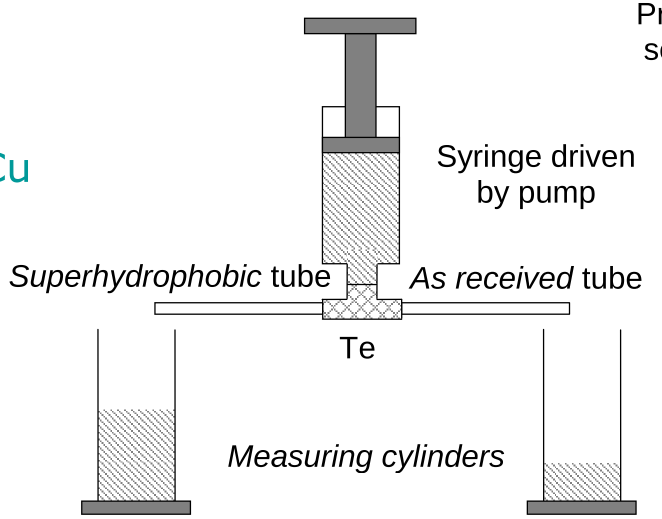
Quantitative Experiment

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

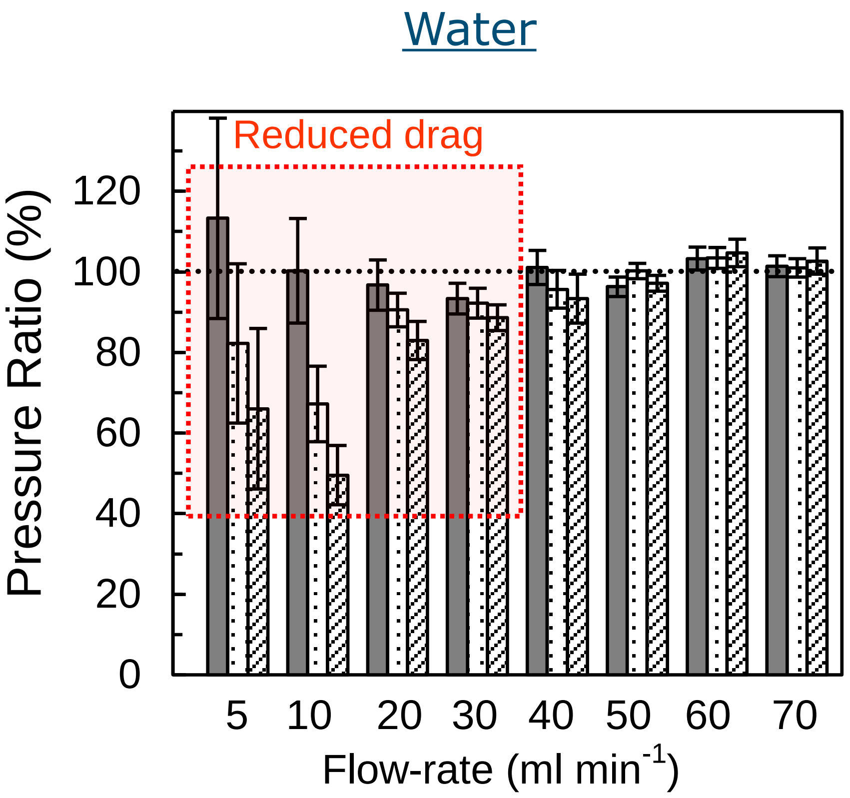


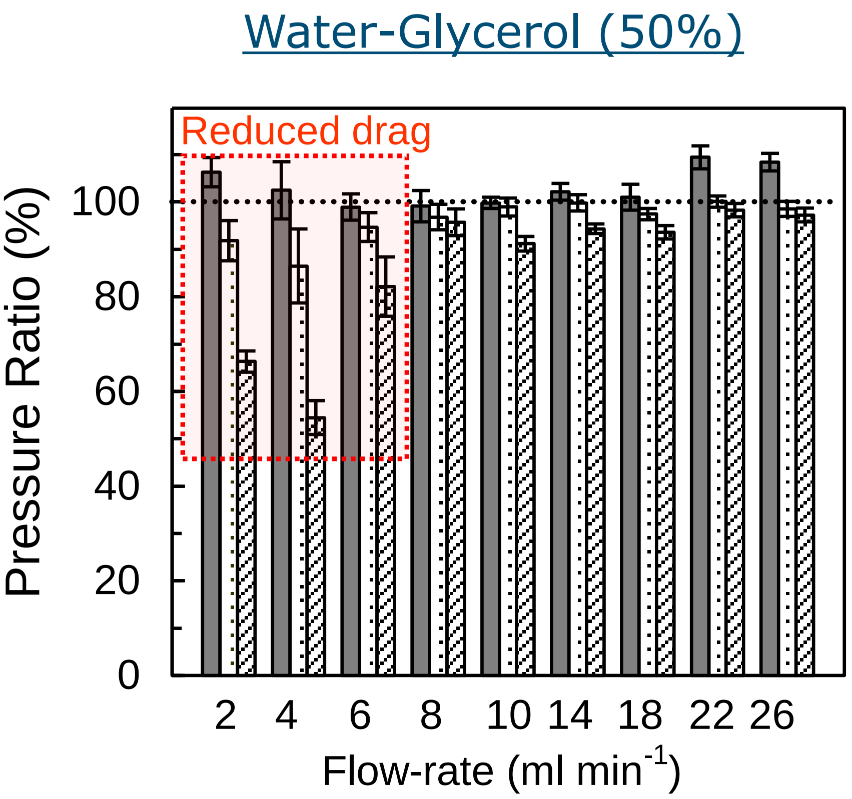
Visualization Experiment

1. 2 tubes in T-arrangement
2. Cu and hydrophobic nanoribbon Cu
3. Syringe pump to force flow
4. Outlet volumes collected



