NOTTINGHAM
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Superhydrophobic Surfaces

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Overview

1. Water repellence in nature
2. Basic concepts
3. A selection of surfaces
4. Switching and superspreading
5. Complex surfaces
6. Porosity and loose surfaces
7. Back to nature

Water Repellence in Nature

Sinking and Falling?

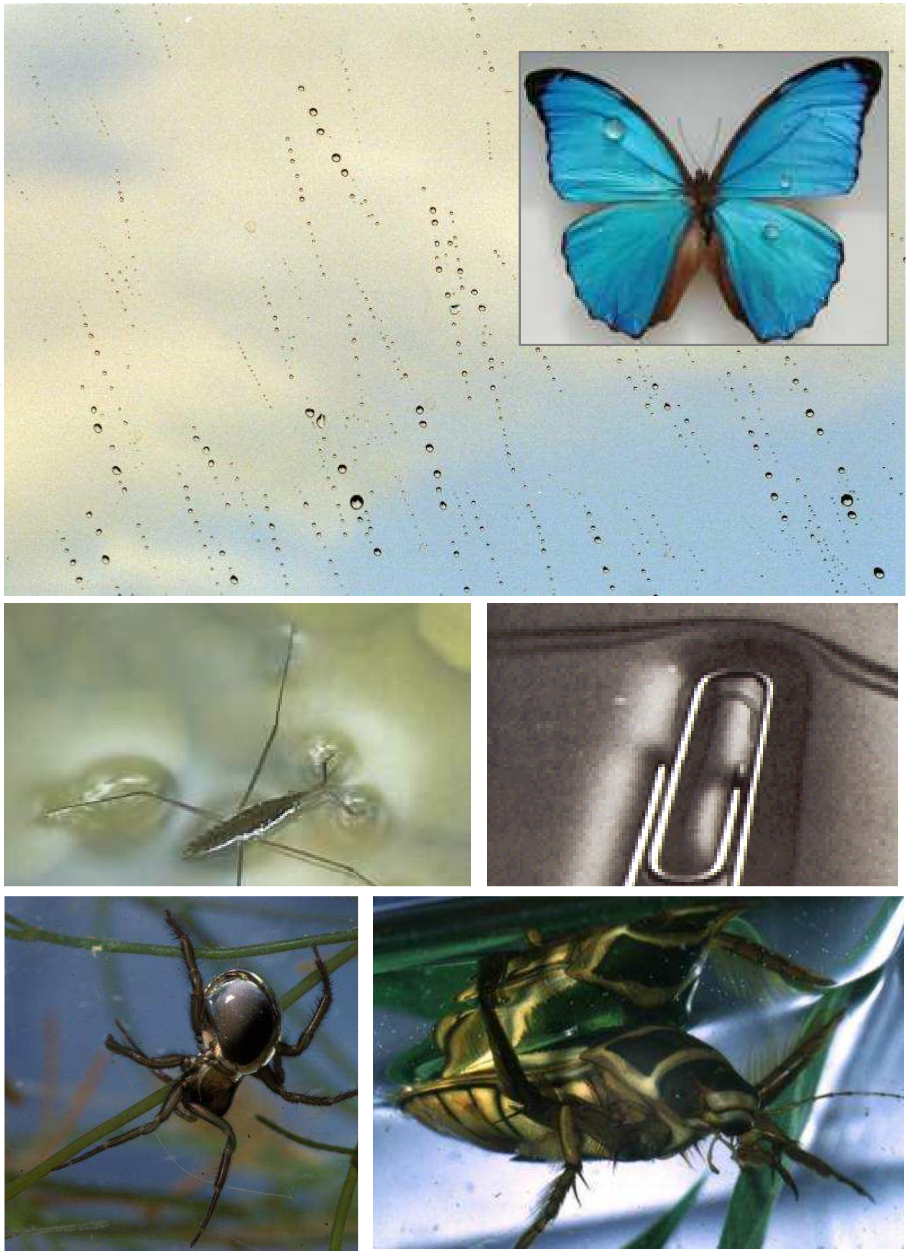
Water-on-Solids

- Liquids sometimes form drops, and sometimes spread over a surface and wet it. Why does this happen?
- Why are raindrops never a metre wide?
- Why don’t they run down the window?
- Why do butterfly wings survive rain?

Solids-on-Water

- How can pond skaters, and even fishing spiders walk-on-water? Why does this happen?
- How can metal objects “float” on water?

Solids-in & under-Water?



Plants and Leaves

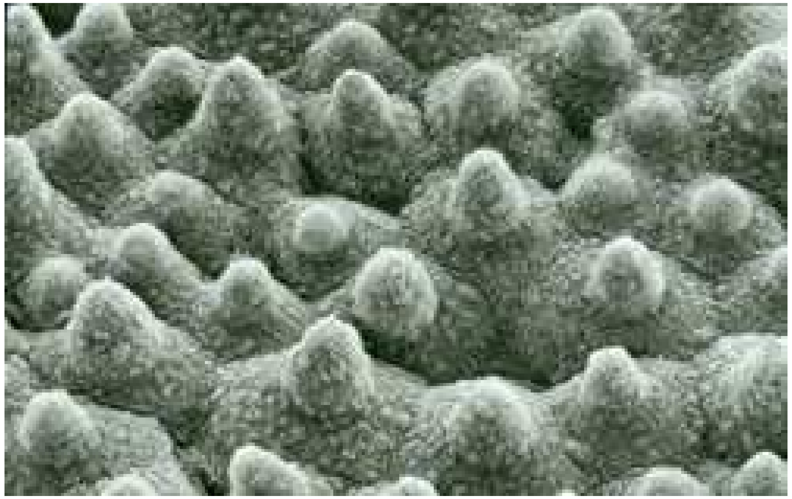
Honeysuckle, Fat Hen, Tulip, Daffodil, Sew thistle (Milkweed), Aquilegia
Nasturtium, Lady’s Mantle, Cabbage/Sprout/Broccoli

The Sacred Lotus Leaf

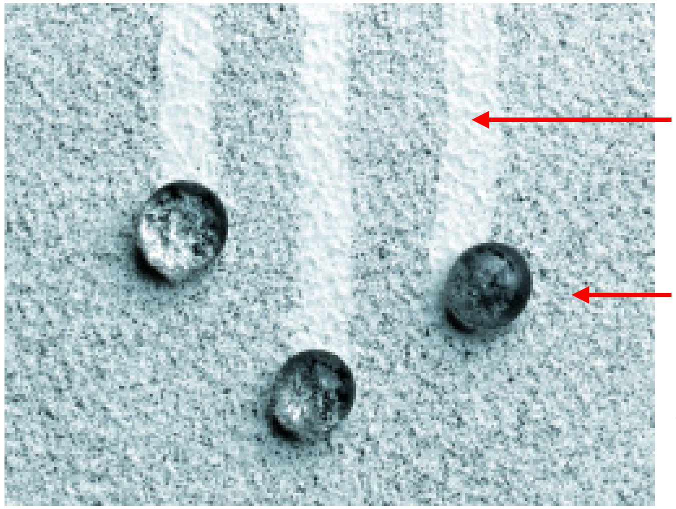
Plants

- Many leaves are super-water repellent
- The Lotus plant is known for its purity
- Superhydrophobic leaves are self-cleaning under the action of rain

SEM of a Lotus Leaf



Self-Cleaning



Dust cleaned away

Dust coated droplet

A “proto-marble”

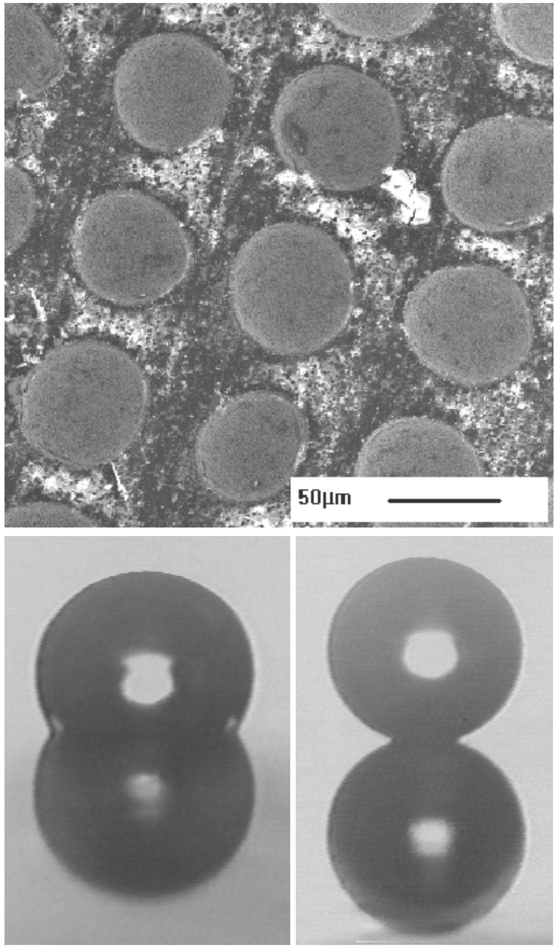
Self-poisoning surface

Acknowledgement   Neinhuis and Barthlott

Basic Concepts

Three Examples

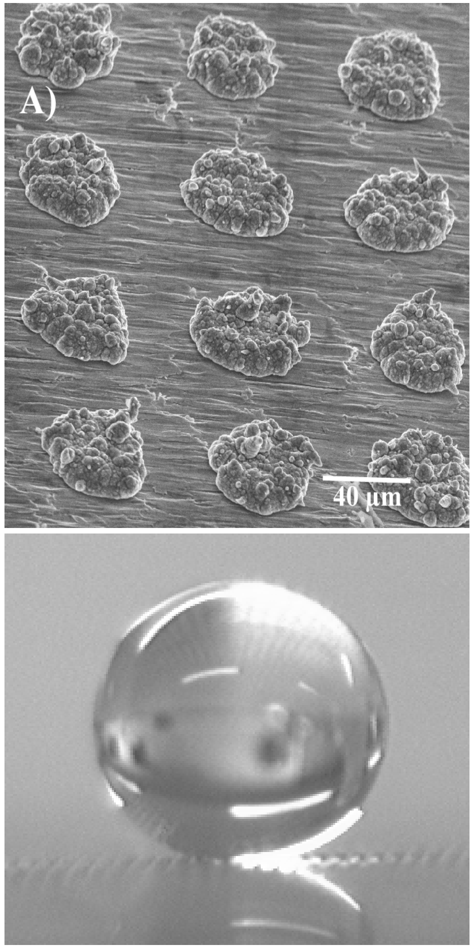
Etched Metal



Flat & hydrophobic

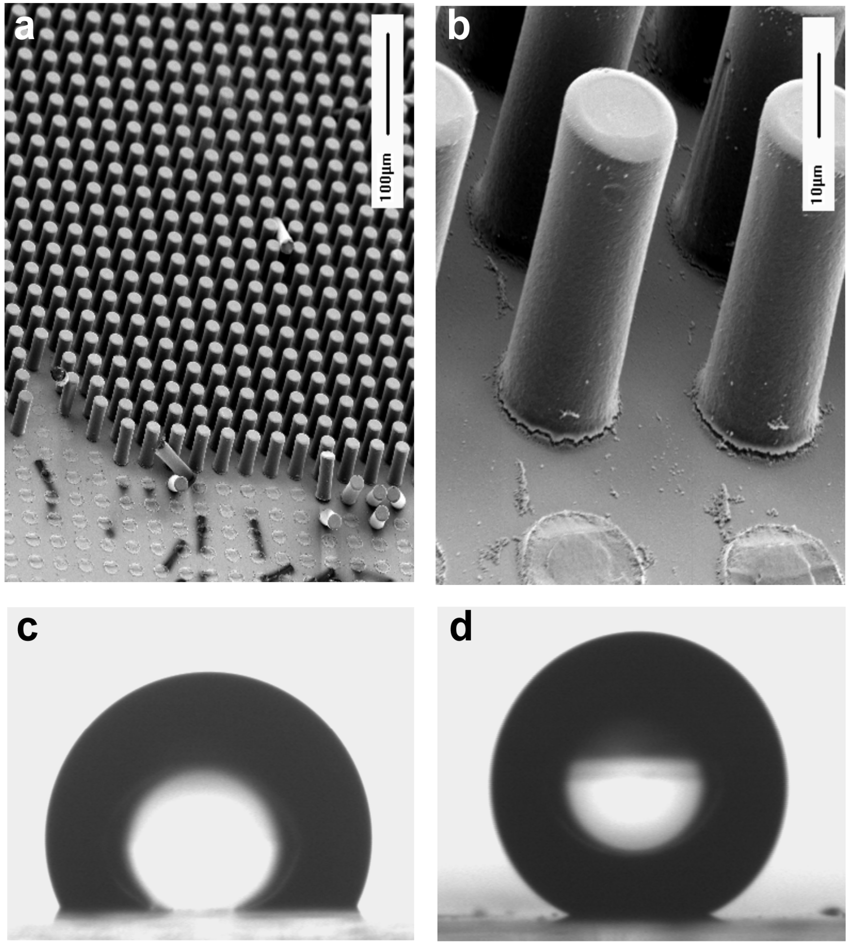
Patterned & hydrophobic

Deposited Metal



Patterned & hydrophobic

Polymer Microposts



Flat & hydrophobic

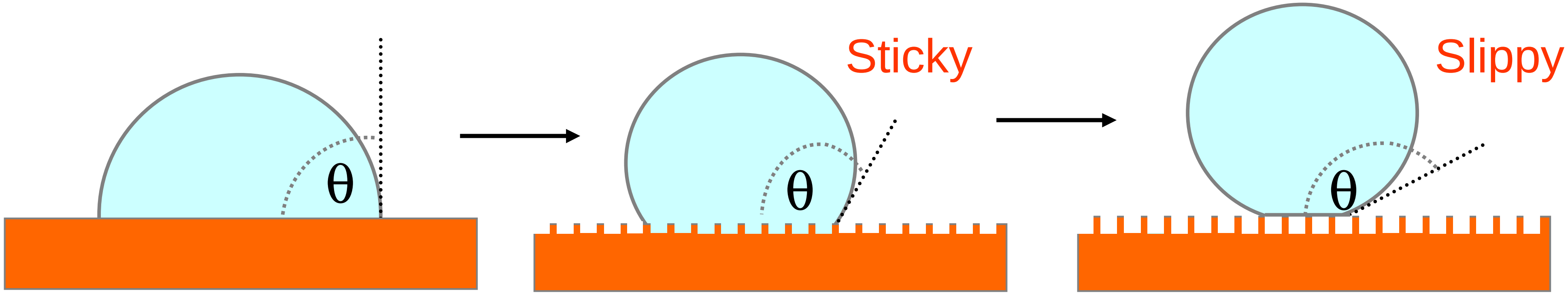
Patterned & hydrophobic

References Shirtcliffe,*et al.*, *Langmuir* **21**, 2005, 937; *Adv. Maters.* **16**, 2004, 1929; *J. Micromech. Microeng.* **14**, 2004, 1384.

Topography & Wetting

Droplets that Impale and those that Skate

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



Young’s Law

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

Chemistry

Wenzel Eq.

