NOTTINGHAM TRENT UNIVERSITY

Super Water-Repellent Surfaces

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Overview

1. Water repellence in nature
2. Basic concepts
3. Creating surfaces
4. Surface and material properties
5. Liquids in motion
6. Back to nature

Water Repellence in Nature

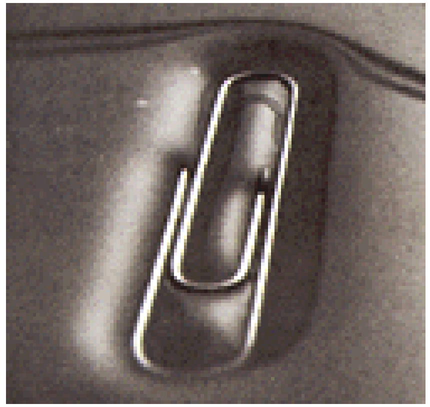
Sinking and Falling?

Water-on-Solids

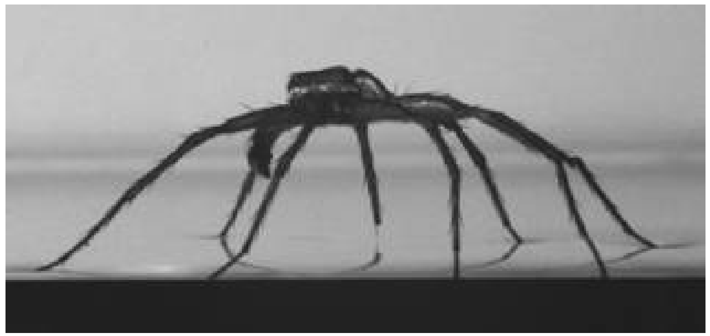
- Liquids sometimes form drops, and sometimes spread over a surface and wet it. Why does this happen?
- Why are raindrops never a metre wide?
- Why don’t they run down the window?
- Why do butterfly wings survive rain?

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?



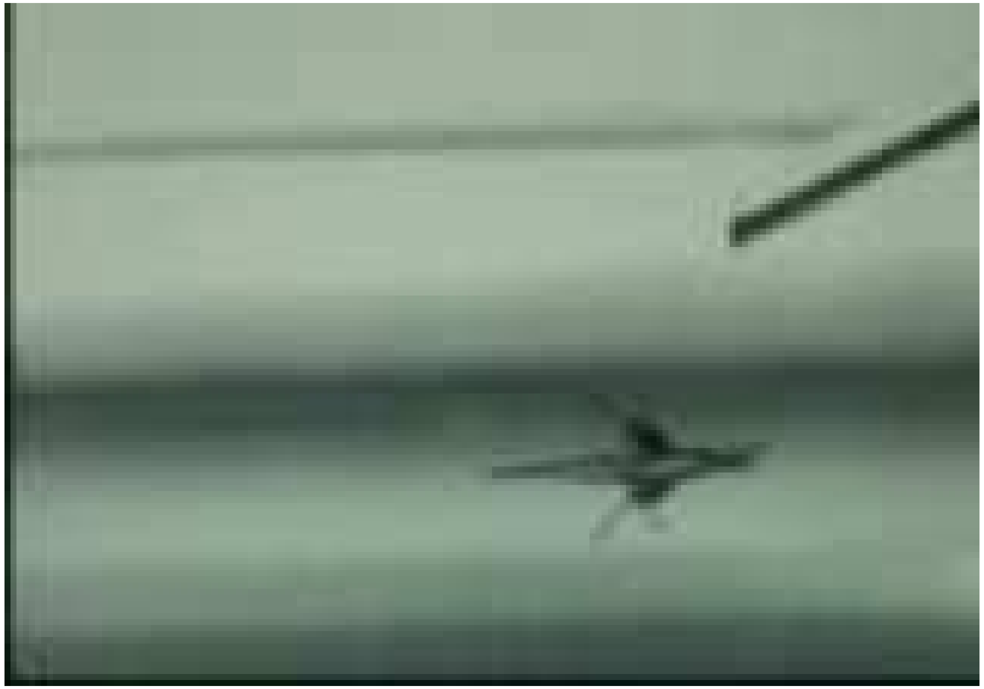
Solids-in & under-Water?