Quantitative Results

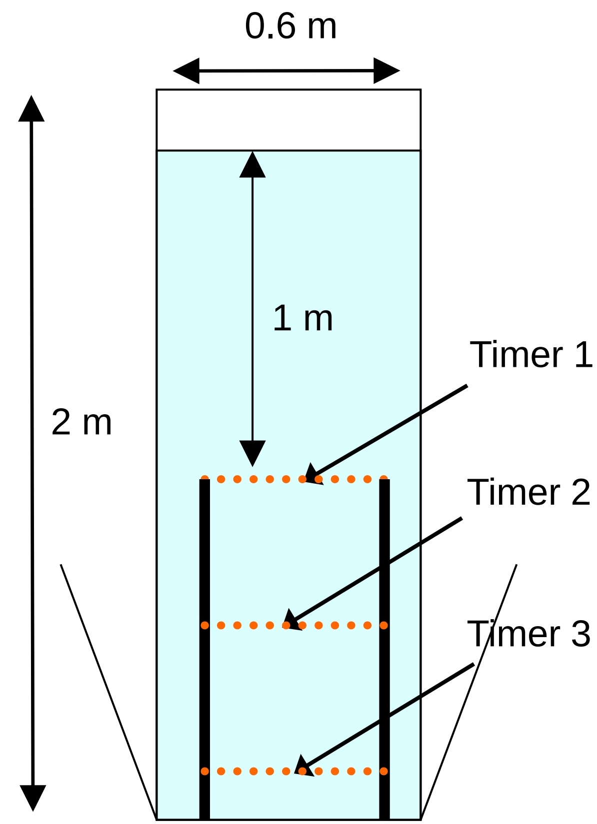




Copper tubes with superhydrophobic inner surfaces show significantly increased flow-rates

Terminal Velocity Experiments

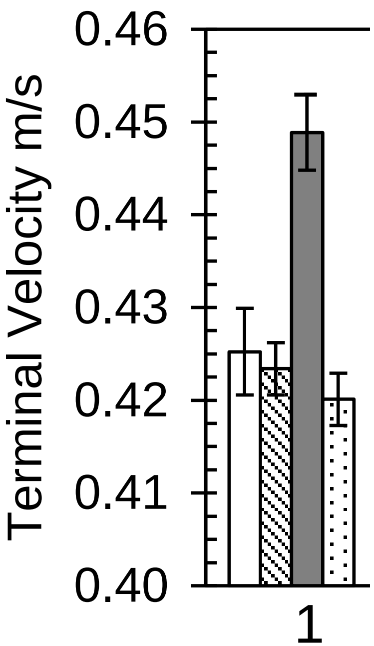
In the presence of a fluid, a falling object eventually reaches a terminal velocity. Textbooks tell us that in water the terminal velocity does not depend on the surface chemistry …. But is that true?