$$\cos\theta_W = r\cos\theta_e$$

Roughness

r = true area/planar projection

Cassie-Baxter Eq

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

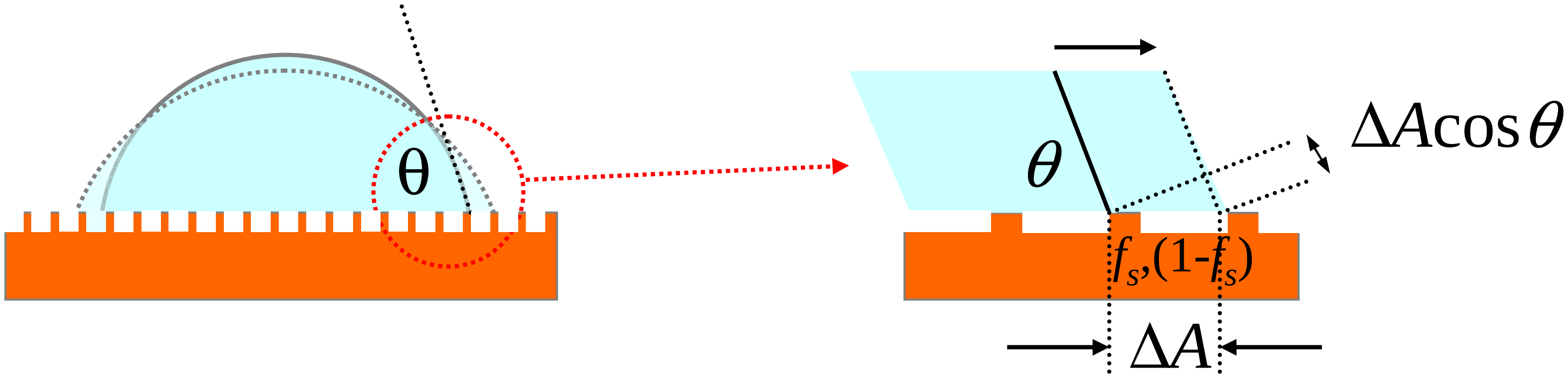
Chemistry

Young’s Law θ_e

Topography

f_s = solid surface fraction

Origin of Cassie-Baxter Equation



Change in surface free energy is

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

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

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

Cassie-Baxter Eq

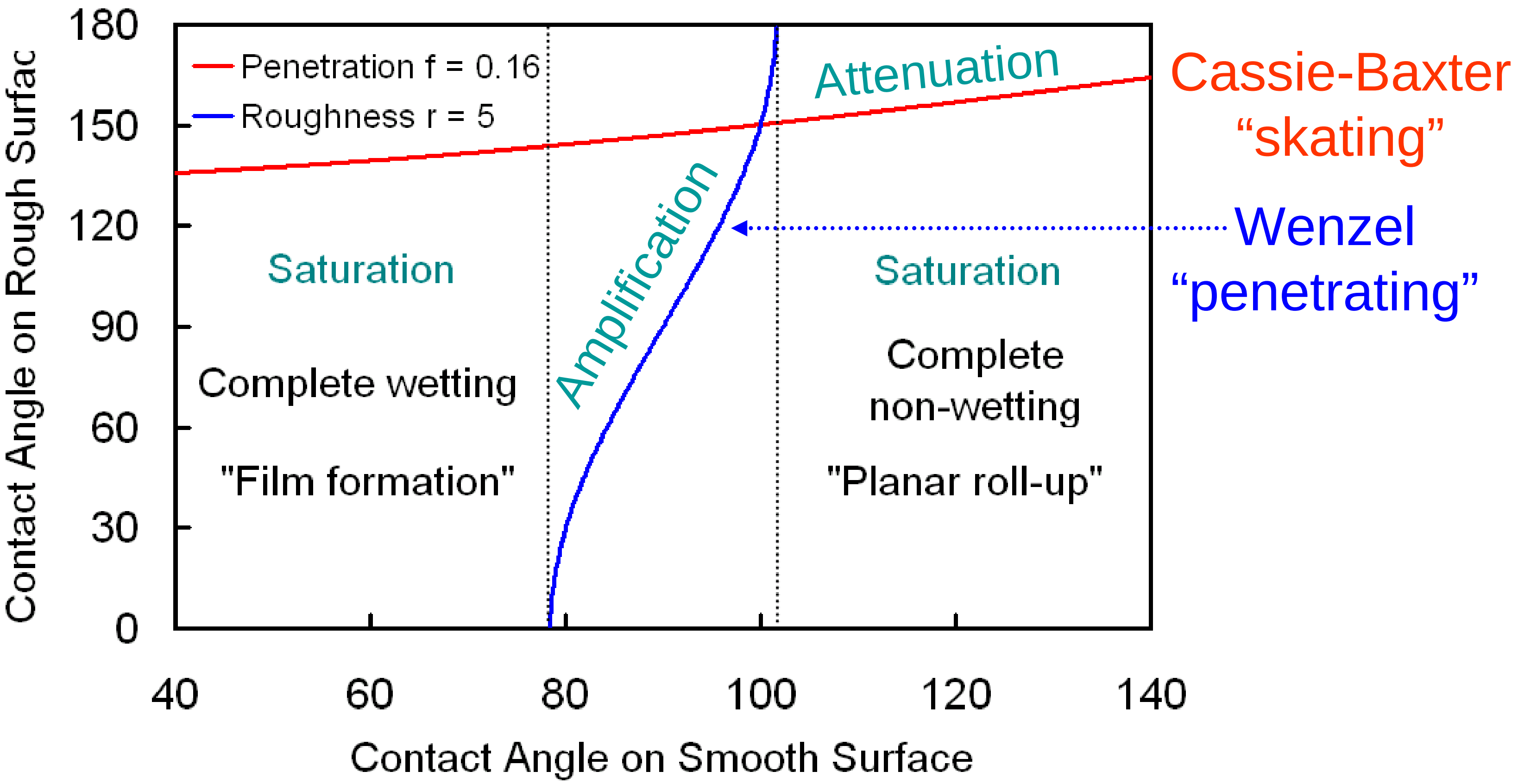
Topography ⇒ f_s = solid surface fraction

Chemistry ⇒ Young's Law θ_e

Air gaps ⇒ cos(180°)=-1

Weighted average using f_s and $(1-f_s)$

Effect of Topography - Theory



Roughness/Topography

θ_e^s > threshold

⇒ enhances repellence

θ_e^s < threshold

⇒ enhances film formation

Superhydrophobic

“Skating case”

⇒ most existing examples

Pressure

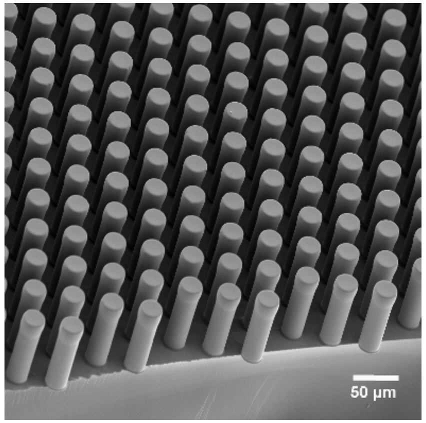
⇒ transition to penetrating

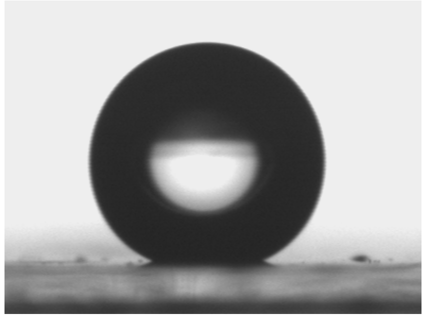
Skating-to-Penetrating Transition

Micro-Structured Surface

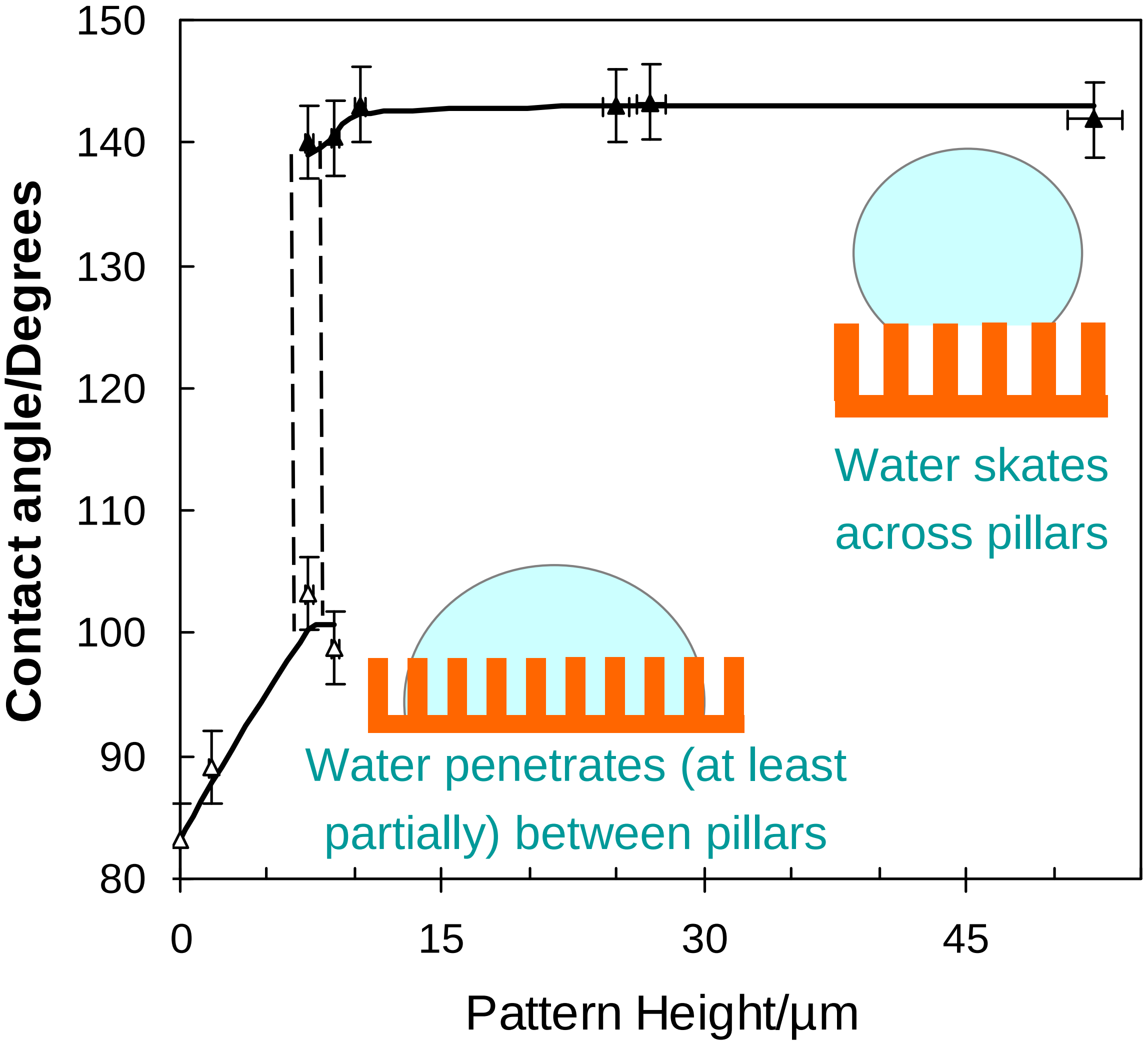
SU-8 pillars 15 µm

Hydrophobic treatment





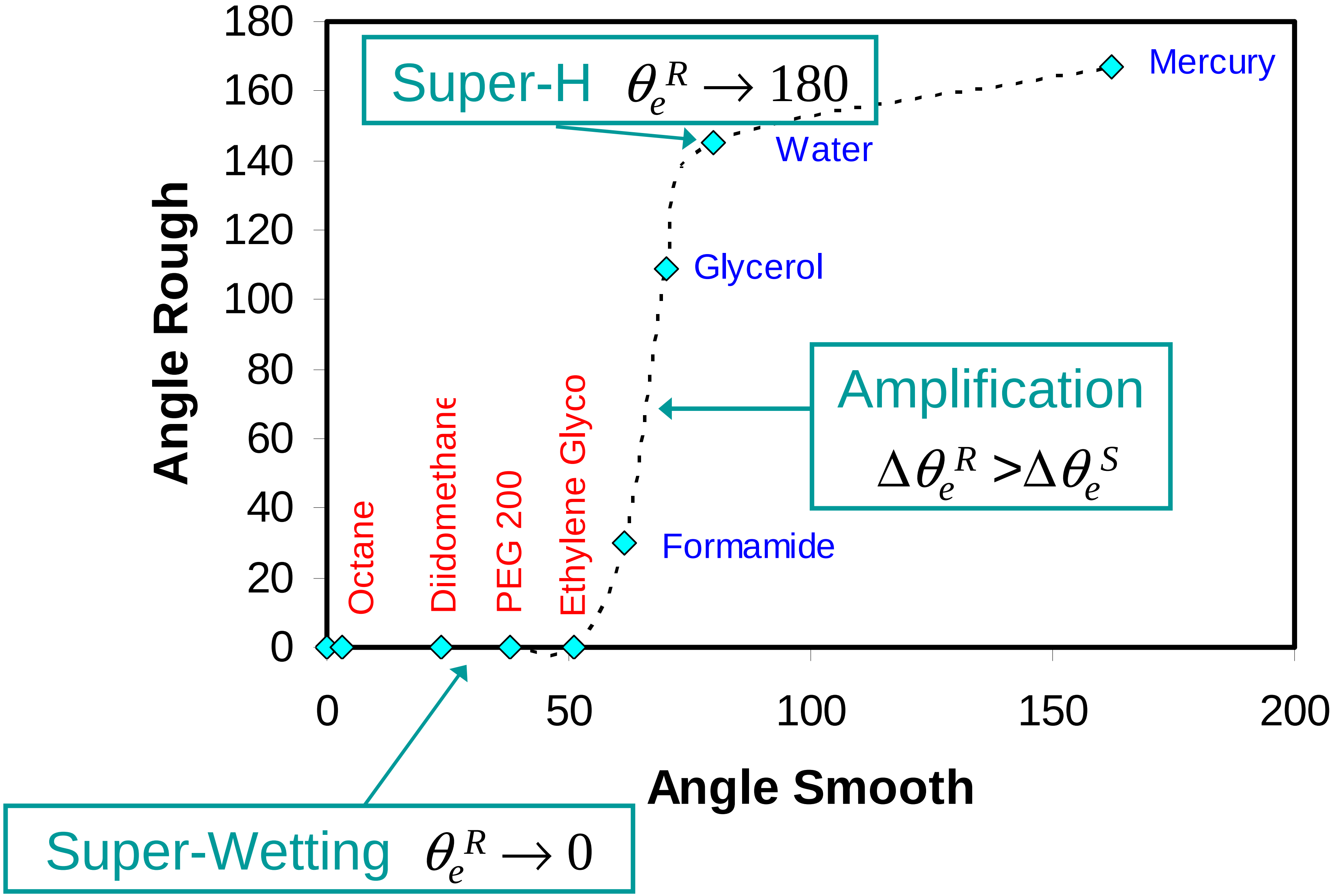
Change of Pillar Height



Water skates across pillars

Water penetrates (at least partially) between pillars

Different Liquids on a SuperH Surface



Super-H $\theta_e^R \rightarrow 180$

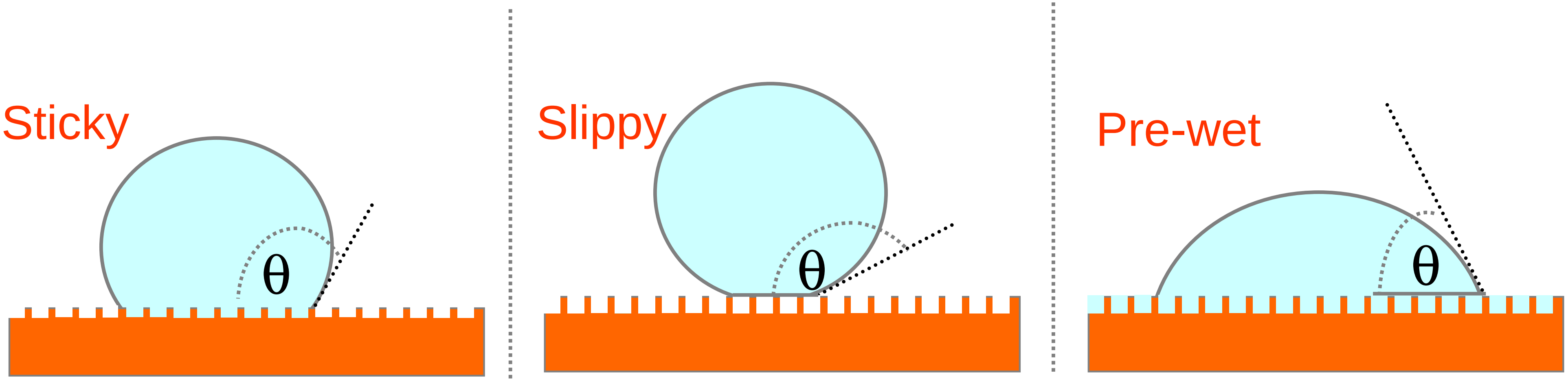
Amplification

$\Delta\theta_e^R > \Delta\theta_e^S$

Super-Wetting $\theta_e^R \rightarrow 0$

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

Pre-existing Wetness



Weighted average of fractions f_s and $(1-f_s)$ with $\theta_{gap}=0^{o}$ or 180^{o}

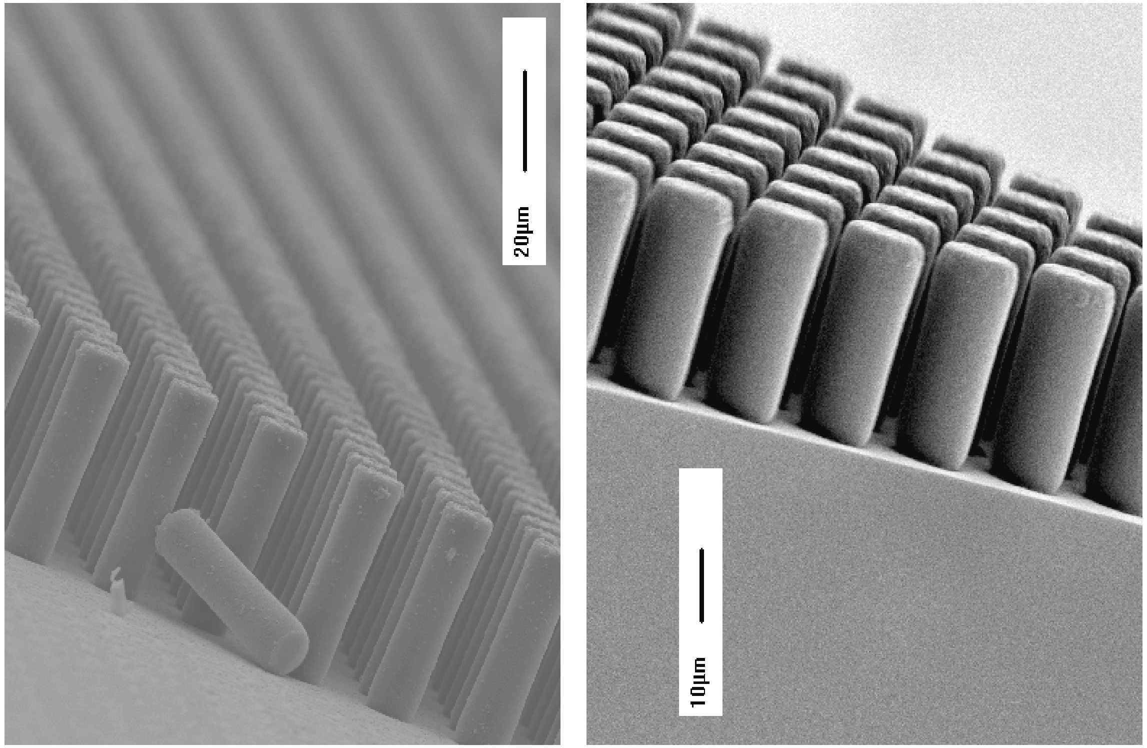
ie. use $\cos(180^{o})=-1$ or $\cos(0^{o})=+1$ in Cassie-Baxter equation