Plants and Leaves

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

Movies: Pond Skaters



Movie of Infant

Movie of Adult

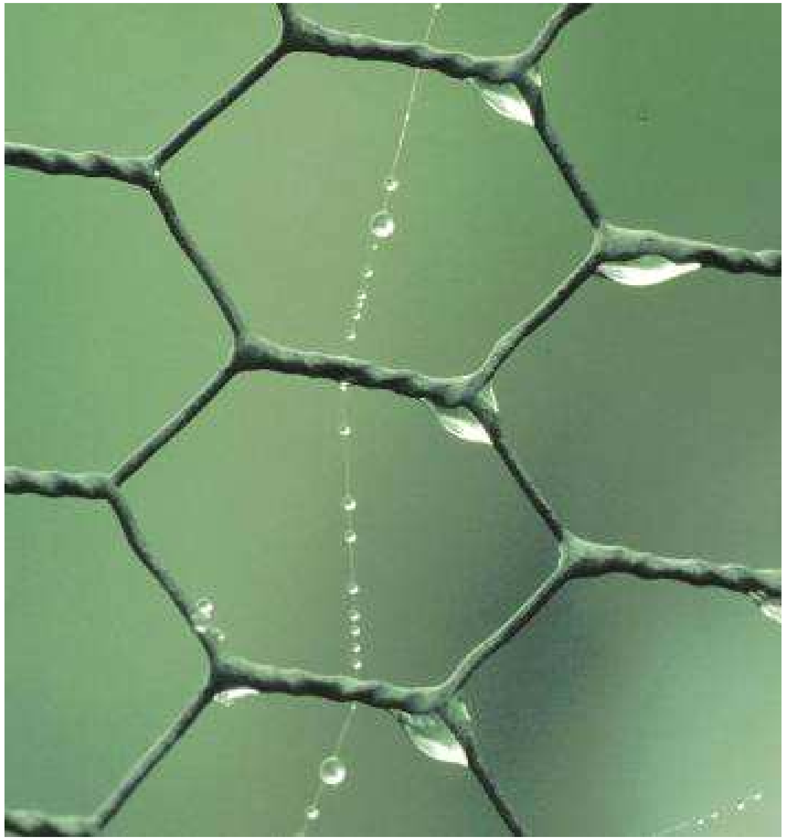
Surface Tension

Molecules at the Surface

- Have fewer neighbours
- Have higher energy than ones inside the liquid

Liquid Surface

- Behaves as if it is in a state of tension
- Tend to minimize its area in any situation
- For a free blob, the smallest area is obtained with a sphere



Surface Tension v Gravity

- Surface tension forces scale with length
- Gravity forces scale with $length^3$
- Small sizes $\Rightarrow$ Surface tension wins

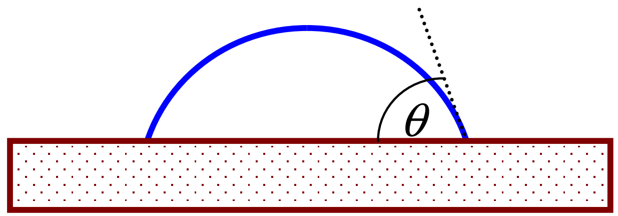
Acknowledgement www.brantacan.co.uk

Water Repellency (Hydrophobicity)

Surface Chemistry

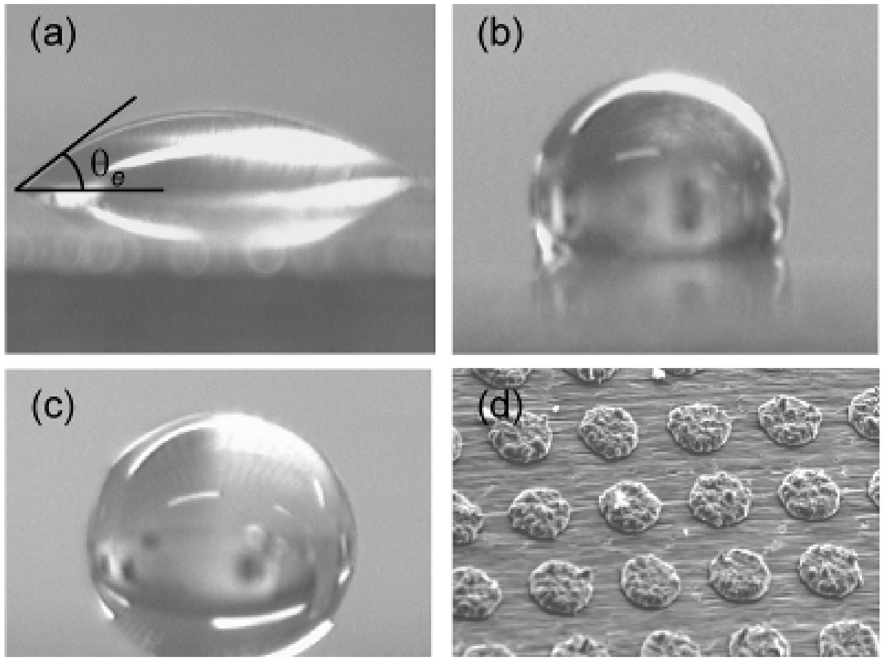
- Terminal group determines whether surface is water hating
- Hydrophobic terminal groups are Fluorine (F) and Methyl (CH_3)