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

Terminal Velocity Results

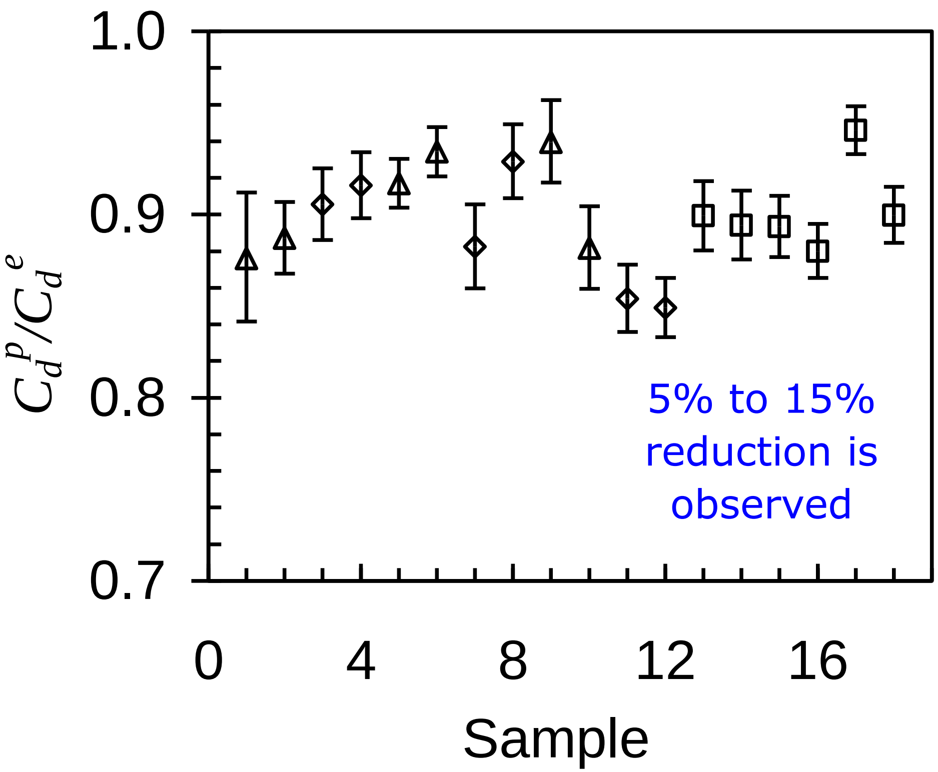
Results for 1-inch Diameter Sphere



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



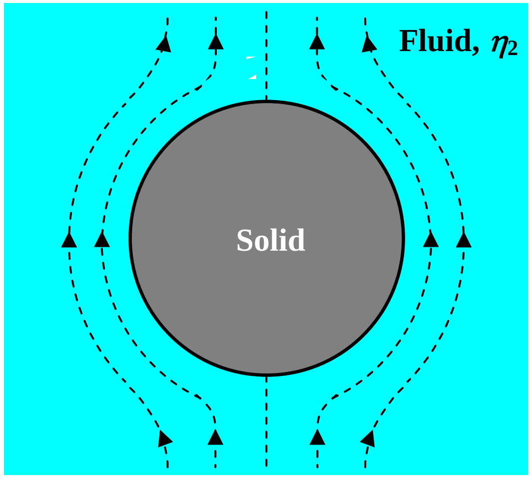
Superhydrophobicity alone is not enough. Also need a plastron to persist to achieve drag reduction

Drag Reduction – Boundary Conditions

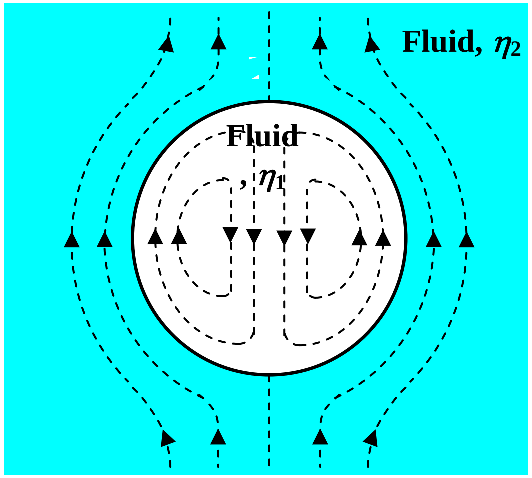
Fundamental boundary condition is not "no-slip", but is continuity of shear stress

Well-known drag reduction effects for gas bubbles with non-rigid interfaces in water

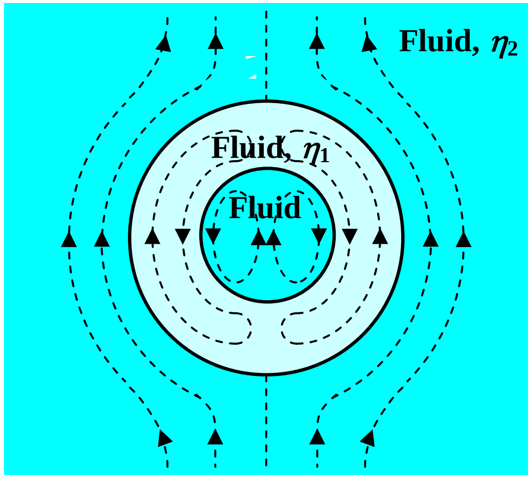
Stokes Drag (Low Re)