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

A Selection of Surfaces

SU-8 Photoresist Pillars

SEMs of Pillars

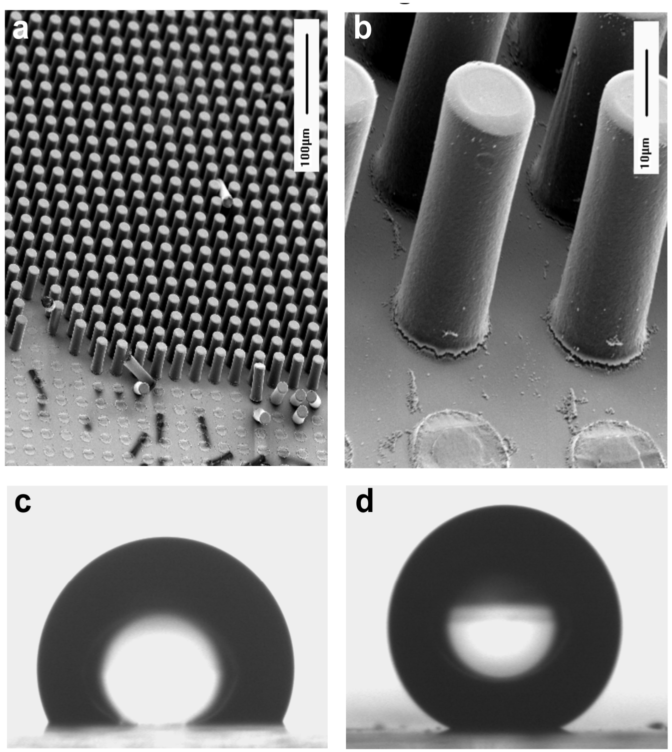


Tall structures to 45-75 μm

smooth and straight walls

Aspect ratios up to ~ 7

Effect on Water



a), b) Pillars D=15 μm, $L = 2D$

c) Flat and hydrophobic

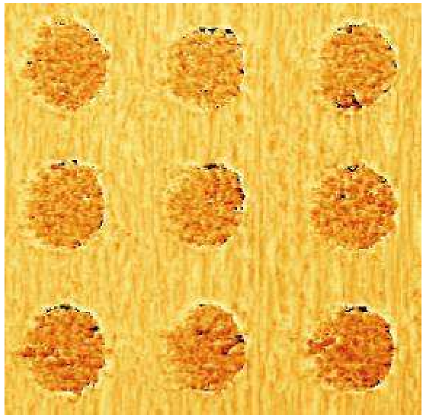
d) Tall and hydrophobic

Reference Shirtcliffe *et al*, J. Micromech. Microeng. 14 (2004) 1384-1389.

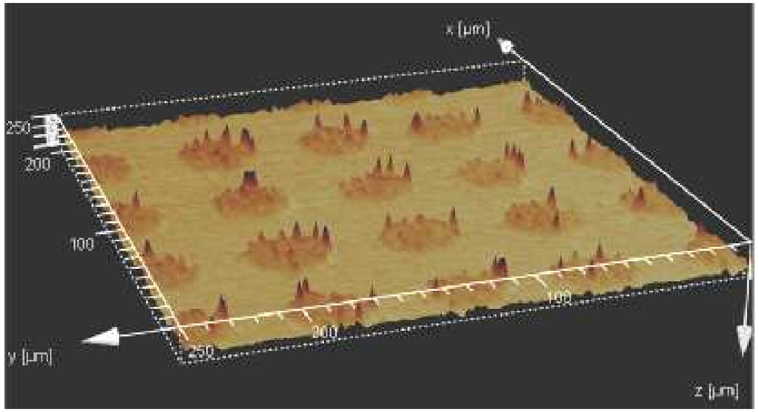
Electrodeposited Surfaces

Diffusion limited aggregation –copper acid bath, fractal roughness

Base Cu electroplated surface

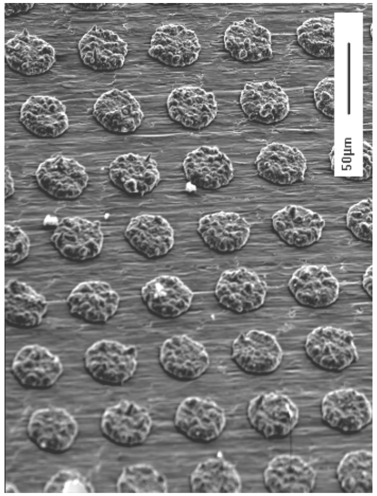


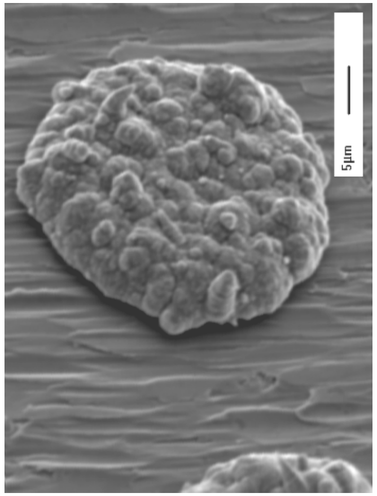
Confocal image of a 30μm textured electroplated Cu

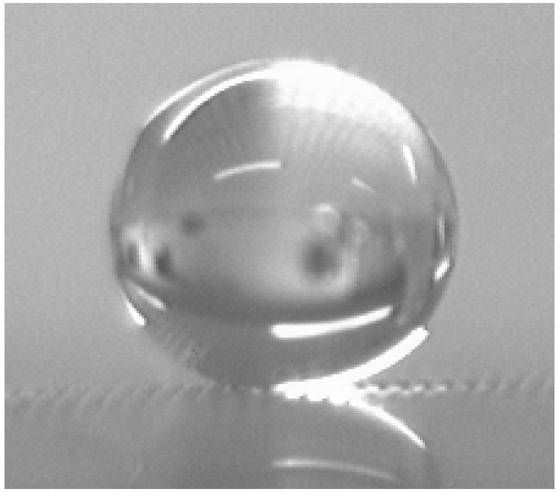


3D view of a electroplated copper sample

“Chocolate Chip Cookies” - Electroplating through a mask



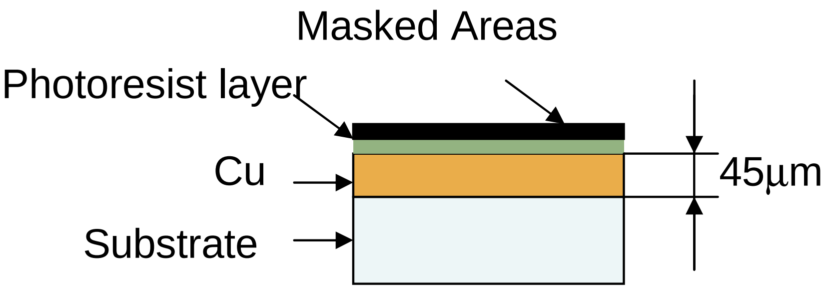


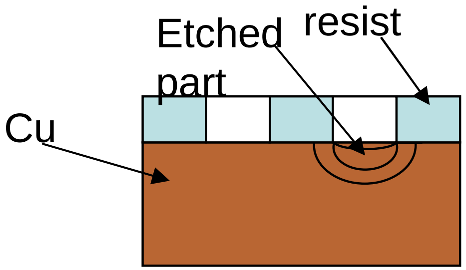


Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932; Shirtcliffe *et al*, Langmuir 21 (2005) 937-943.

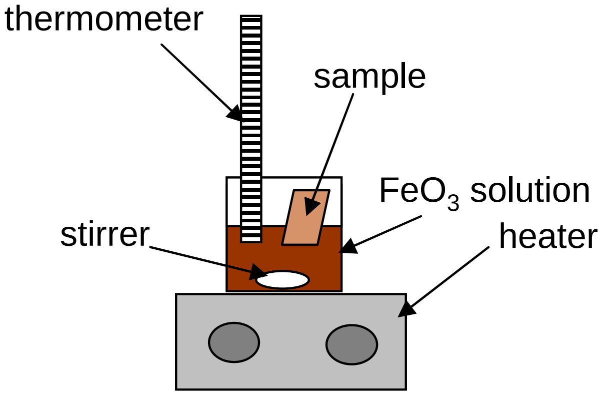
Etched Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

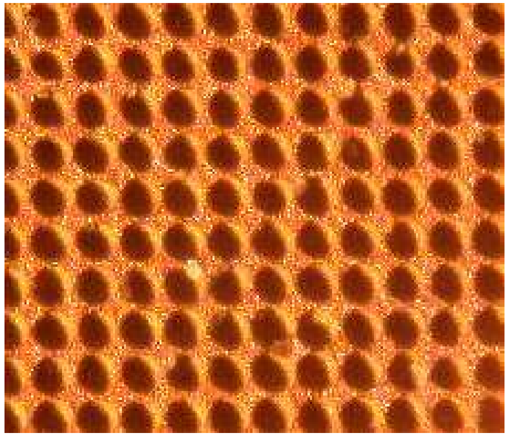




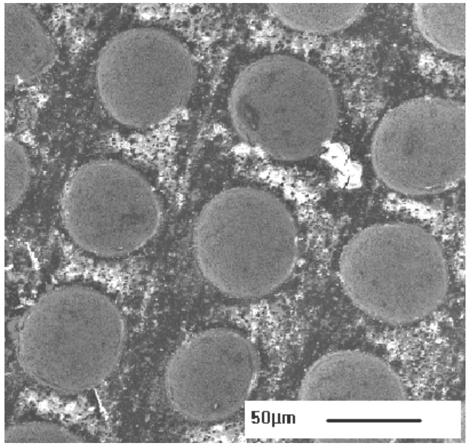
hole growth



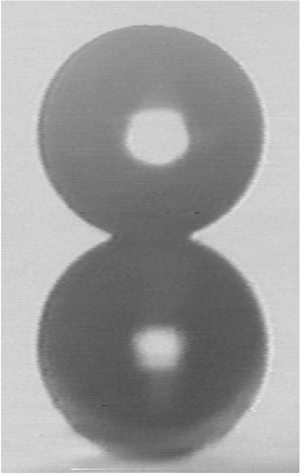
Setup of the copper etching



Copper sample etched through a 30 µm pattern



SEM picture of the pattern of the etched copper surface



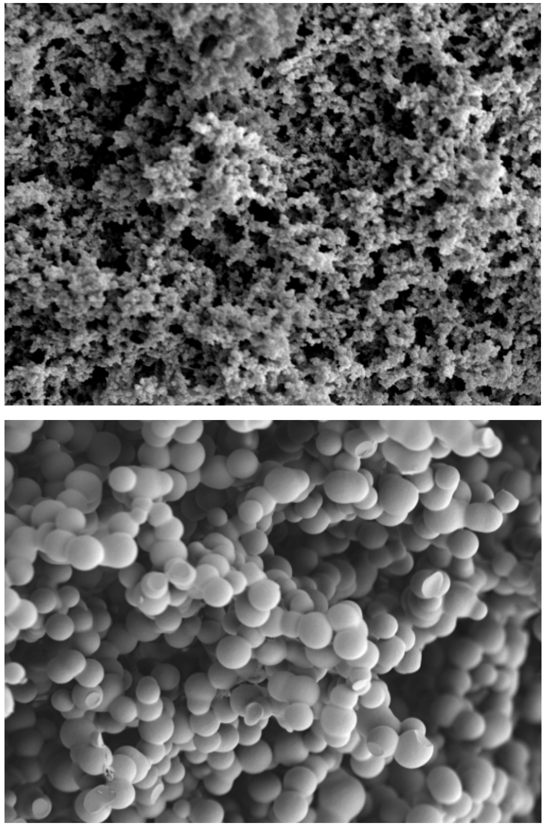
Water drop and reflection on an etched copper surface

Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932; Shirtcliffe *et al*, Langmuir 21 (2005) 937-943.

Organo-Silica Sol-Gel Foam Surfaces

- Sol-Gel = preparation of oxide materials from solution
  - Usually organosilicon compounds hydrolysed to form intermediates
  - Partially & fully hydrolysed silicates can link together
  - Solvent creates porous structure unless complete phase separation occurs
  - Hydroxide and organic groups usually present until thermally treated
  - MTEOS sol-gel using 1.1 M & 2.2 M ammonia

- Advantages
  - Intrinsically hydrophobic
  - *Abradable (renewable) superhydrophobic surfaces*
  - Pore size controllable nano- to macro-porous
  - Contact angle hysteresis as low as 4^o
  - Hydrophobic-to-hydrophilic transition by heating

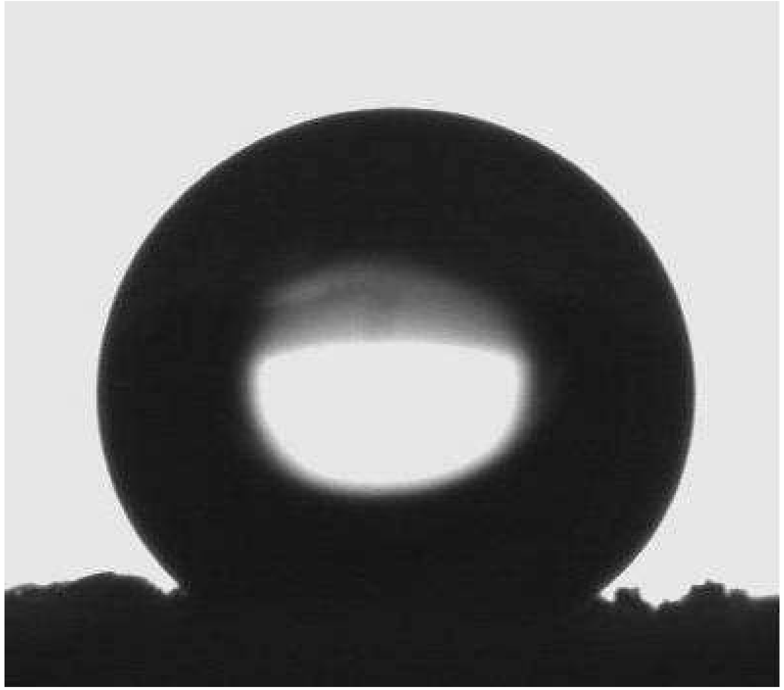


10 µm

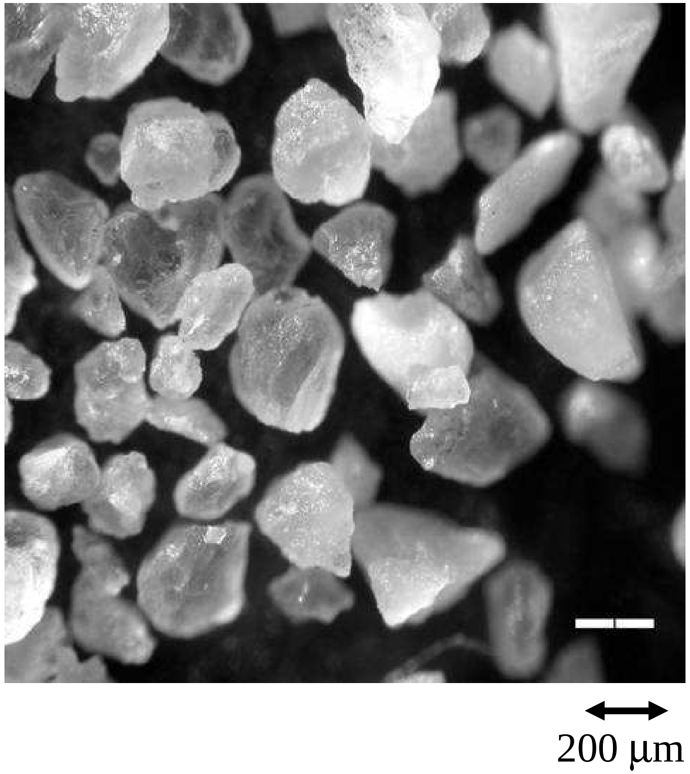
<u>Reference</u> Shirtcliffe *et al*, Langmuir <u>19</u> (2003) 5626-5631

Super Water-Repellent Sand/Soil

Sand with139°



Shape and Packing



Comments

1. Effect occurs naturally, but can also be reproduced in the lab
2. Water droplet doesn't penetrate, it just evaporates
3. Need to use ethanol rich mixture to get droplet to infiltrate (MED test)

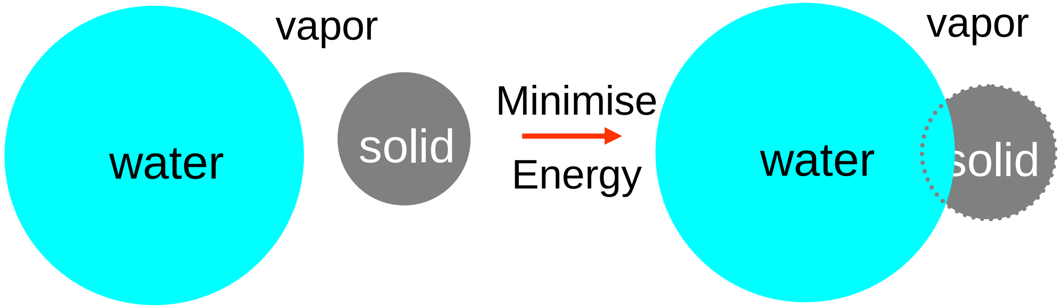
Reference McHale *et al*, Eur. J. Soil Sci. 56 (2005) 445-452; McHale *et al*, Hydrol. Proc. 21 (2007) 2229-2238.