Contact Angles



- Characterises hydrophobicity
- Water-on-Teflon gives ~ 115^{o}
- The best that *chemistry* can do

Physical Enhancement



(a) is water-on-copper

(b) is water-on-fluorine coated Cu

(c) is a super-hydrophobic surface

(d) “chocolate-chip-cookie” surface

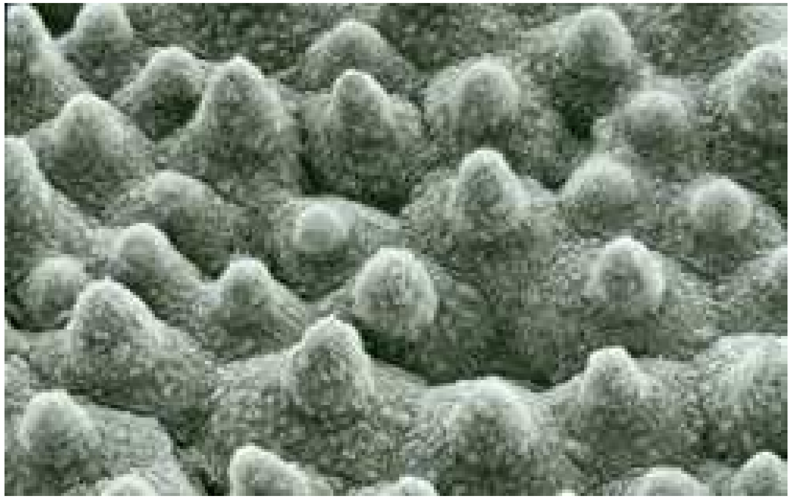
> Superhydrophobicity is when the contact angle is larger than 150^{o}