Hadamard-Rybczynski



Encapsulated Droplet

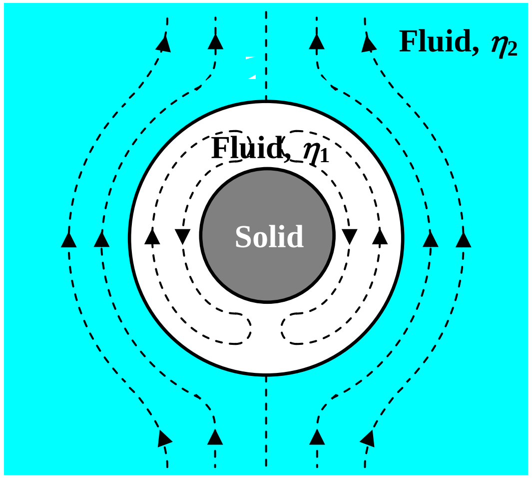


Hadamard-Rybczynski drag is 25% less than Stokes drag

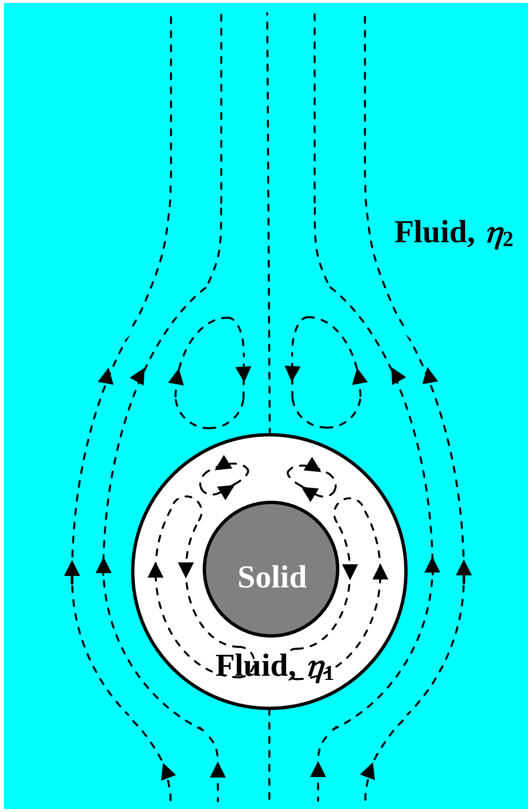
Reference McHale, G., *et al*., Soft Matter 6 (2010) 714-719.

Low and Intermediate *Re* numbers?

At low *Re*, a plastron/air layer may cause a Hadamard-Rybzcynski effect and reduce drag



At intermediate *Re*, an air layer is likely to alter flow patterns and modify wake separation – possibly reducing drag

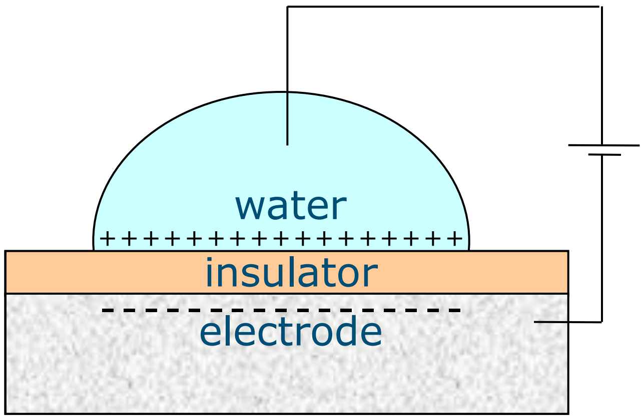


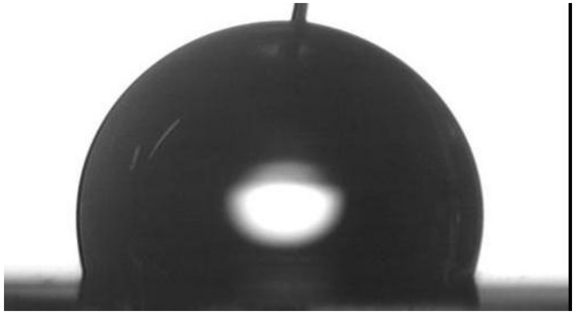
A persistent plastron/air layer is needed to achieve drag reduction

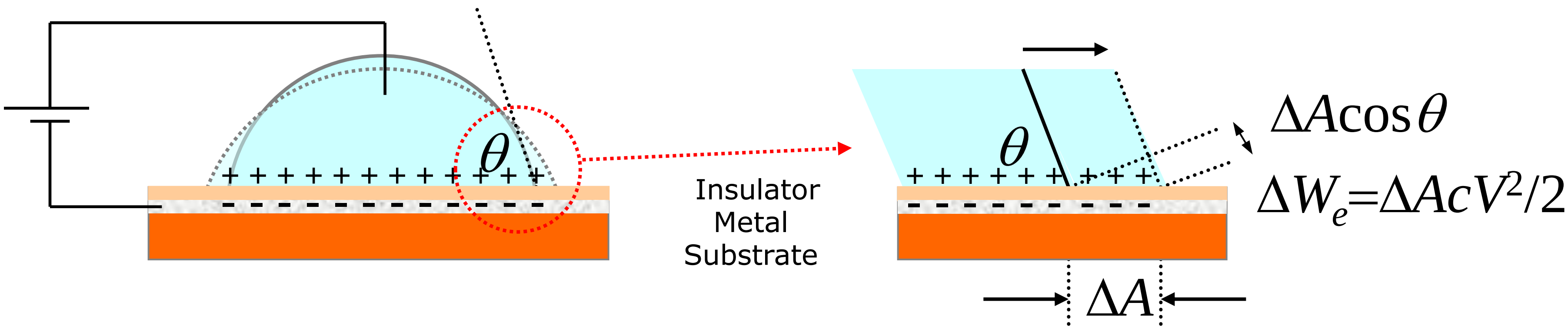
6. Dielectrowetting

Led by Prof. Carl Brown

The Principle of Electrowetting-on-Dielectric







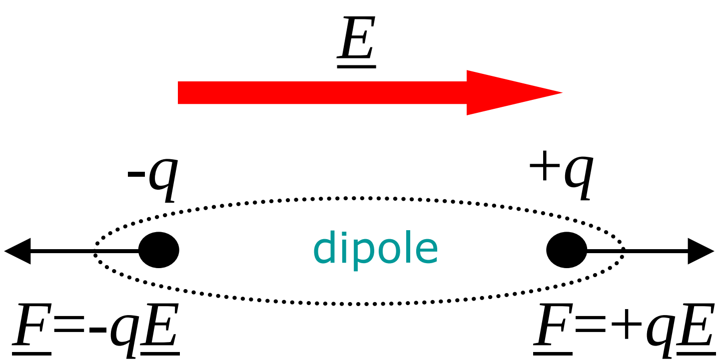
$\Rightarrow$ $$\cos\theta_e(V) = \cos\theta_e(0) + \varepsilon_r\varepsilon_o V^2/2d\gamma_{LV}$$