Liquid Marbles

Loose Surfaces

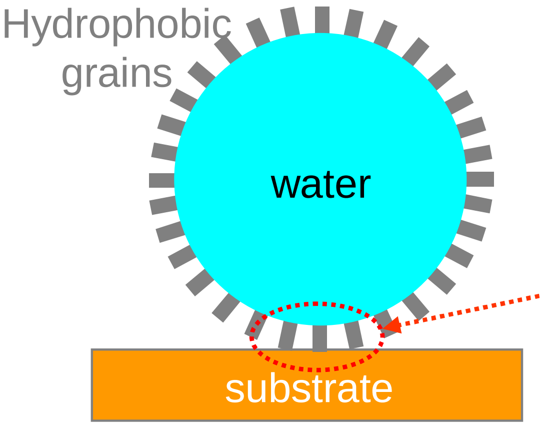
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

Hydrophobic Grains and Water

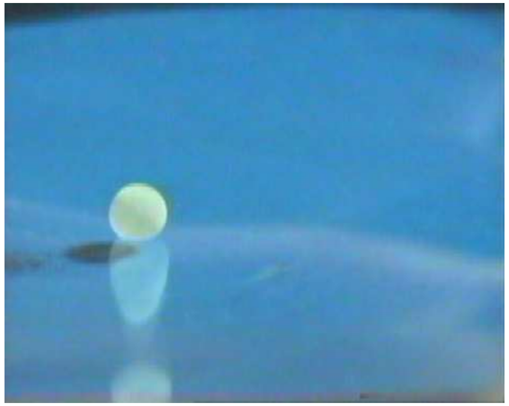


$$\Delta F = -\pi R_g^2 \gamma_{LV} (1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment

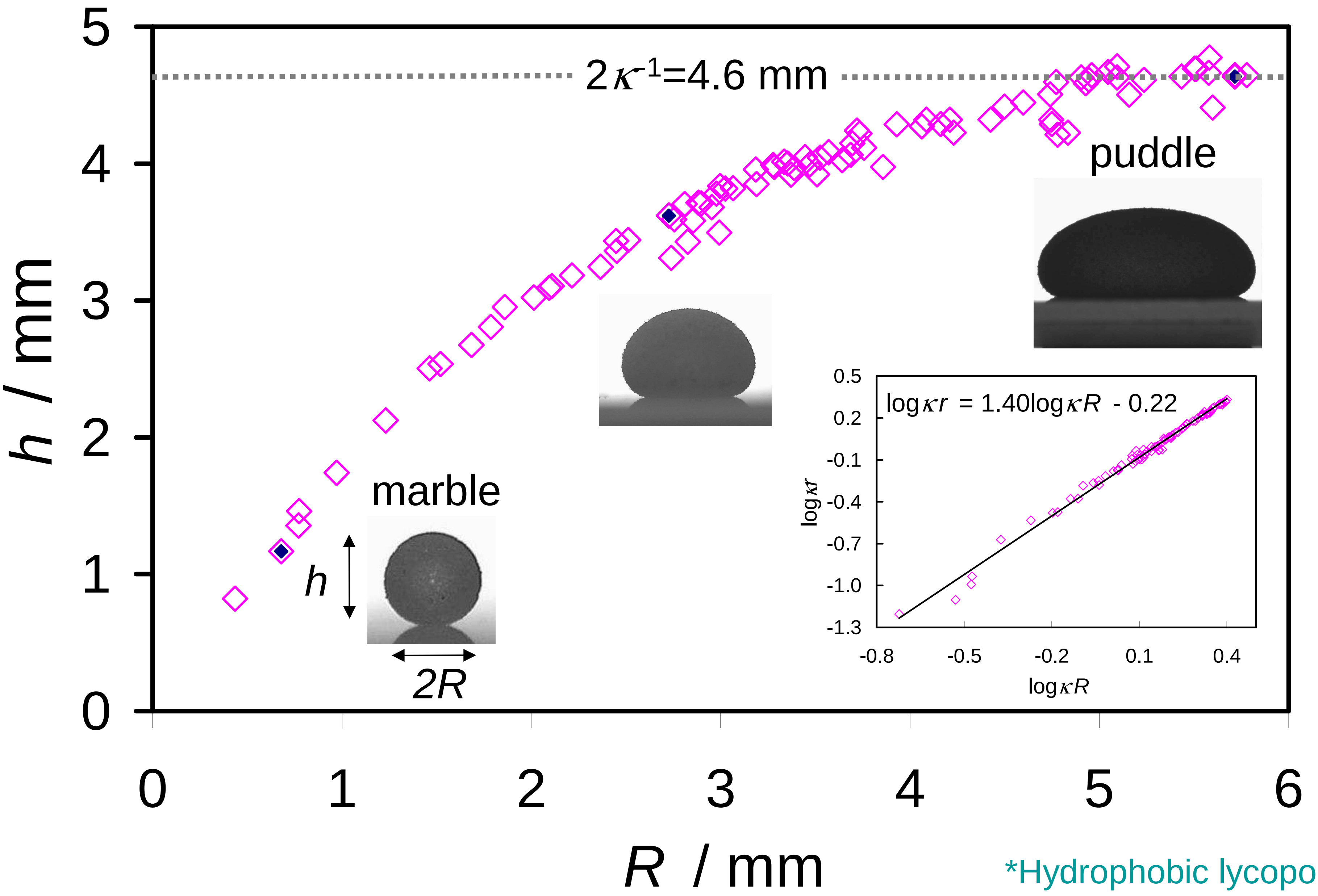


Similar to pillars, but solid conformable to liquid



Reference Aussillous, P.; Quéré, D. Nature 411, (2001), 924-927

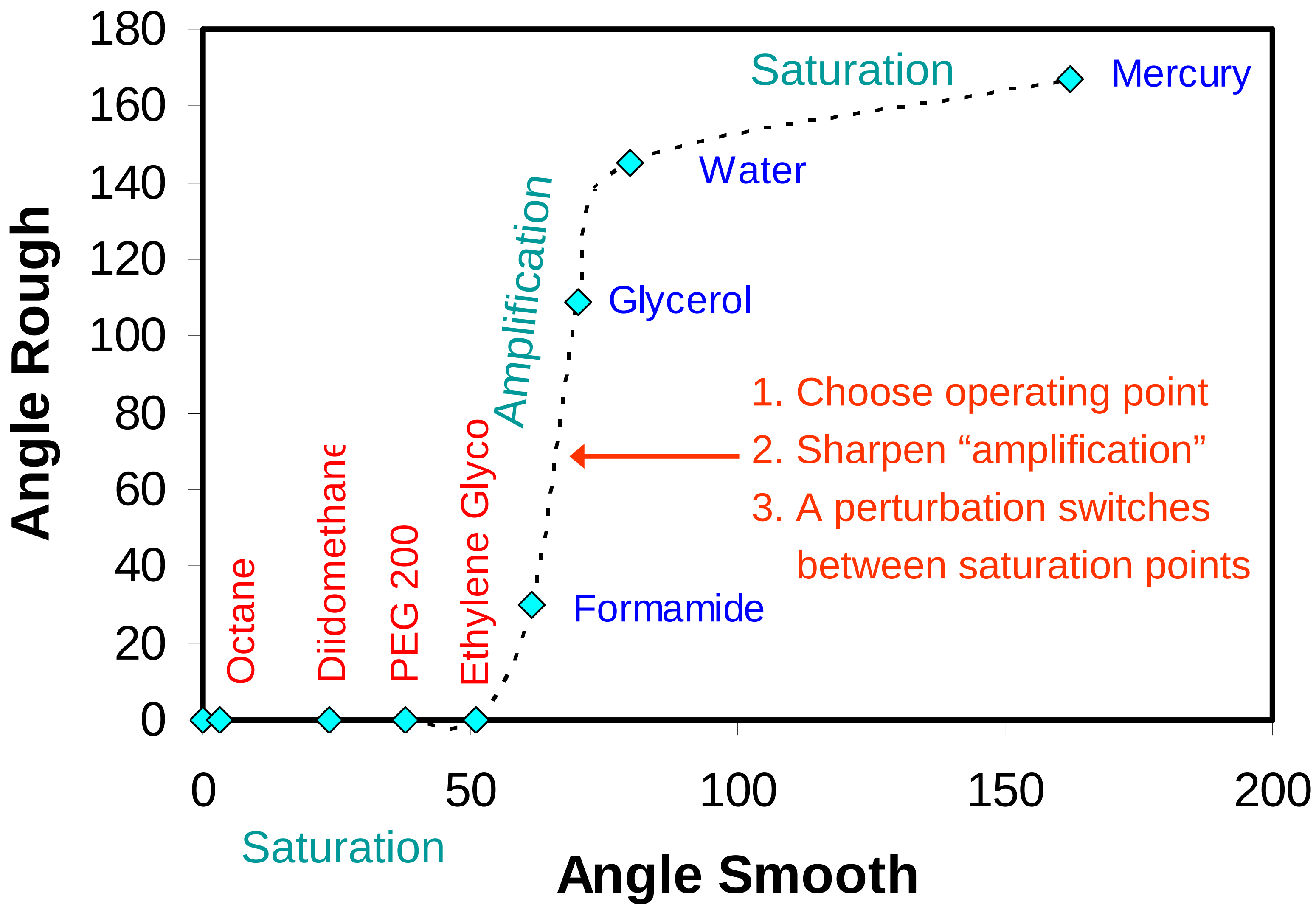
Perfect Non-Wetting Marbles*



*Hydrophobic lycopodium

Switching and Super-spreading

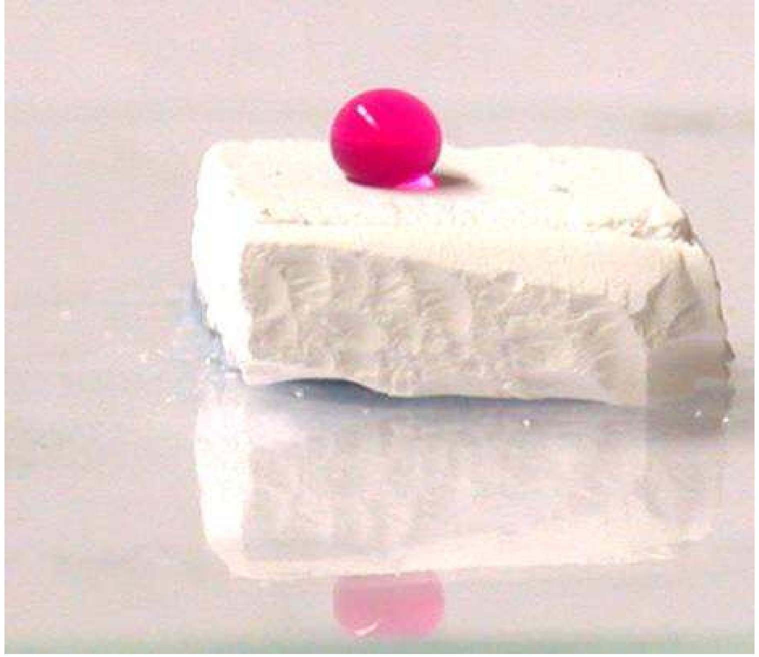
“Digital” Switching - Recall



1. Choose operating point
2. Sharpen “amplification”
3. A perturbation switches between saturation points

<u>Reference</u> McHale *et al*, Analyst <u>129</u> (2004) 284-287.

Sol-Gel Foams – Switching from S/H

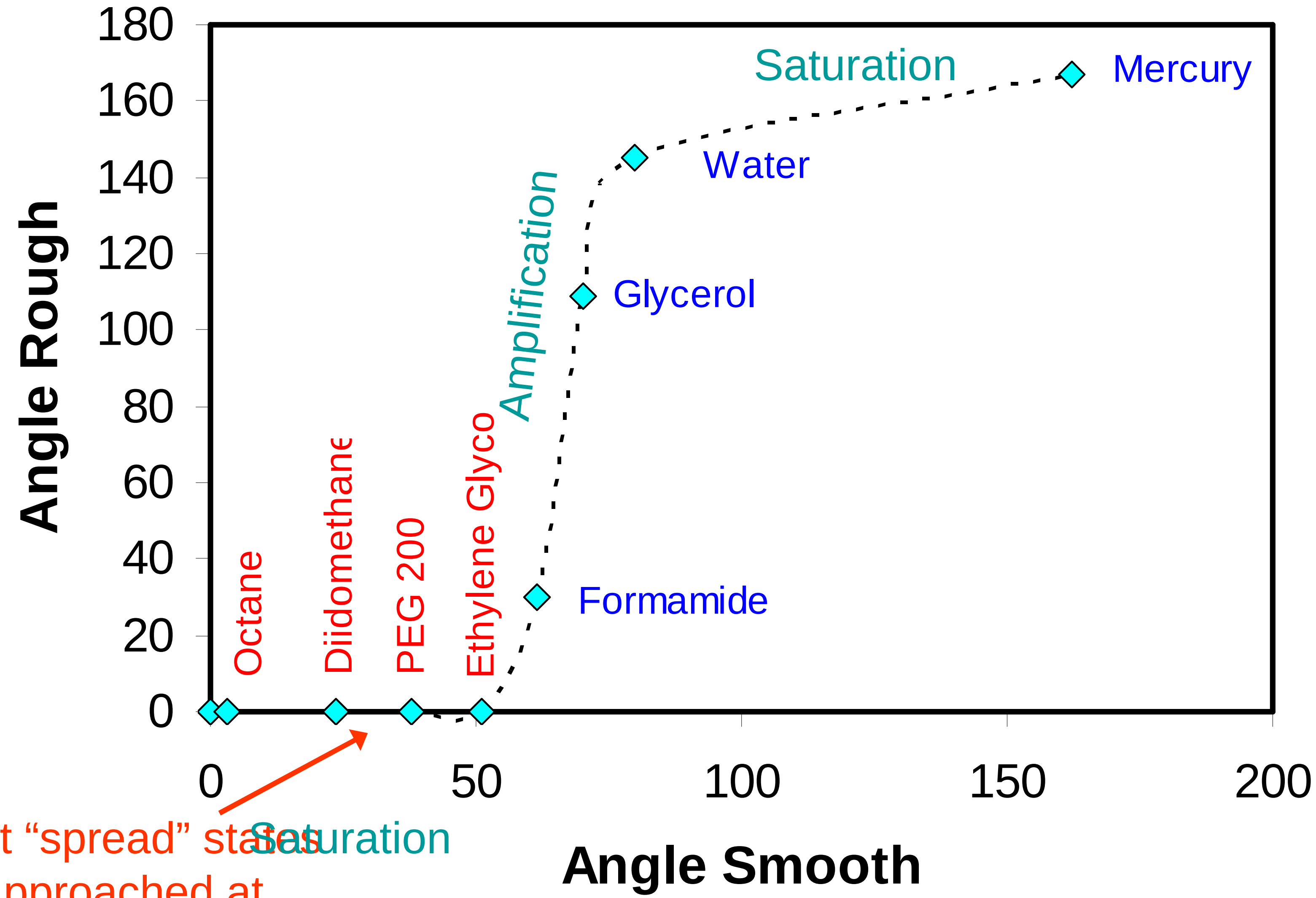


Foam heated
(and cooled)
prior to droplet
deposition

- Mechanisms for Switching
  - Temperature history of substrate
  - Surface tension changes in liquid (alcohol content, surfactant, …)
  - “Operating point” for switch by substrate design

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

“Super-spreading” - Recall



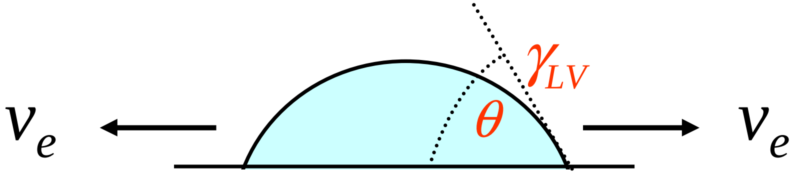
Different “spread” states
are approached at
different rates

Reference McHale *et al*, Analyst 129 (2004) 284-287.

Super-spreading and "*Driving Forces*"

Drop spreads radially until contact angle reaches equlibrium

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



Smooth/rough solid

Smooth Surface

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

Cubic drop edge speed

$$\Rightarrow v_E \propto \theta(\theta^2 - \theta_e^2)$$

Wenzel Rough Surface

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

Linear droplet edge speed

$$\Rightarrow v_E \propto \theta((r-1)+((\theta^2 - r\theta_e^2)/2)$$

Prediction

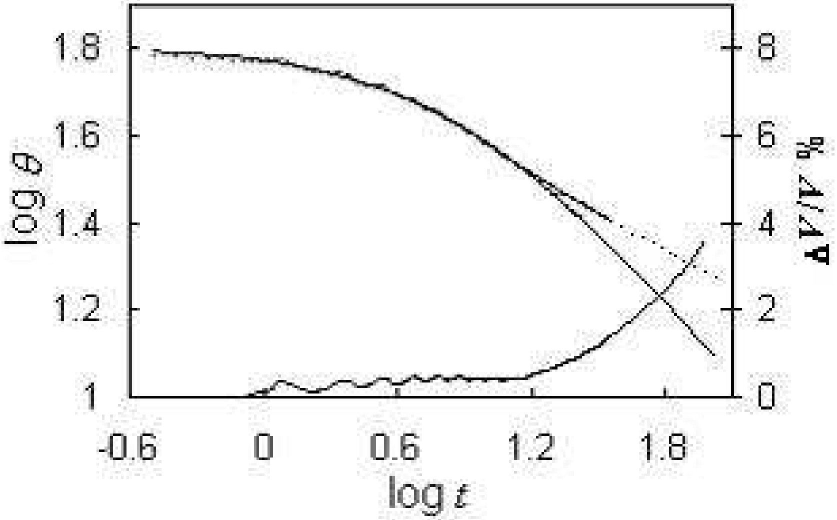
Weak roughness (or surface texture) modifies edge speed:

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

Reference McHale and Newton, Colloids & Surfaces, A206 (2002) 193-201.