The Sacred Lotus Leaf

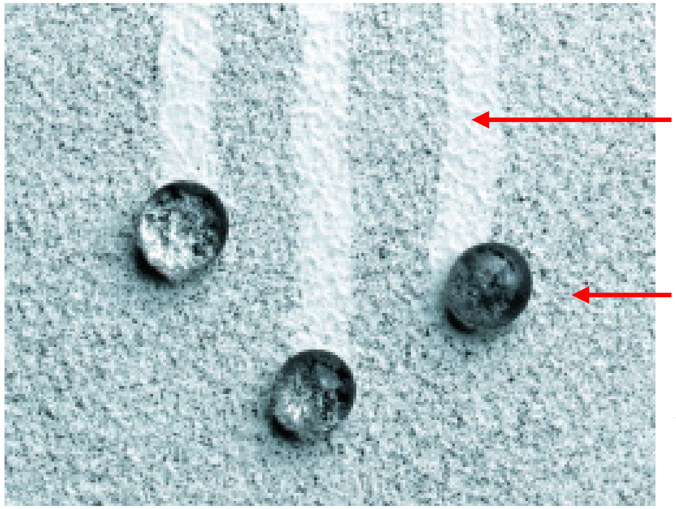
Plants

- 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

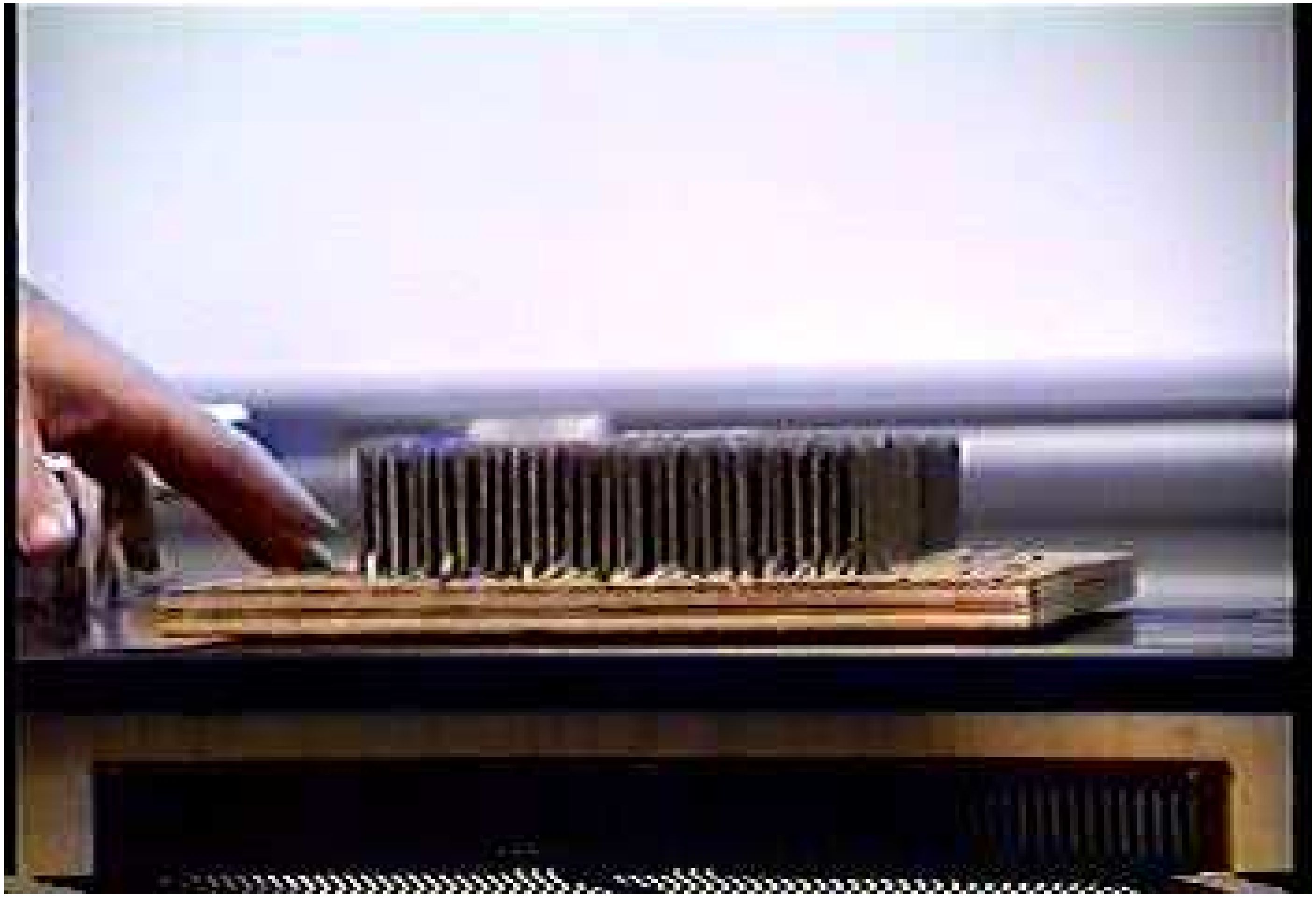
A “proto-marble”