EWOD Modified Young's Law

Dielectrophoretic (DEP) Forces

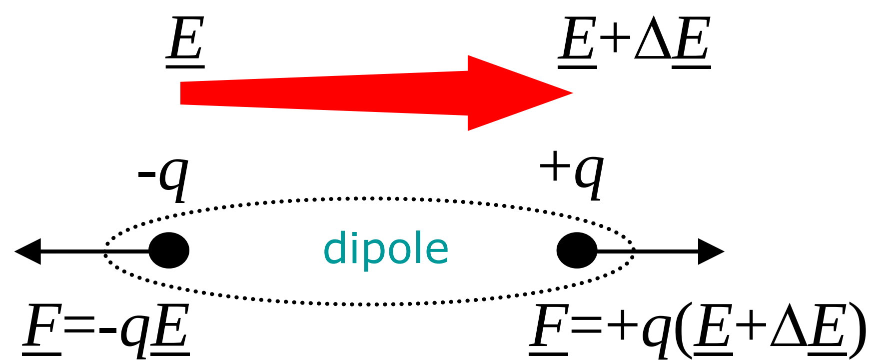
Force on a dipole in a dielectric material caused by a non-uniform electric field

Uniform Electric Field Applied



Zero net force on dipole

Non-Uniform Electric Field Applied



Net force on dipole = $+q\Delta\underline{E}$

In a dielectric liquid a non-uniform electric field causes liquid motion

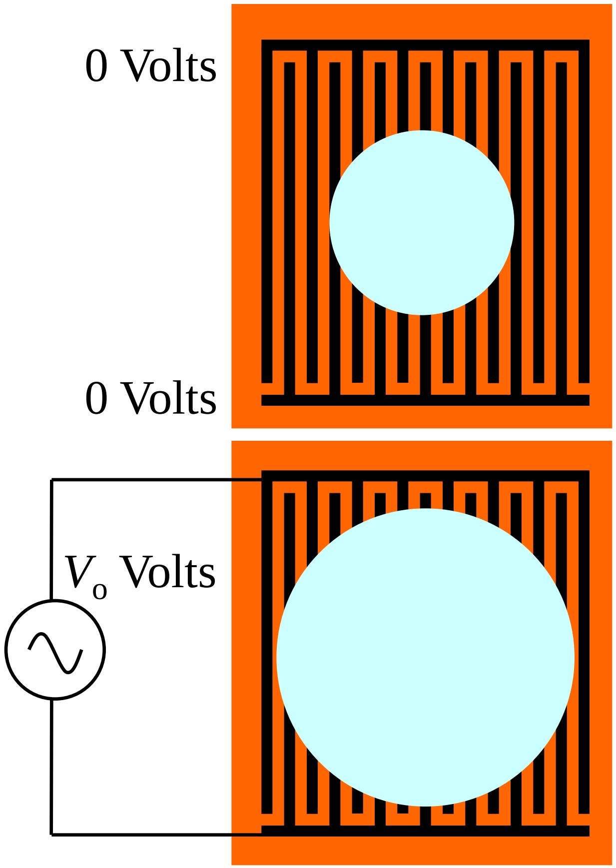
L-DEP Comparison to Electrowetting-on-Dielectric (EWOD)

1. L-DEP acts on the bulk material, but EWOD acts at the contact line
2. L-DEP uses dielectric liquids, but EWOD uses conducting liquids
3. L-DEP does not require electrical contact, but EWOD does require a contact