Superspreading of PDMS on Pillars

Hoffmann/Tanner Laws for exponents *p* & *n* (cubic to linear transition)

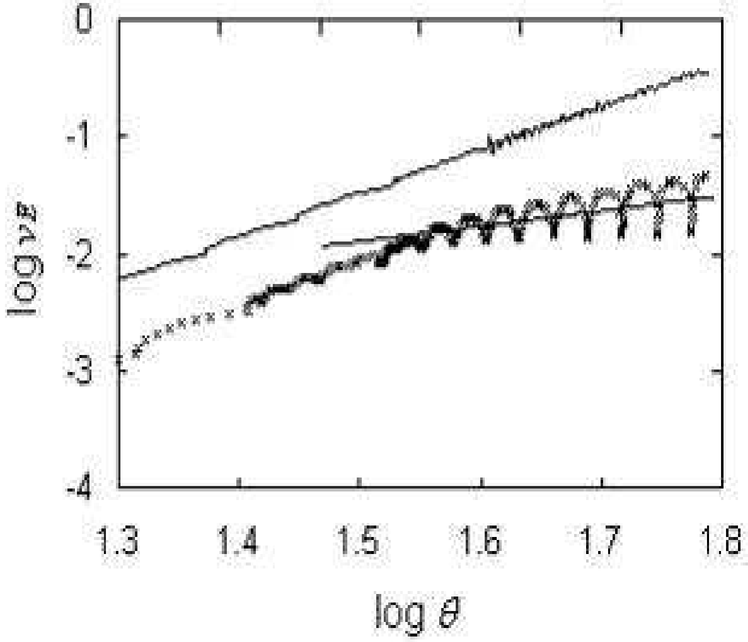


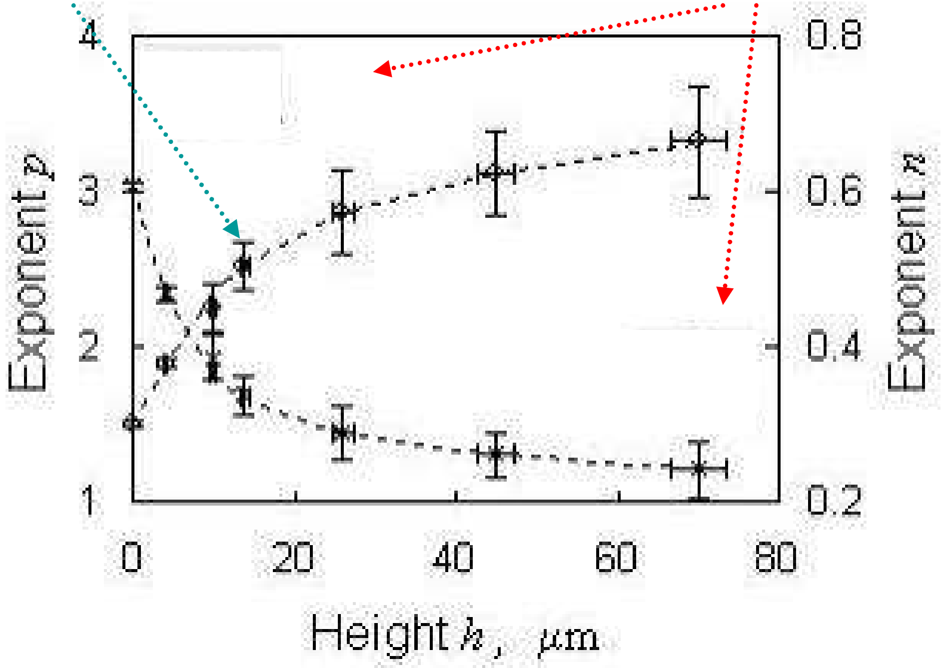
$$v_E \propto v^* \theta^p$$

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

Effect of substrate on PDMS

Effect of substrate on water

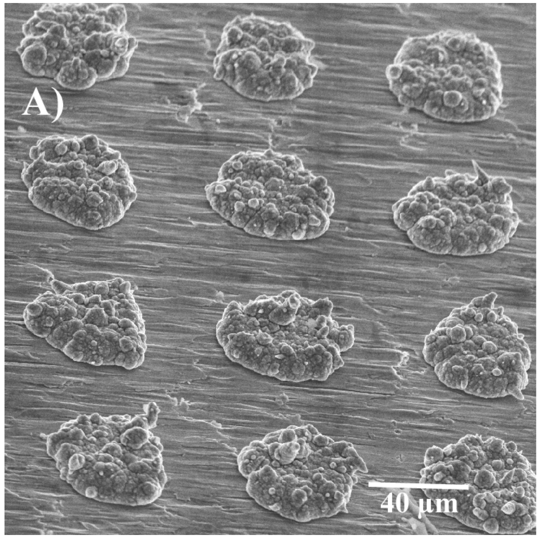


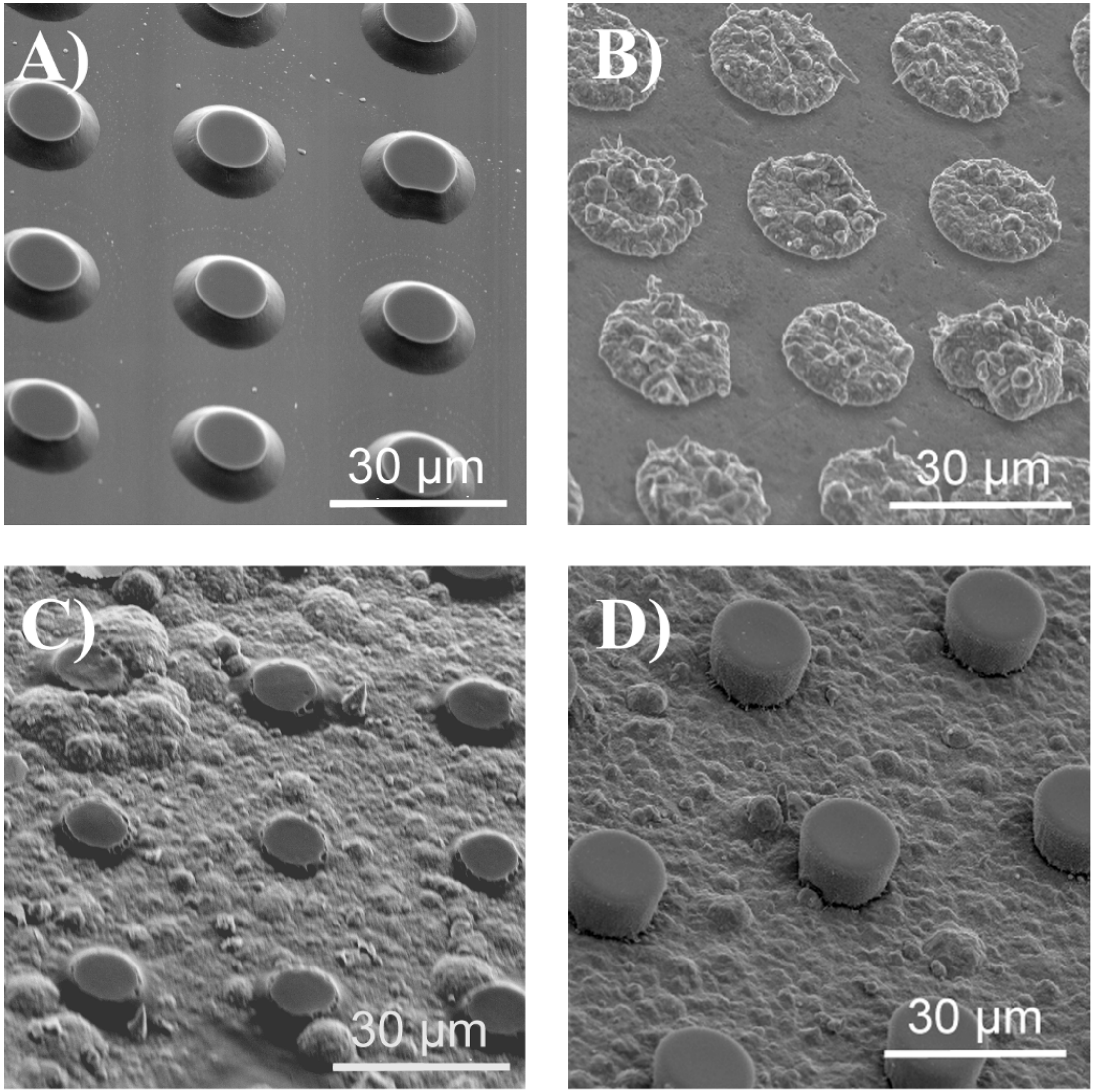


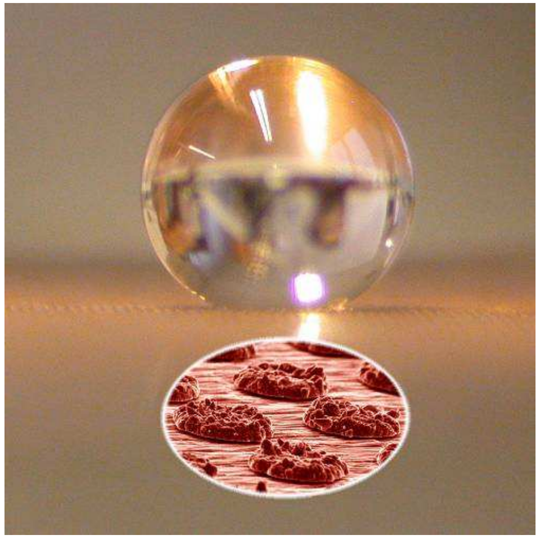
References McHale□, *et al*, Phys. Rev. Lett. 93, (2004) art. 036102; Nature Maters. 6 (2007) 637-628.

Complex Surfaces

Double Length Scale Systems







Reference   Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932.

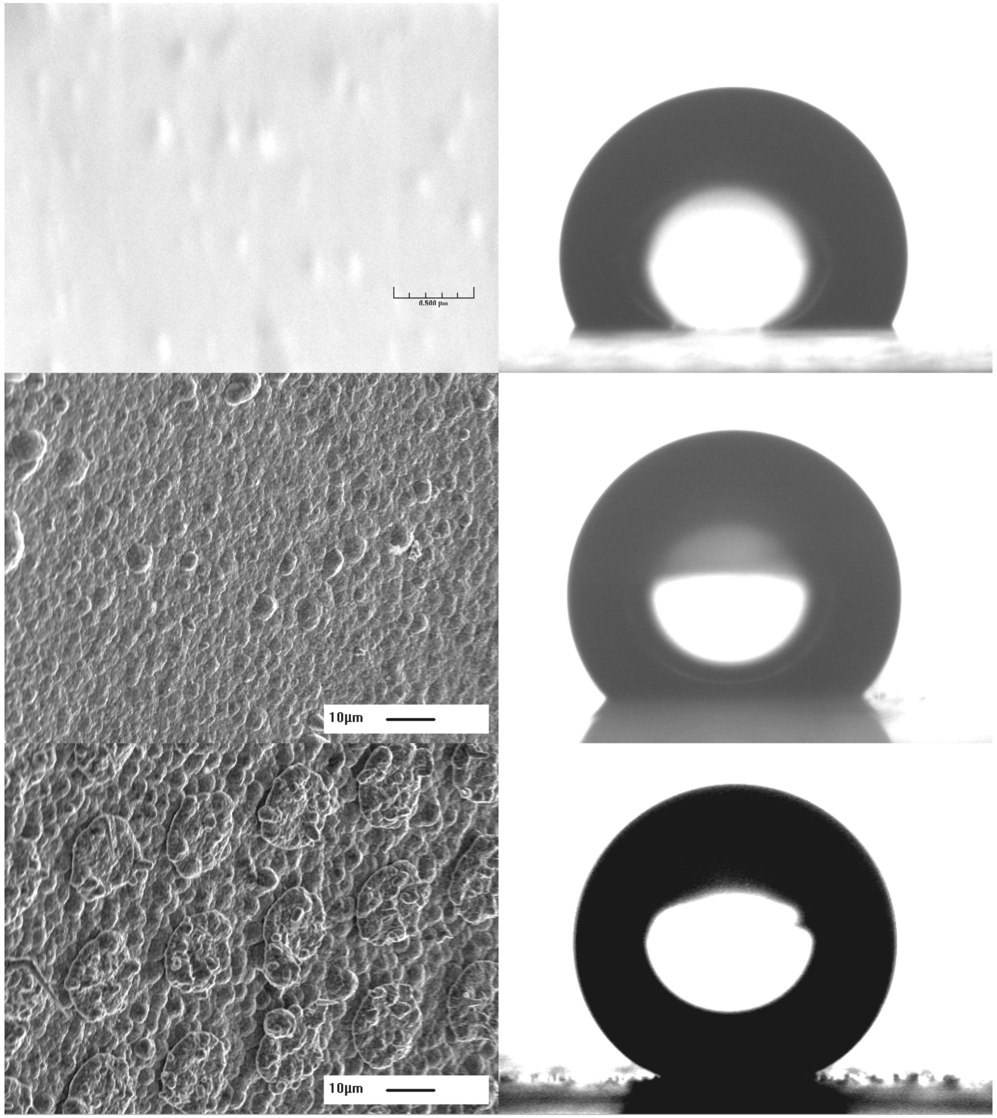
Combining Slight Roughness and Texture

- Smooth and Hydrophobised 115°

- Slightly Rough and Hydrophobised 136°

- Slightly Rough, Textured and Hydrophobised 160°

Two length scales is extremely effective



Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932 (Theory is in the supplementary information).

Patterns in Superhydrophobicity

Local Cassie-Baxter Contact Angle

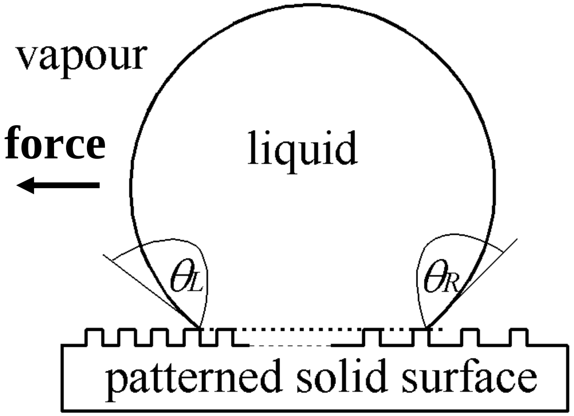
Make contact angle depend on position and surface chemistry $\theta(x, \theta_e^s)$

Same surface chemistry, but vary Cassie-Baxter fraction across surface

$$\cos\theta_{CB}(x) = f(x)\cos\theta_e^s - (1 - f(x))$$

Driving Force

Droplet experiences different contact angles ⇒ driving force



$$Force \propto \gamma_{LV}(\cos\theta_R - \cos\theta_L)$$
$$\propto \gamma_{LV}(f_R - f_L)(\cos\theta_e^s + 1)$$

Need to overcome contact angle hysteresis

Reference Quéré *et al* (unpublished); McHale *et al*, Analyst 129 (2004) 284-287; McHale, Langmuir 23 (2007) 8200-8205.

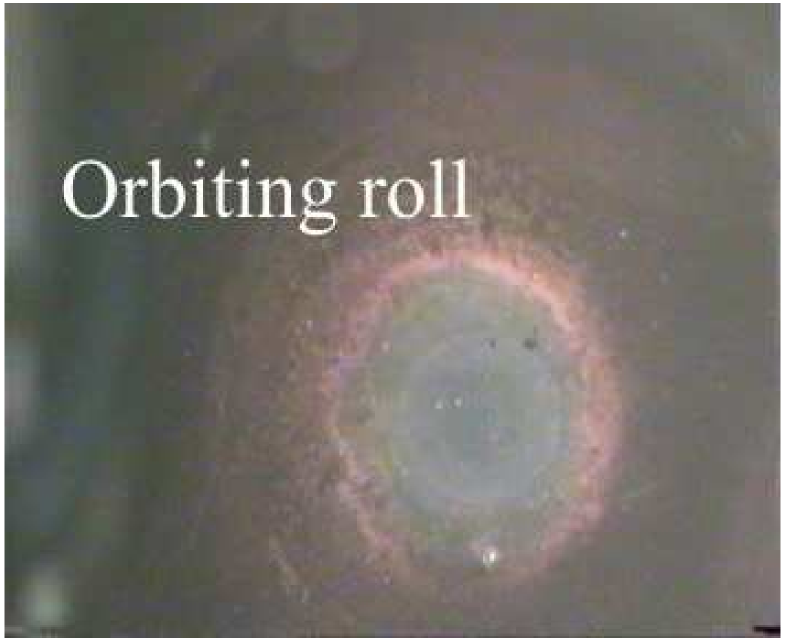
Self-Actuated Motion

Radial Gradient in Contact Angle

Electrodeposited copper – Diffusion limited aggregation

Fractal–like to overcome contact angle hysteresis

Radial gradient $\theta(r)$=110° → 160°

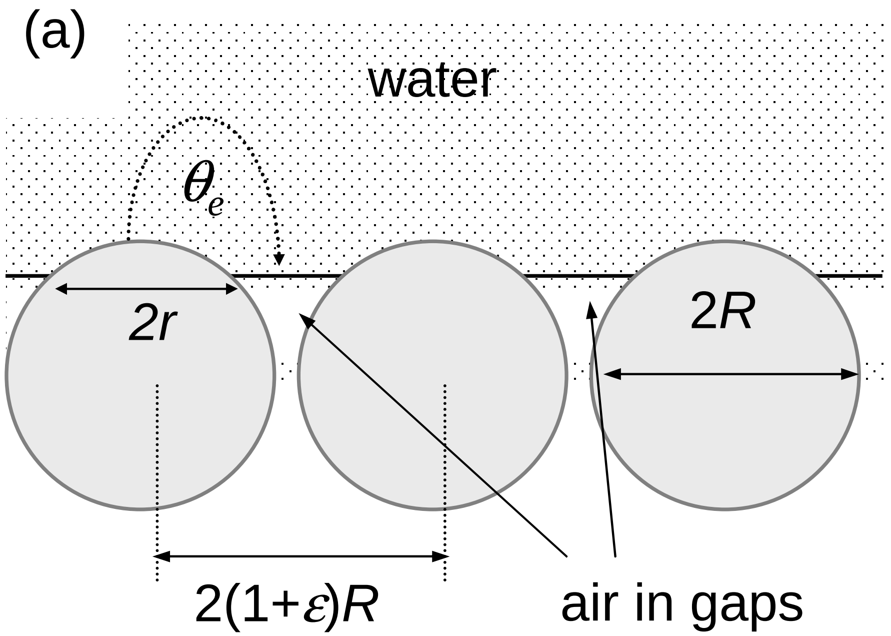


Reference McHale *et al*, to be submitted…….