Self-poisoning surface

Acknowledgement Neinhuis and Barthlott

Basic Concepts

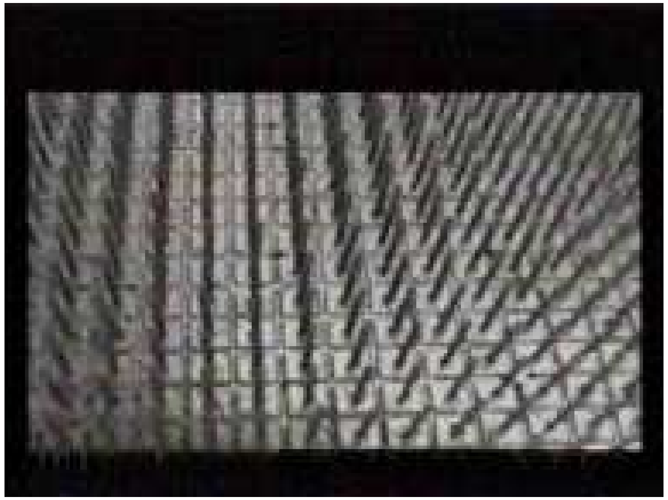
A “Bed of Nails” Effect



Balloon on a Bed of Nails

Acknowledgement Wake Forest University

A “Bed of Nails” Effect



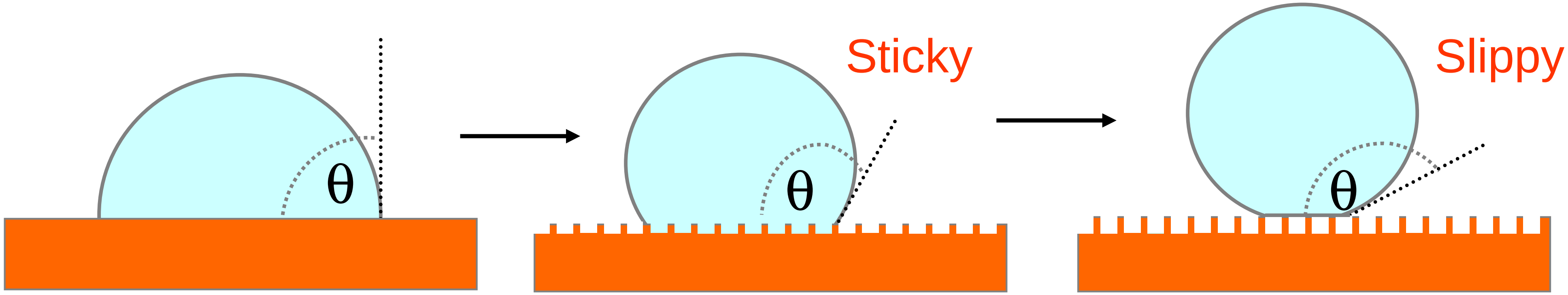
Movie of A Professor on a Bed of Nails

Acknowledgement Mahanakorn University Physics

Topography & Wetting

Droplets that Impale and those that Skate

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



Young’s Law	Wenzel	Cassie-Baxter
$\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$	$\cos\theta_W = r\cos\theta_e$	$\cos\theta_{CB} = f_s\cos\theta_e - (1 - f_s)$

Chemistry

Roughness

Chemistry

Young’s Law θ_e

Topography

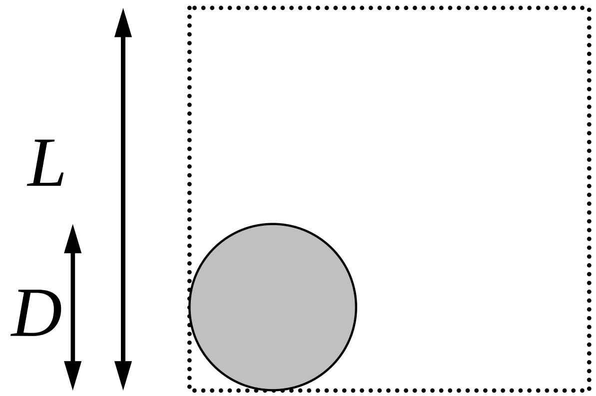
r = true area/planar projection

f_s = solid surface fraction

Texture Example

Circular Pillars

- Diameter *D*, box side *L*, height *h*



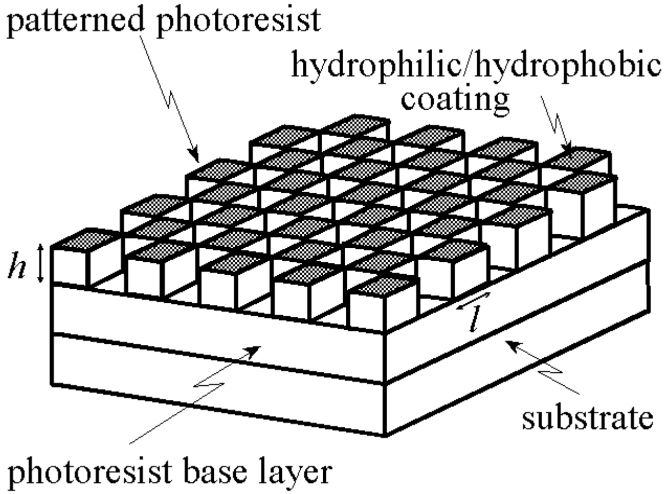
$$f_s = \frac{\pi D^2}{4L^2} \qquad r = 1 + \frac{\pi}{4}\left(\frac{h}{D}\right)$$