L-DEP Driven Spreading

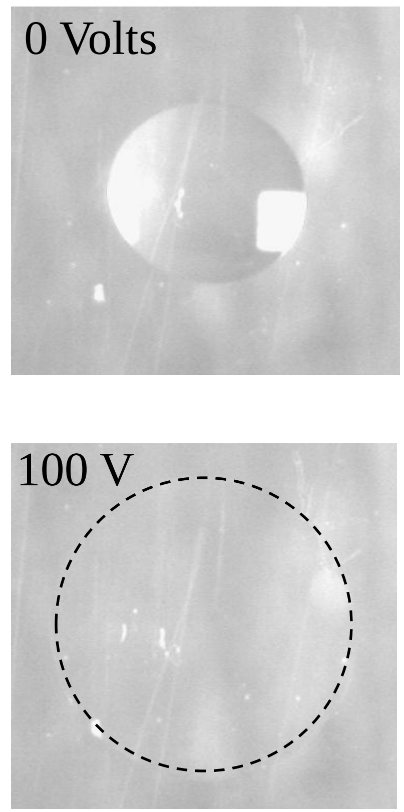
Interdigital Transducers

Top view



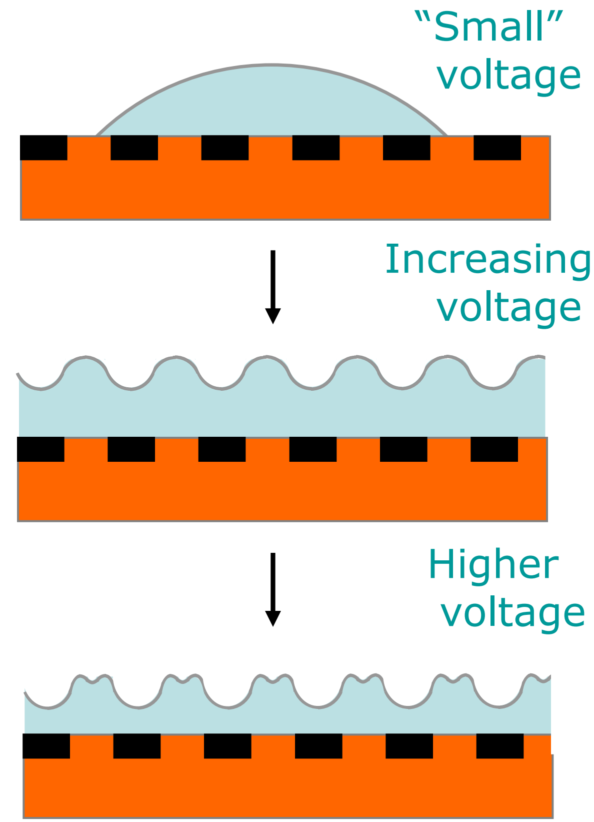
Castor Oil Droplet

Top view*



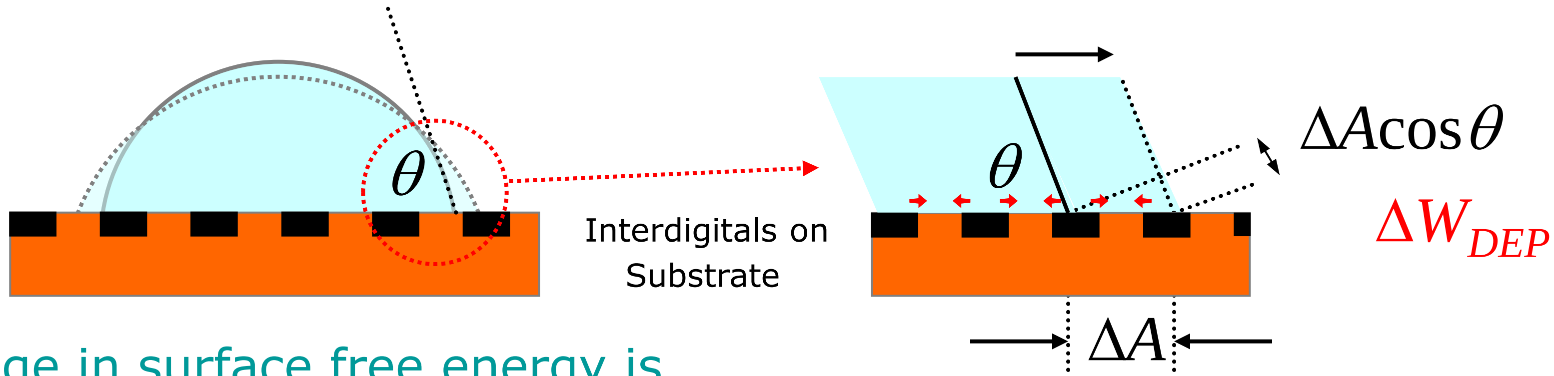
Droplet to Wrinkled Film

Side view



*Acknowledgement: Images courtesy of Mr Naresh Sampara (NTU)

Surface Free Energy: Droplet Spreading



Change in surface free energy is

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

Exponential field decay into liquid, $E_z = \alpha V\exp(-\alpha z) \Rightarrow$ pen. depth $z \sim 1/2\alpha$.

L-DEP energy change is, $\Delta W_{DEP} = \varepsilon_r \varepsilon_o \alpha^2 V^2 \Delta A / 4\alpha$, assuming a thick droplet

Equilibrium is when $\Delta F = 0$

$$\Rightarrow \quad \cos\theta_e(V) = \cos\theta_e(0) + \varepsilon_r \varepsilon_o \alpha V^2 / 4\gamma_{LV}$$

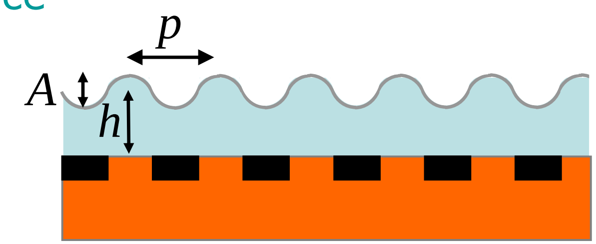
L-DEP Modified Young's Law

Reference McHale, G., *et al.*, to be submitted to Langmuir (2011).