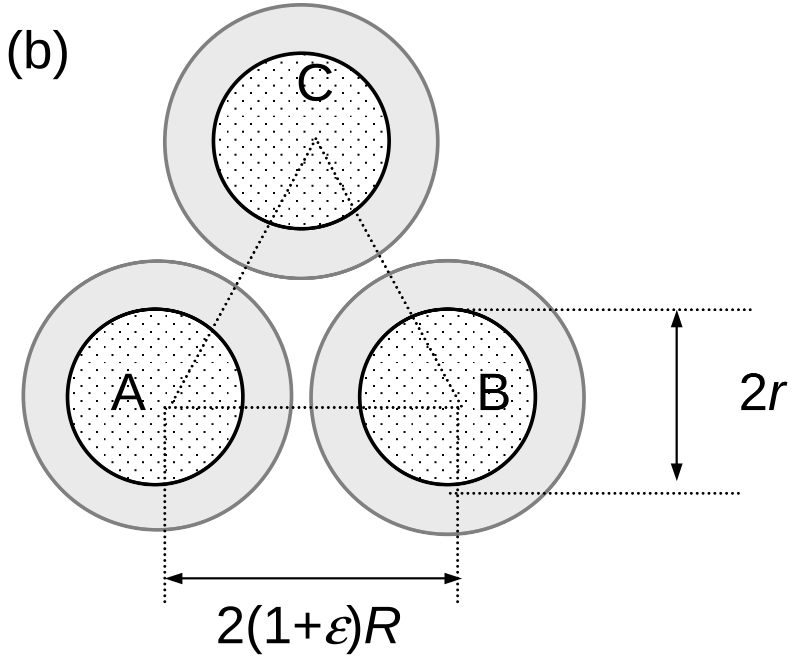
Wetting to Porosity

Simple Model of Soil

Side View



Top View



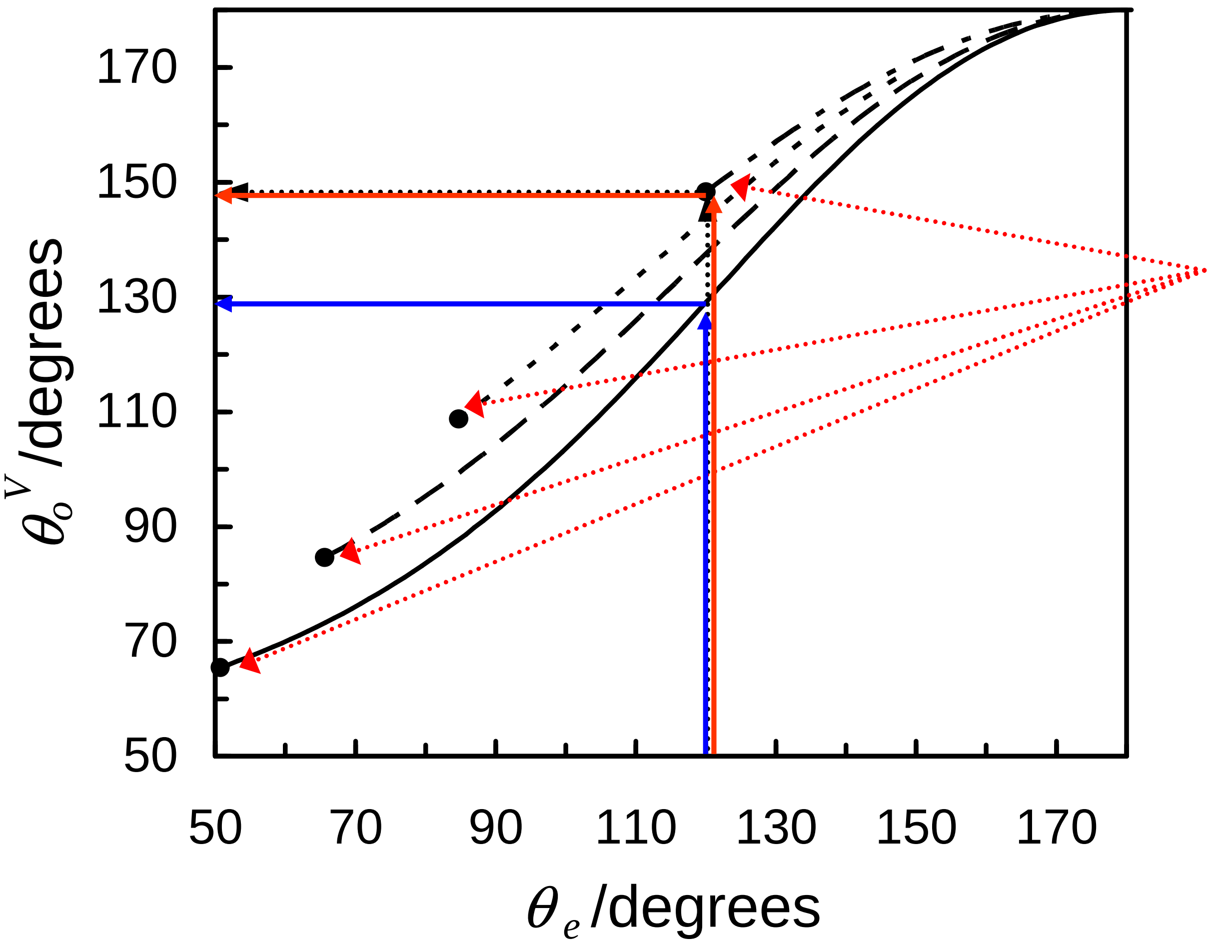
Assumptions

1. Uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges air gaps horizontally between spheres
3. Capillary (surface tension) dominated size regime of gaps<<κ^{-1}=2.7 mm

Reference McHale *et al*, Eur. J. Soil. Sci. 56 (2005) 445-452; Hydrol. Proc. 21 (2007) 2229-2238.

Dry Soil – Water Repellence Enhancement

Water repellence increases with spacing of grains



Minimum Hydrophobicity

$$\cos\theta_e^{\min} = -1 + 2\sqrt{\frac{2-2\varepsilon-\varepsilon^2}{3}}$$

i.e. Solid point at start of each curve

Separation when bead pushes up through hole is $\varepsilon_{max}=\sqrt{3}-1=0.732$

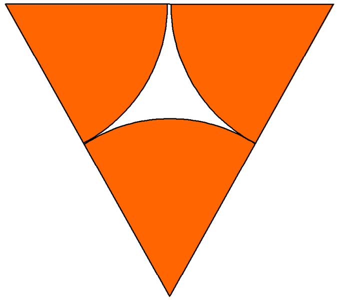
Reference McHale *et al*, Hydrol. Proc. 21 (2007) 2229-2238.

Transition from Wetting to Porosity

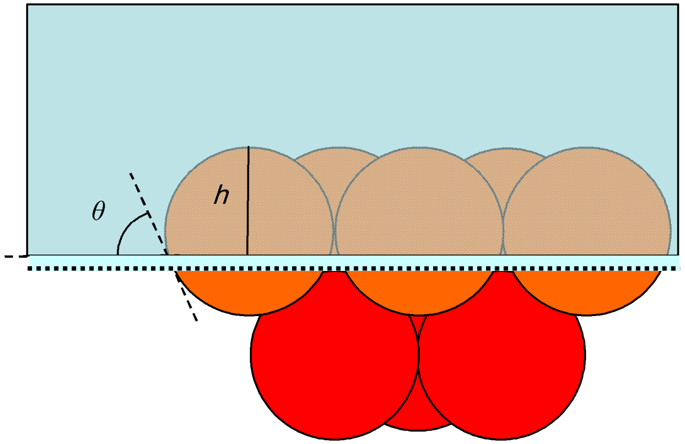
Assumptions

1. Spherical particles radius R
2. Fixed & hexagonally packed
3. Planar meniscus with Young's law contact angle, θ_e
4. Minimise surface free energy, F

Top View



Side View



Results for Close Packing

1. Change in surface free energy with penetration depth, h, into first layer of particles
2. Equilibrium exists provided liquid does not touch top particle of second layer
3. If liquid touches second layer at depth, h_c, then complete infiltration is induced
4. Critical contact angle, θ_c, when h_c reached

$$\Delta F = -\pi R\gamma_{LV}\left[\cos\theta_e + \left(1-\frac{h}{R}\right)\right]\Delta h$$

$$h_c = \sqrt{\frac{8}{3}}R = 1.63R$$

$$\boxed{\theta_c = 50.73^{\circ}}$$

*Consistent with experiments**

References Shirtcliffe *et al*, Appl. Phys. Lett. 89 (2006) art 094101; *S. Bán, E. Wolfram, S. Rohrsetzher 22, (1987) 301-309.

Infiltration into Bead Packs & Sand

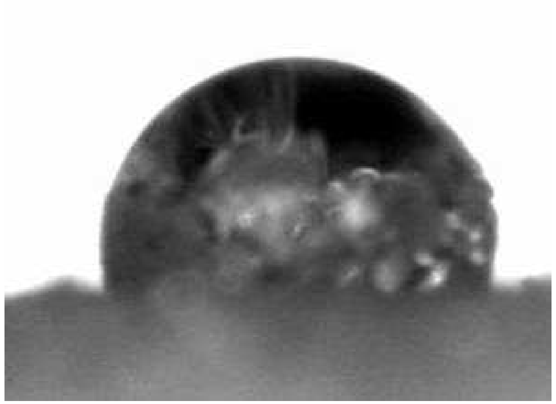
Fluorocarbon Bead Packs

1. Fluorocarbon coated glass beads (size = 75 μm) on glass slides
2. Range of hydrocarbon liquids
3. Penetration occurs for pentane, but not for hexane

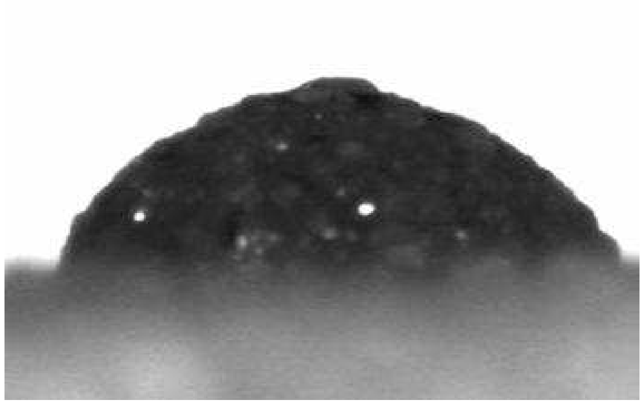
Liquid	***θ* on fluorocarbon coated glass slides / °±4**
Octane	72°
Heptane	65°
Hexane	61°
Pentane	52°

Fluorocarbon Coated Sand

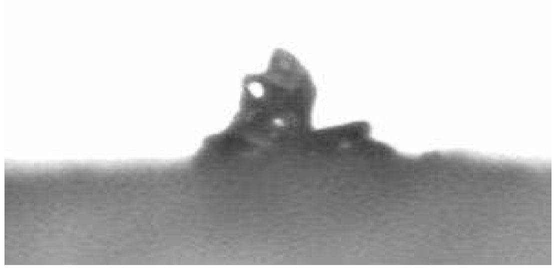
Penetration occurs for hexane



Octane (72°)



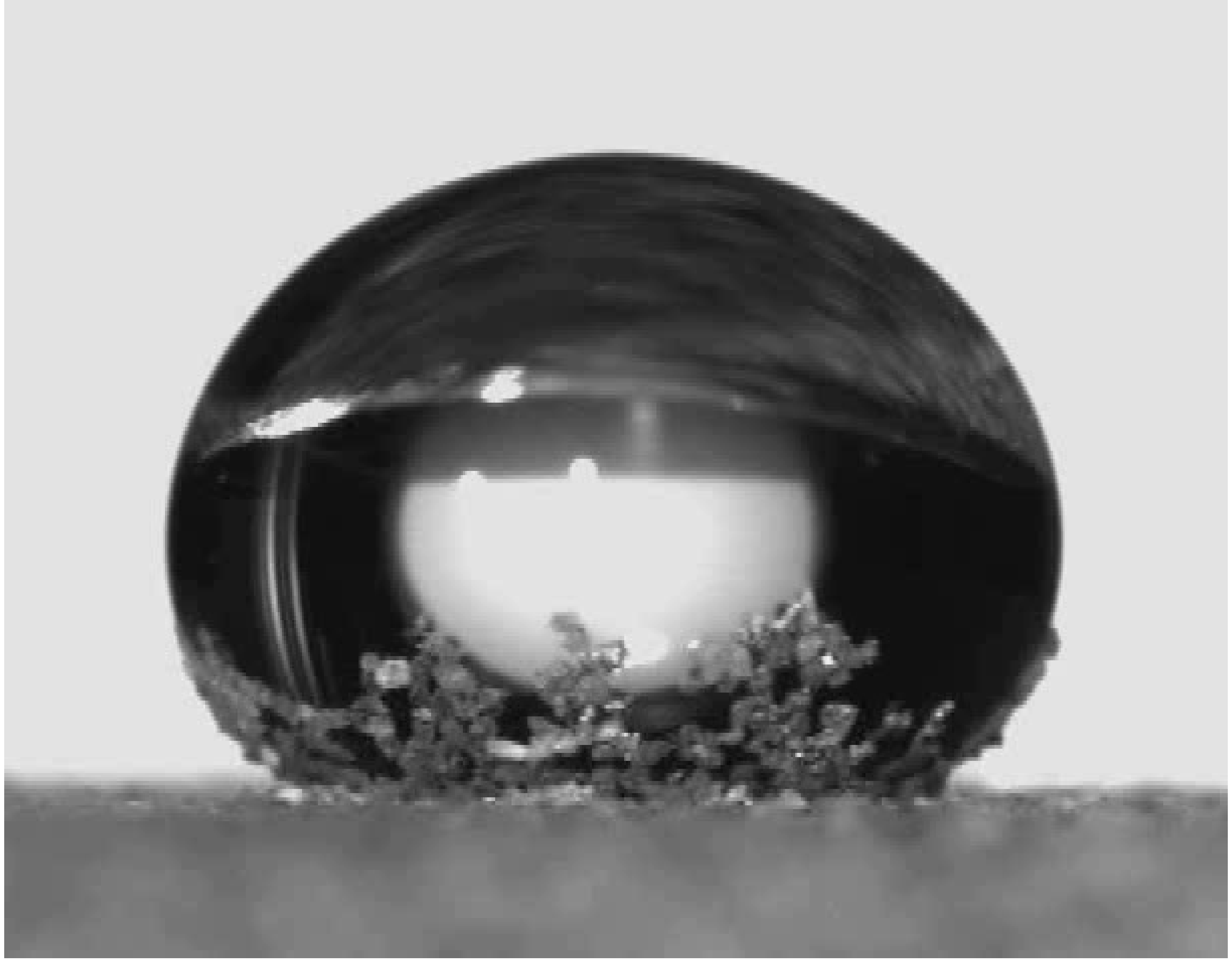
Heptane (65°)



Hexane (61°)

Reference Shirtcliffe *et al*, Appl. Phys. Lett. 89 (2006) art 094101

Water Droplet Evaporation on Hydrophobic Sand



Reference Shirtcliffe *et al.*, Appl. Phys. Lett. 90 (2007) art. 054110.