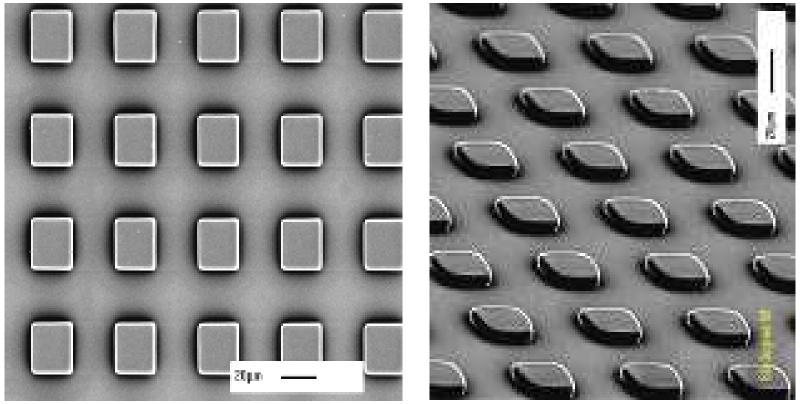
Numerical Example

L=2D	and	f_s=0.196	with θ_e^s=115°	gives	θ_e^c=152°
D=15 µm	need	*h*=21 µm	to achieve		θ_e^w=152°
D=5 µm	need	*h*=7 µm	to achieve		θ_e^w=152°