Surface Free Energy: Sinusoidal Wrinkles

Thin Droplet Case (Far-field Wrinkles)

1. Electric field penetrates to upper liquid-air interface
2. Deformation of liquid-air interface can change surface energy
3. Redistribution of liquid in a pattern following "smoothed" field of IDT alters capacitive energy



Additional surface area: $\Delta A_{LV}=\pi^2 A^2/2p$

Decrease in capacitive energy: $\Delta W_{DEP}=\Delta C V(z)^2/2 \approx \Delta C V^2 \exp(-2\pi h/p)/2$

Capacitance is a function of h/p and scales with $\varepsilon_r\varepsilon_o$, i.e. $C=\varepsilon_r\varepsilon_o f(h/p)$

Change in capacitance is: $\Delta C=(\varepsilon_r\varepsilon_o A/p)[\mathrm{d}f/\mathrm{d}u]_{u=h/p}$

Minimizing energy with respect to changes in amplitude A,

$$\Rightarrow \quad A \propto \varepsilon_r\varepsilon_o V^2 \exp(-2\pi h/p)/4\gamma_{LV}$$

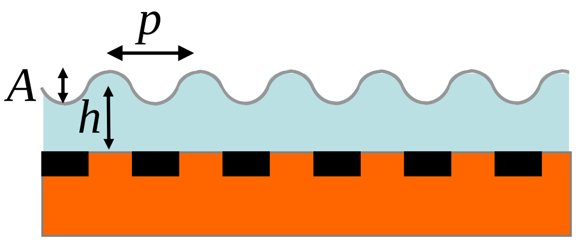
Amplitude Scaling Law*

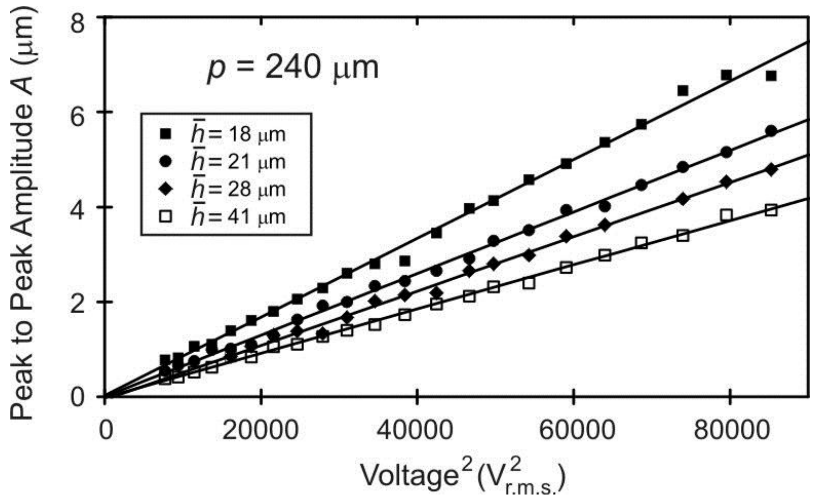
**Full solution of Maxwell's equation gives same results*

References Brown, C.V.; *et al.*, Appl. Phys. Lett. 97 (2010) art. 242904; *Submitted to J. Appl. Phys. (2011).

Experimental: Observed Scaling Laws

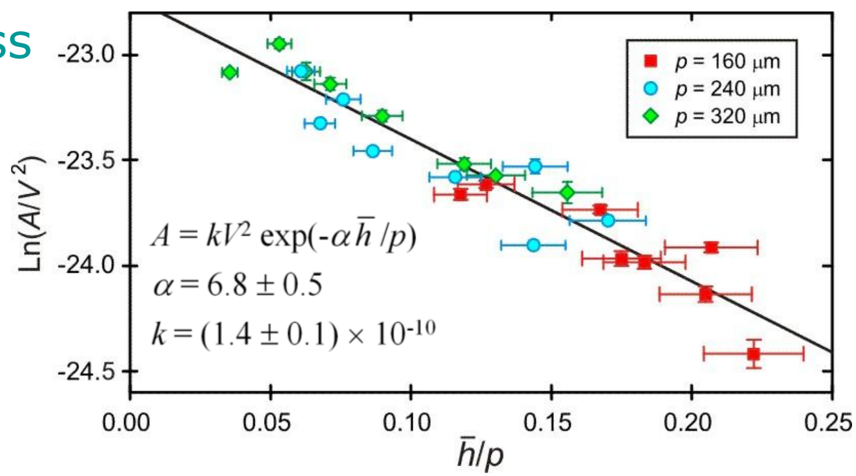
10 kHz sinewave, 1-decanol oil
p=160, 240 and 320 μm