Evaporatively Driven Sorting

Surface Free Energies

When two particles of the same size, but different wettabilities, compete for a reducing air-water interface the one with its contact angle θ_e closest to 90^o should win and remain at the interface

Ejection: Surface–into-Air

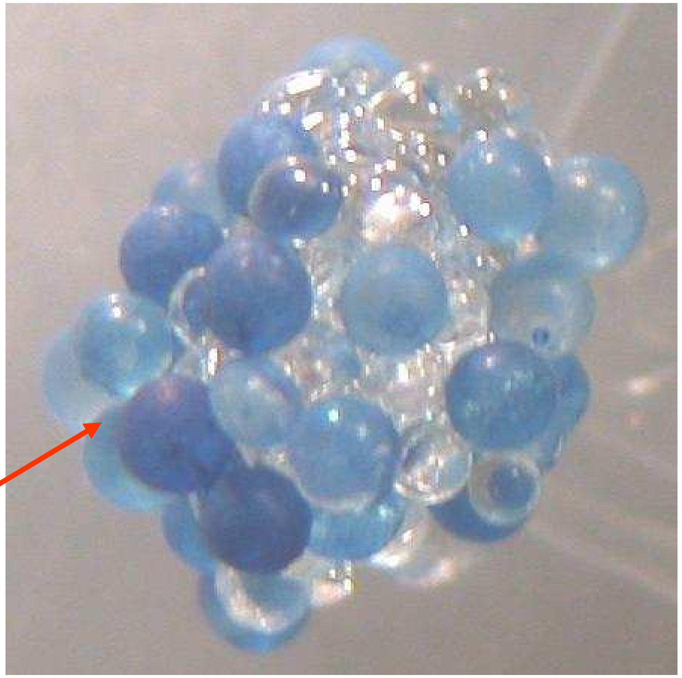
$$\Delta F = \pi R^2 \gamma_{LV} (1 + \cos\theta_e)^2$$

Ejection: Surface–into-Liquid

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

Experimental Test

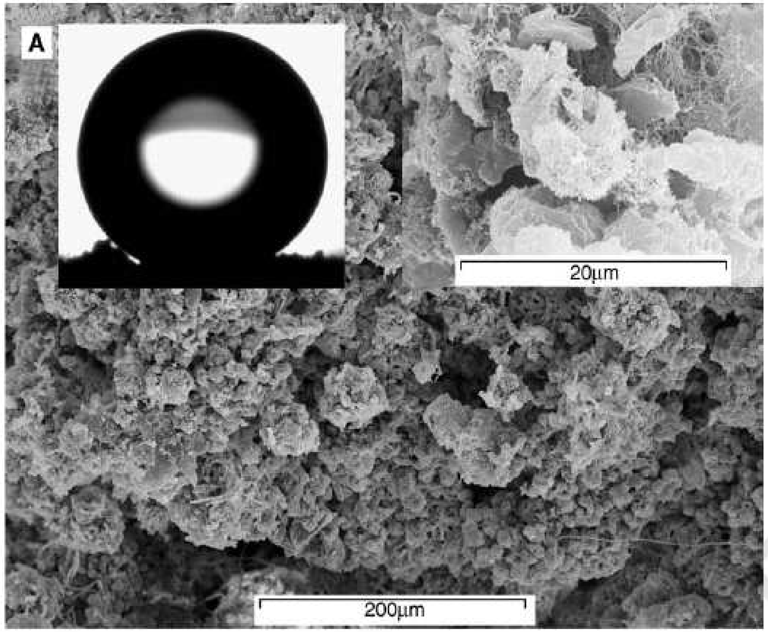
1. Bed of blue hydrophobic (115^o) spheres of diameter 500 μm and transparent hydrophilic (17^o) spheres of diameter 700 μm
2. Allow droplet to evaporate and clump to form



After evaporation blue particles are on outside of clump

Back to Nature

Pollution Tolerant Lichens



1. Live on hard surfaces without penetrating them
2. Susceptible to airborne pollution
3. Open structure and tendency to dry and rehydrate in response to drought
4. Exposed to large quantities of unbuffered water $\Rightarrow$ *intrinsically sensitive to pollution*
5. Lichens growing on basic surfaces are more resistant $\Rightarrow$ *water buffered by the surface*

Mechanism for Pollution Tolerance?

1. Breathable Gore-Tex® type membrane
2. Promoting water runoff from top surface
   - allows gas exchange even during rainfall
   - reduces direct exposure to rainwater
3. Absorbing water via lower surface gives buffered and filtered water

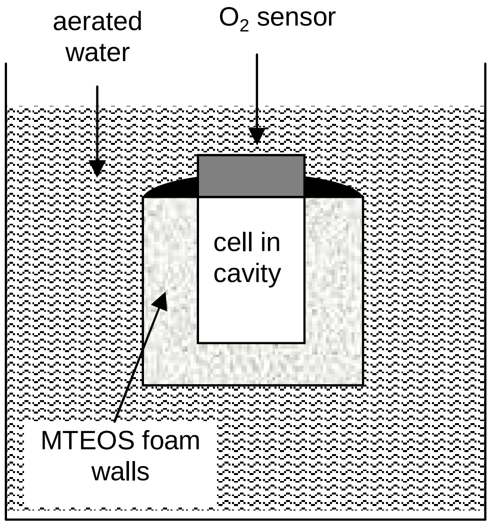
Resistance to acid rain?

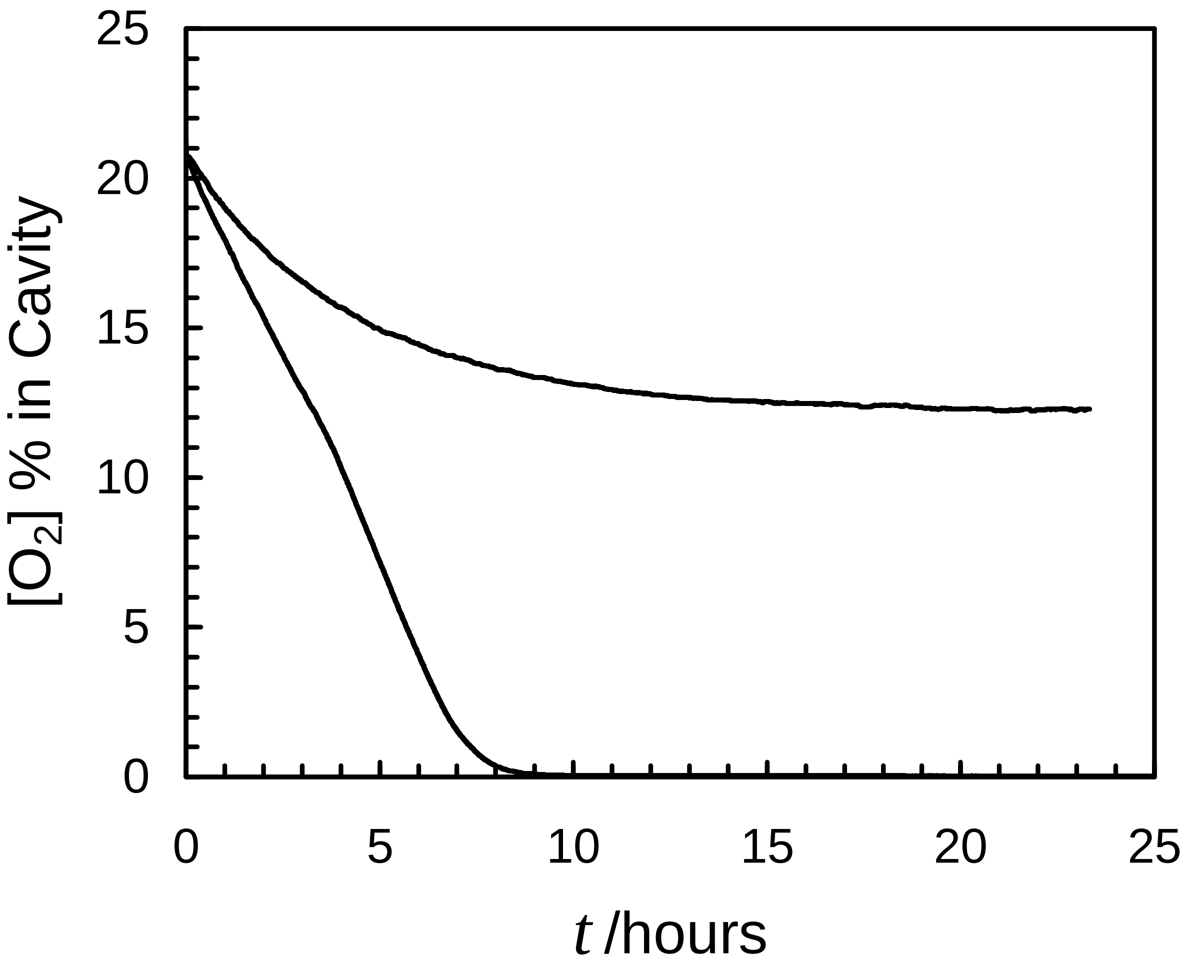
Reference Shirtcliffe *et al.*, J. Plant. Phys. 163 (2006) 1193-1197.

Plastron Respiration

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

Superhydrophobic Plastron: Respiration





Reference Shirtcliffe *et al.*, Appl. Phys. Lett. 89 (2006) art 104106.


SNIGGER
BEETLES MAY HOLD THE SECRET OF BREATHING UNDERWATER
FRAN
OH COME ON, I BET PEOPLE THOUGHT SCUBA GEAR LOOKED SILLY WHEN IT WAS FIRST INVENTED

The End

COST

Acknowledgements

Funding Bodies

- EU COST D19 and P21 Programmes
- EPSRC EP/E063489/1, EP/E043097/1, EP/D500826/1, EP/C509161/1, GR/R02184/0, GR/S34168/01

    Exploiting the solid-liquid interface
    Enhancing water sports performance
    Superhydrophobic & superhydrophilic surfaces (also Dstl/MOD JGS)
    Electrowetting & superhydrophobic surfaces (also Dstl/MOD JGS)
    Extreme soil water repellence
    Drag reduction & slip at the solid-liquid interface

- NERC NER/J/S/2002/00662, NERC NEC003985/1 (SD)

    Advanced Fellowship for Dr Stefan Doerr
    Fundamental controls on soil hydrophobic behaviour

People

- PhDs, PDRAs (Dr Evans, Roach and Shirtcliffe), Other staff at NTU (Dr Newton, Prof. Perry & Pyatt), and external collaborators

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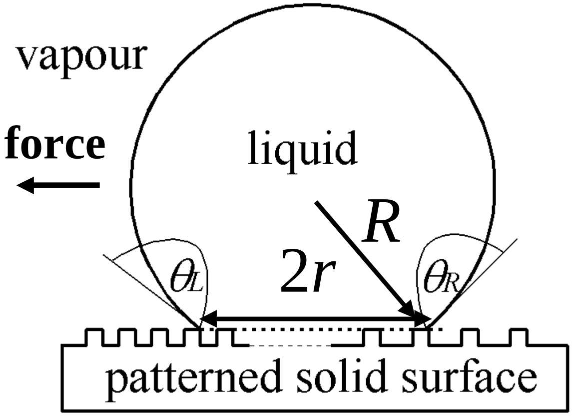
Conditions for Motion

Spherical Cap



Assume small contact area:

$$2r \approx 2R\,[2f_{\mathrm{ave}}(x)(1+\cos\theta_e^{s})]^{1/2}$$

$$\mathit{Force/length} = \gamma_{LV}(f_R - f_L)(\cos\theta_e^{s} + 1)$$

$$= 2R\,\gamma_{LV}[2f_{\mathrm{ave}}(x)]^{1/2}(1+\cos\theta_e^{s})]^{3/2}(\mathrm{d}f/\mathrm{d}x)$$

Defect Based Hysteresis Force

$$\mathit{Force/length} = \gamma_{LV}\Delta(\cos\theta) \approx \gamma_{LV} f(x)\log f(x)$$

Drive Condition

$$(\mathrm{d}f/\mathrm{d}x) > \mathrm{constant} \times f_{\mathrm{ave}}(x)^{1/2}\log f_{\mathrm{ave}}(x)/[R(1+\cos\theta_e^{s})^{3/2}]$$

More superhydrophobic

Larger droplets

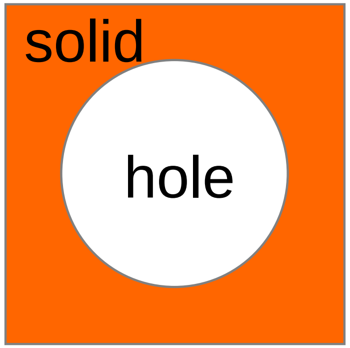
Reference Joanny & de Gennes (1984) (cited by Quéré); McHale *et al*, to be submitted.

Cylindrical Model for Capillary Infiltration

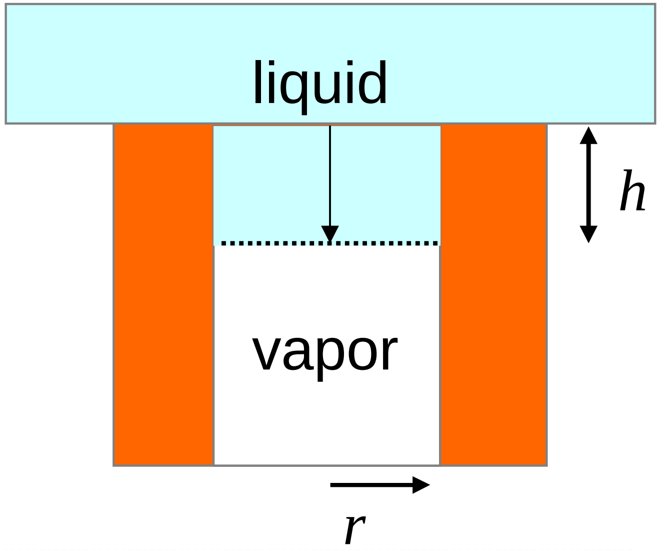
Assumptions

1. Fixed cylindrical pipe
2. Meniscus with Young's law
   contact angle, $\cos\theta_e = =(\gamma_{SV}-\gamma_{SL})/\gamma_{LV}$
3. Minimise surface free energy, F

Top View



Side View



Change in surface free energy = solid-liquid energy per unit area × gain of wall area minus solid-vapor energy per unit area × loss of wall area

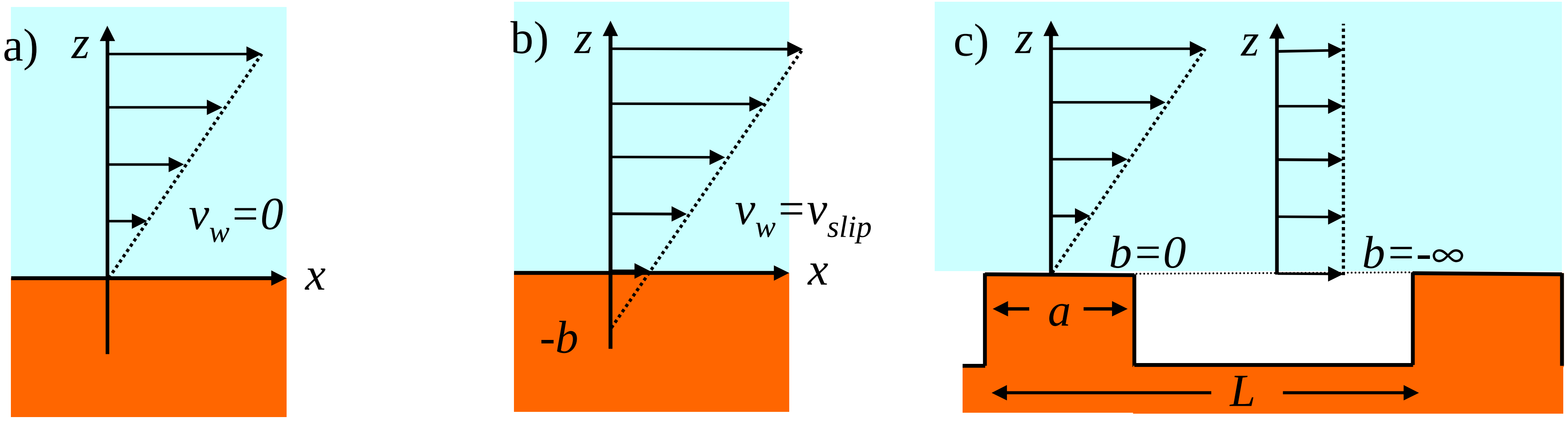
$$\Delta F=(\gamma_{SL}-\gamma_{SV})2\pi r\Delta h \overset{\text{Young's Law}}{\Rightarrow} \Delta F=-\gamma_{LV}\cos\theta_e 2\pi r\Delta h$$

Spontaneous infiltration when ΔF is negative $\Rightarrow$ $\boxed{\theta_e<90^o}$