Lithographic Structures

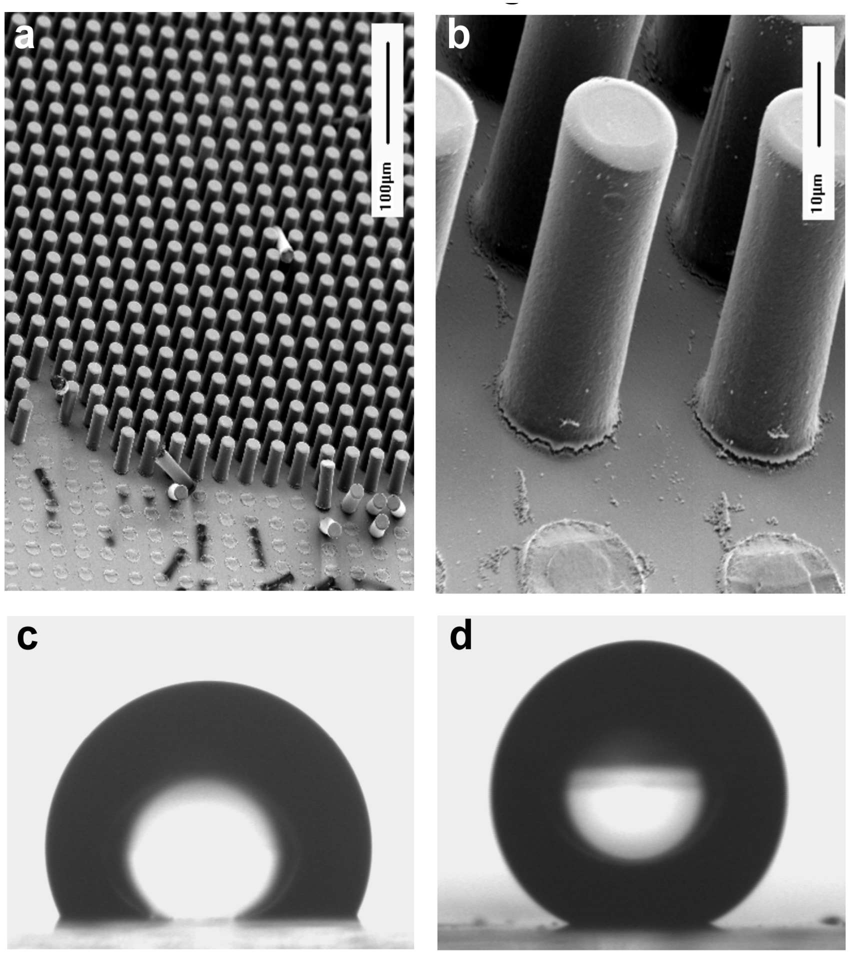
Principles





Microfabricated surfaces

Practice: Polymer microposts



Flat & hydrophobic

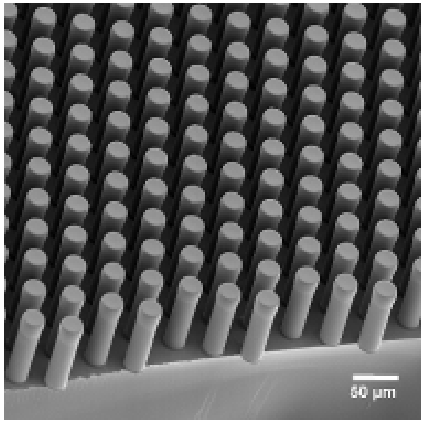
Patterned & hydrophobic

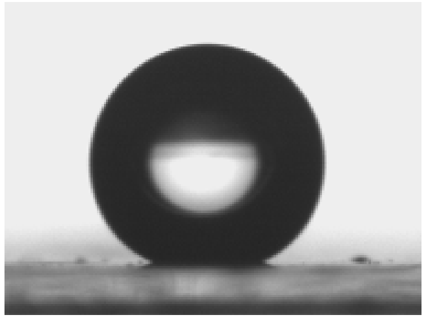