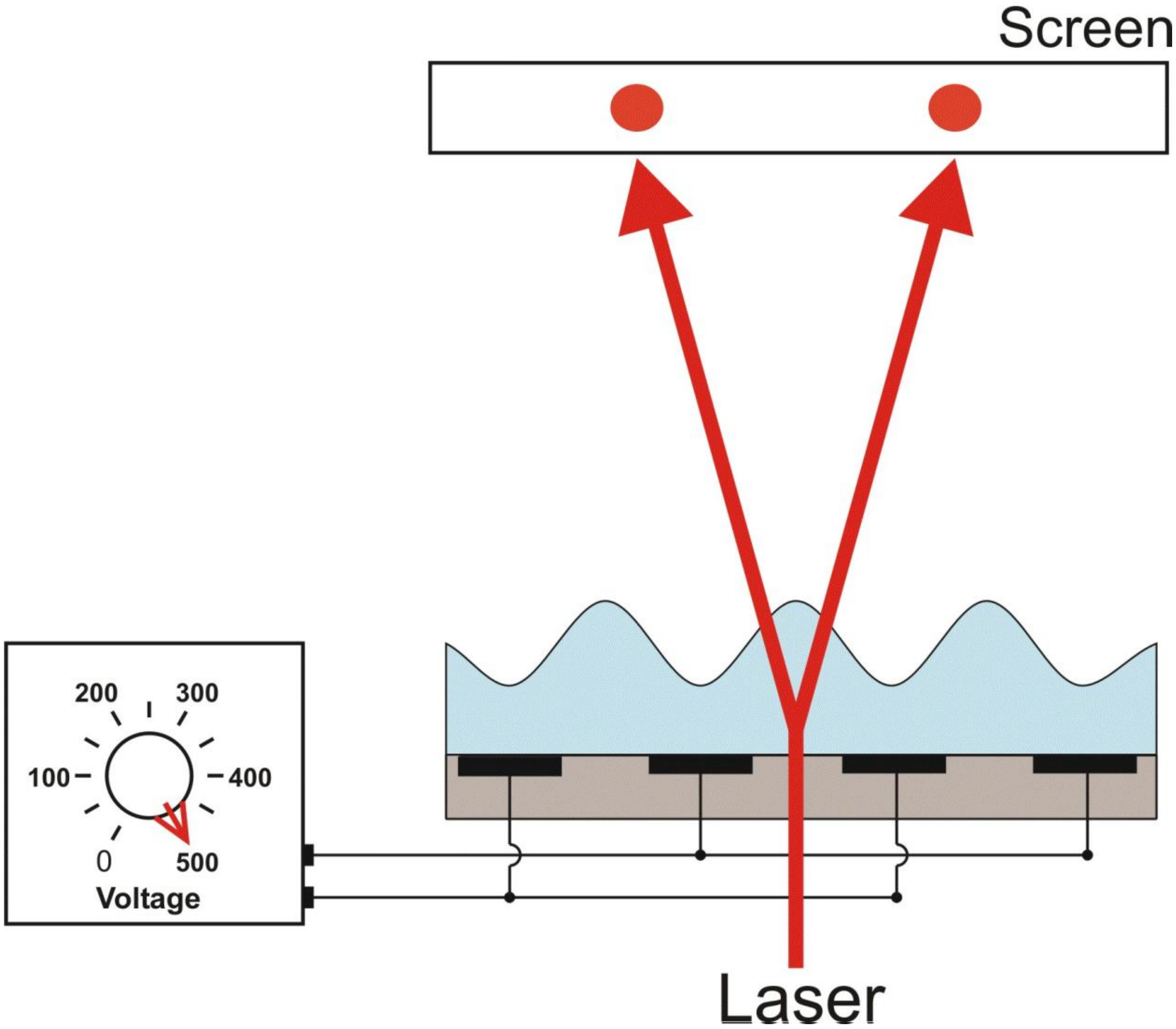
Scaling of amplitude with thickness to electrode periodicity:

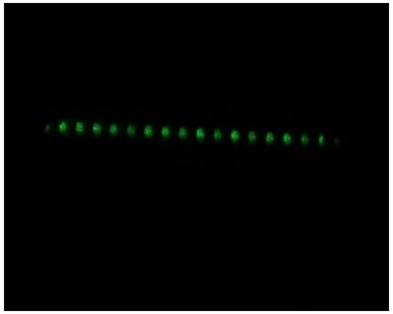
$$A = kV^2 \exp(-2\pi h/p)$$

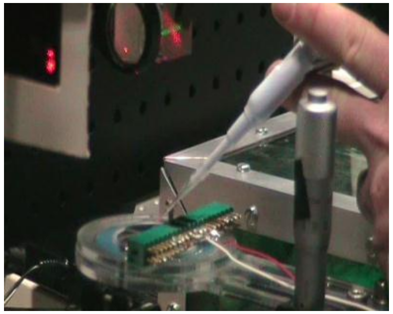


Reference Brown, C.V.; *et al.*, Appl. Phys. Lett. 97 (2010) art. 242904.

Programmable Phase Grating







Reference Brown, C.V.; *et al.*, Nature Photonics. 3 (2009) 403-405.

Summary and Conclusions

1. Topography enhancement of wetting is rich in effects
    - Superhydrophobicity
    - Switching
    - Superwetting and superspreading
2. Substrates can be shaped by the liquid
    - Hydrophobic, but adhesive
    - Liquid Marble
    - Capillary Origami
3. Underwater superhydrophobicity offers functional properties
    - Plastron/underwater respiration without gills
    - Suppression/reduction of adsorption
    - Reduction of drag
4. Dielectrowetting
    - Control of wetting of oils
    - Shaping surfaces
    - Creating optical effects

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Collaborators

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EP/C509161/1 – Extreme soil water repellence

EP/D500826/1 & EP/E043097/1 – Slip & drag reduction

EP/E063489/1 – Exploiting the solid-liquid interface

Dstl via EPSRC/MOD JGS, Kodak European Research

EU COST Action D19 - Chemistry at the nanoscale

EU COST Action P21 - Physics of droplets

Kodak COMIT Faraday Partnership [dstl] COST EPSRC Engineering and Physical Sciences Research Council NATURAL ENVIRONMENT RESEARCH COUNCIL