<u>But soil is not a set of parallel pipes</u>

Slip by Simple Newtonian Liquids

No Slip | Slip | Mixed

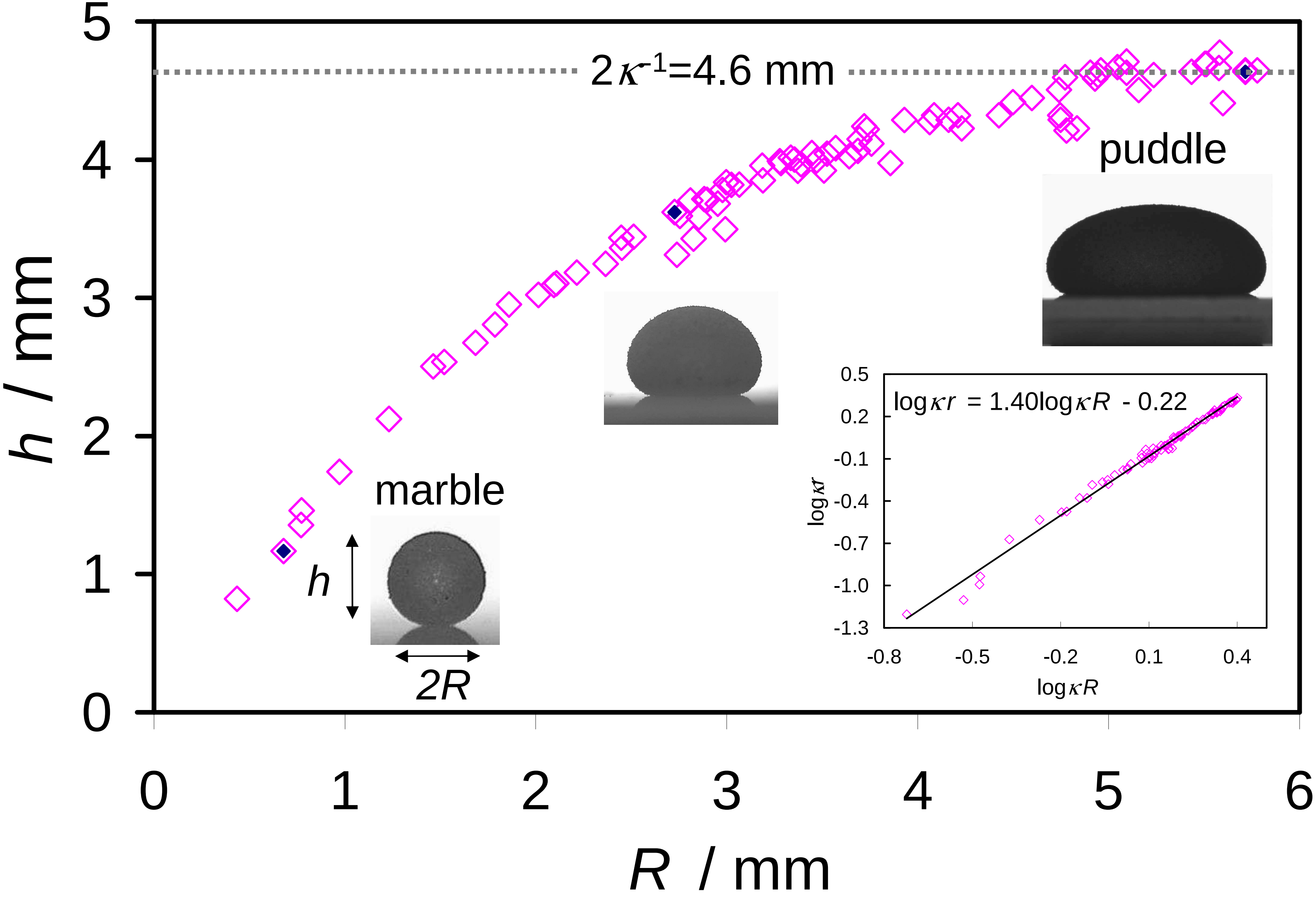


Experimental Evidence – Steady Flow

1. Theory[1,2] supported by simulations suggests $b=L\,f(\varphi_s)/2\pi$
2. Micro-PIV experiments detailing flow profiles[3] ($h=1\text{-}7\ \mu\text{m} \Rightarrow b=0.28L$)
3. Cone-and-plate rheometer experiments[4] – drag reduction > 10%
4. Hydrofoil in a water tunnel experiments[5] – drag reduction of 10%

References [1]Philip, *Z. Angew. Math. Phys.* **23**, 1972; [2]Lauga & Stone, *J. Fluid Mech.* **489**, 2004; [3]Joseph *et al*., *Phys. Rev. Lett.* **97,** 2006;[4]Choi & Kim, *Phys. Rev. Lett.* **96**, 2006; [5]Gogte, *et al. Phys. Fluids* **17**, 2005.

Size Data (Lycopodium)



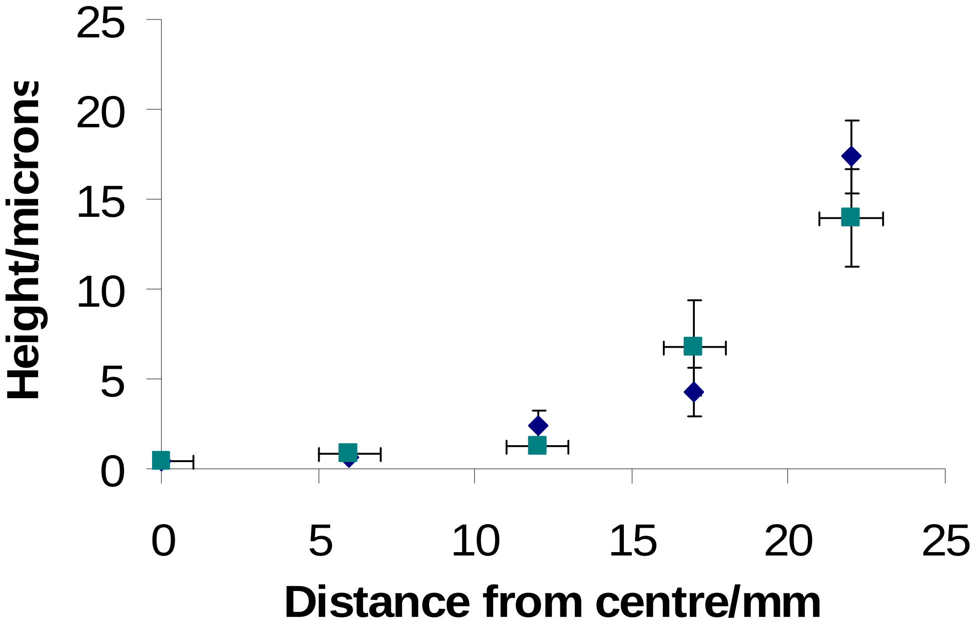
Surface Profile

Mechanism for Motion

Small slope on extremely low hysteresis surface?

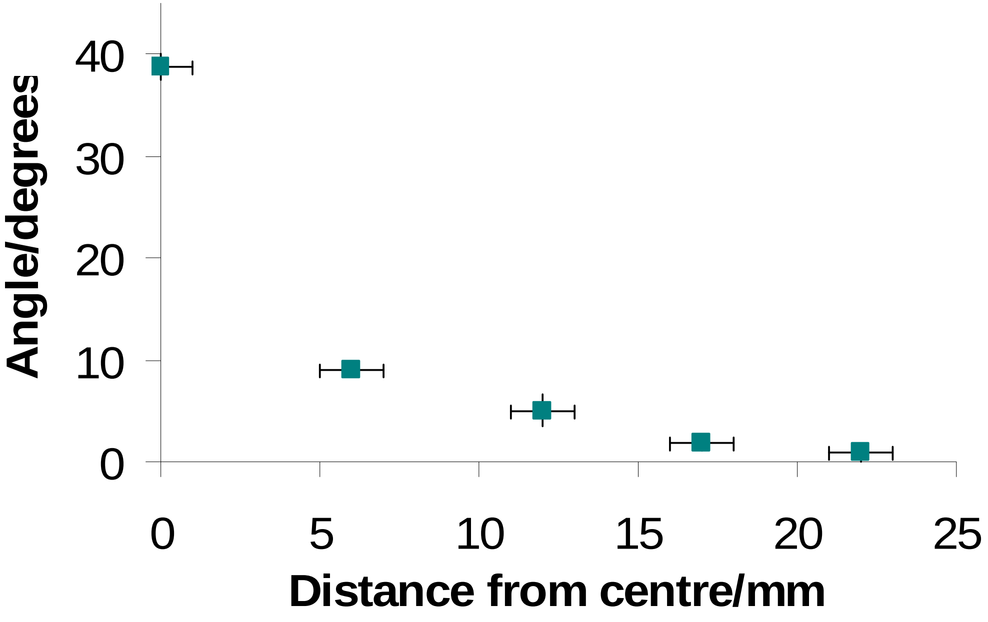
Truly contact angle driven?

Surface Profile



Multiple profiles have been taken
along different radial lines

“Hysteresis”

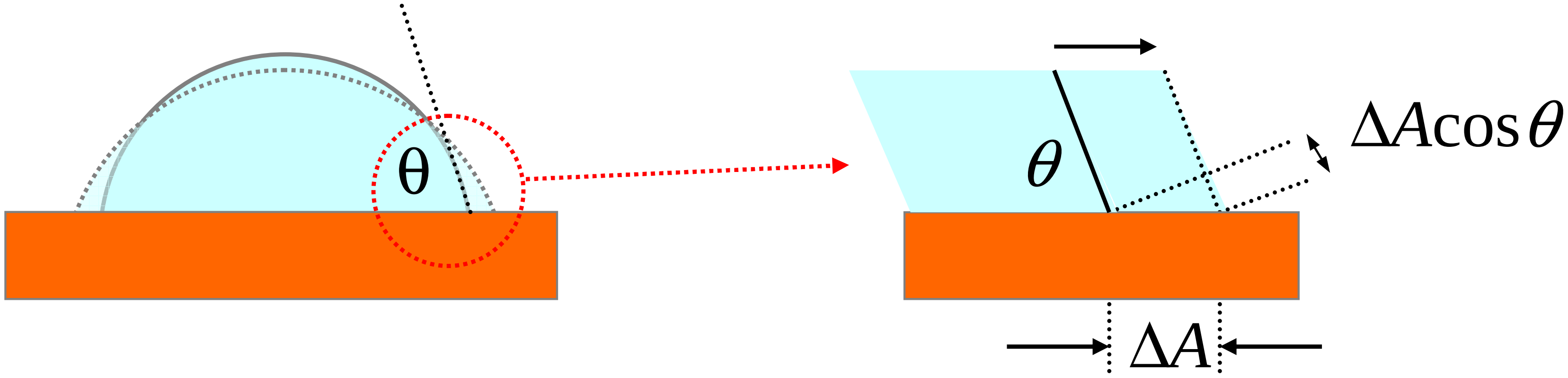


Using radial view and tilt table
tangential to radius

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

$\boxed{\text{solid-liquid energy per unit area} \times \text{gain of substrate area}}$ - $\boxed{\text{solid-vapor energy per unit area} \times \text{loss of substrate area}}$ + $\boxed{\text{liquid-vapor energy per unit area} \times \text{gain of liquid-vapor area}}$

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

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

Conclusions

1. Superhydrophobic Surfaces

    Create by widely different methods – in-lab and natural

    Can be switched to superspreading surfaces

    Surface patterns/gradients can cause self-actuated motion

2. Wetting versus Porosity

    Capillary infiltration occurs for θ_e substantially less than 90º (e.g. 51º-65º)

3. Fixed versus Loose Solid Structures

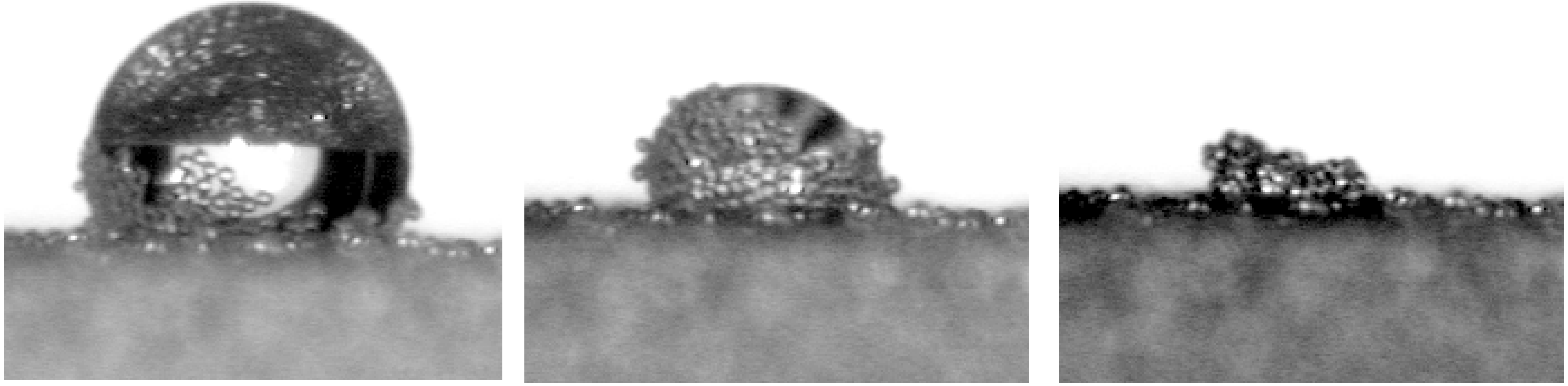
    Grains can re-arrange – droplets become liquid marbles

    Evaporation drives self-coating and grain sorting

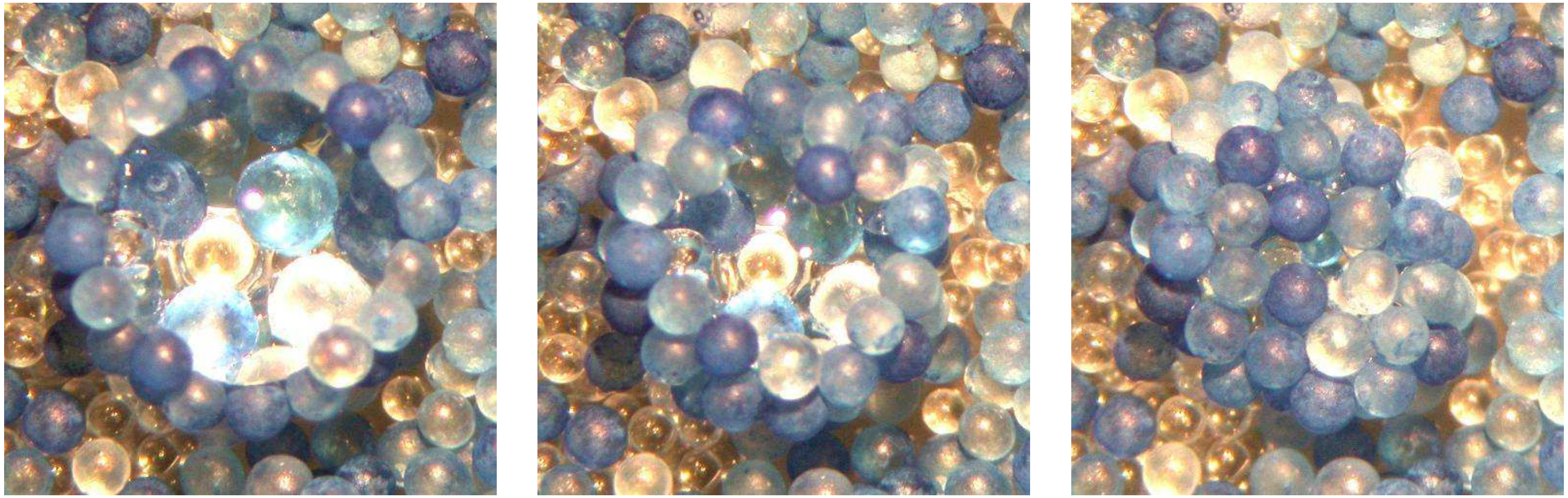
The End

Hydrophobic Granular Self Sorting

Water droplet digging during drying

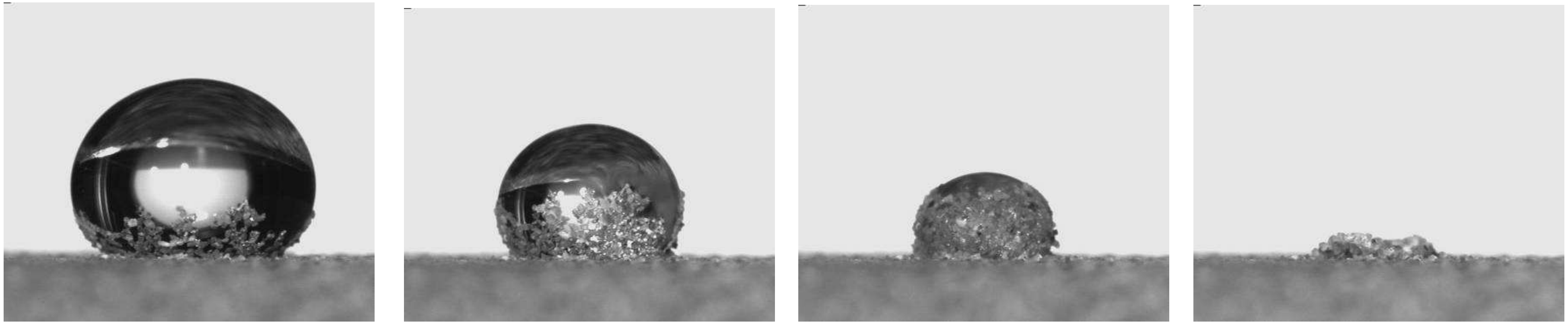


Mixed hydrophobic (blue)/hydrophilic (clear)

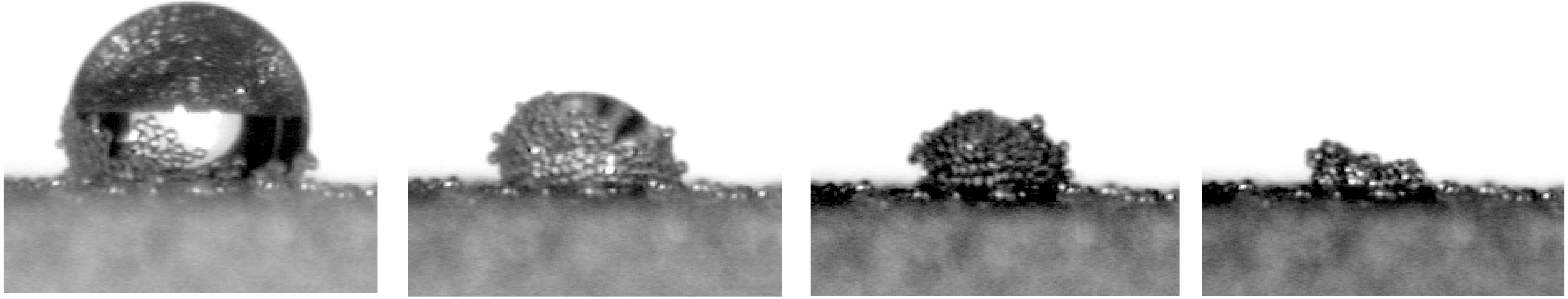


Evaporatively Driven Coating

Water on Hydrophobic Sand



Water on Hydrophobic 75 µm Silica Beads



Reference Shirtcliffe *et al.*, submitted to APL (2006).