Skating-to-Penetrating Transition

Micro-Structured Surface

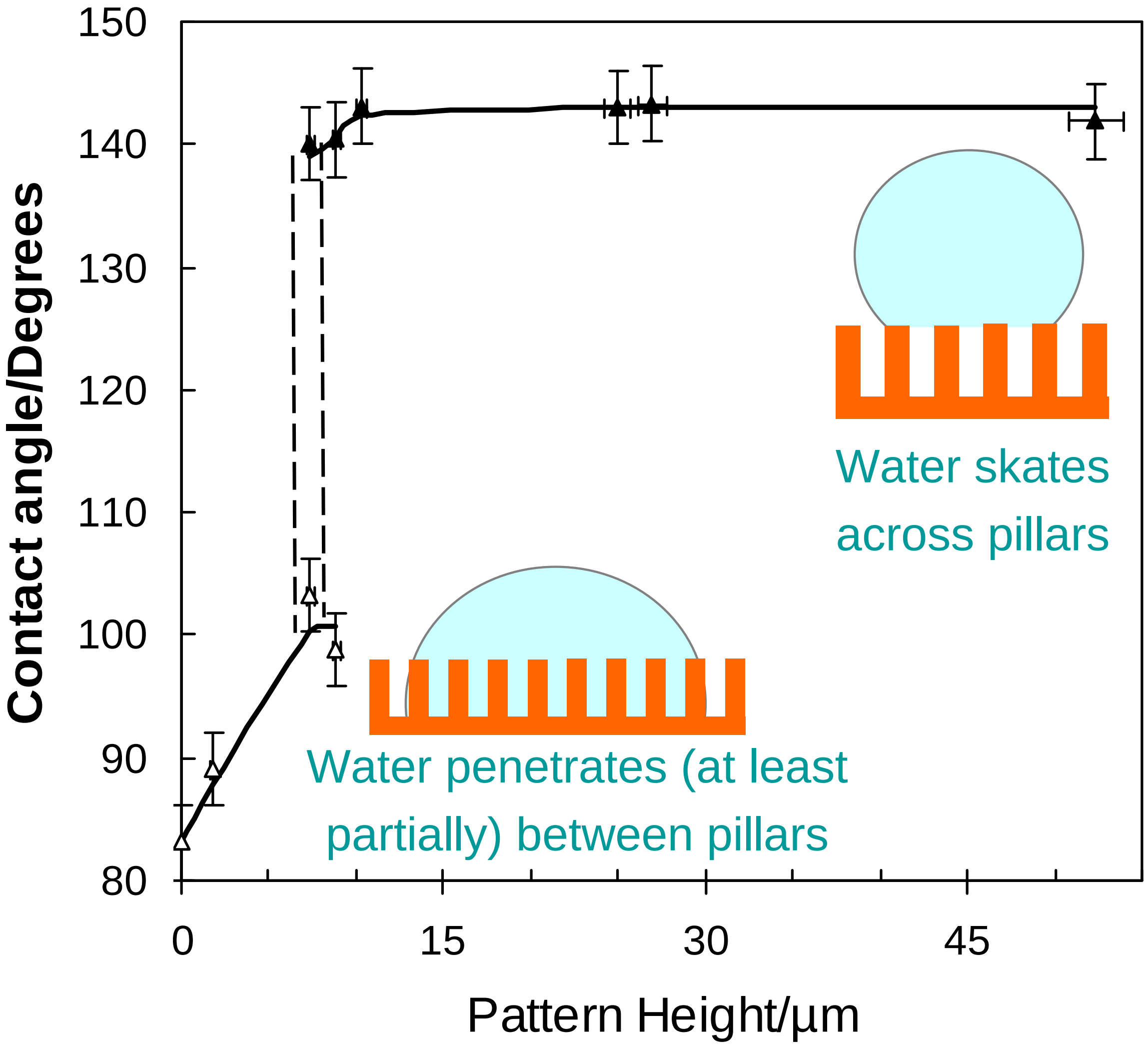
SU-8 pillars 15 µm

Hydrophobic treatment

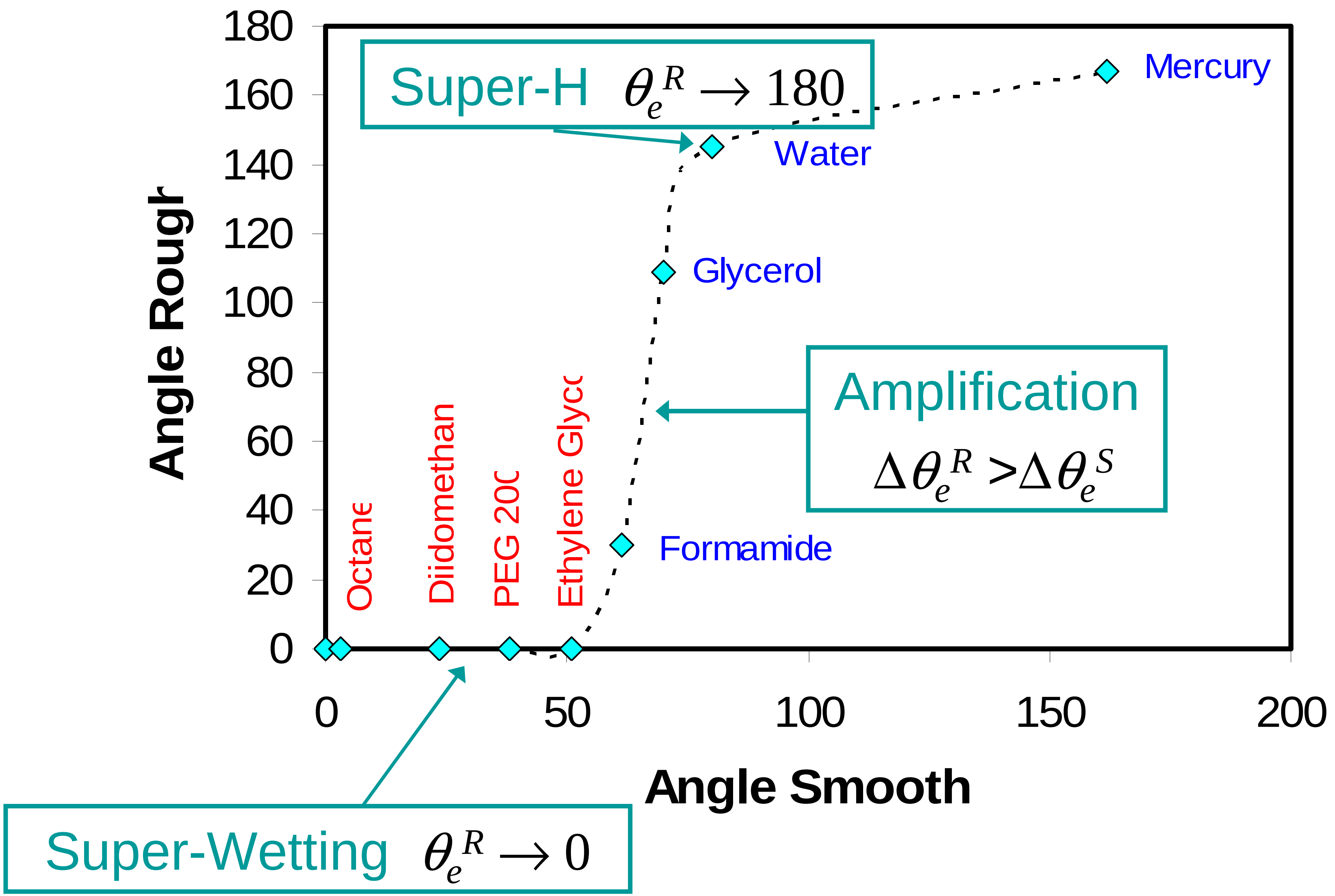




Change of Pillar Height



Different Liquids on a SuperH Surface

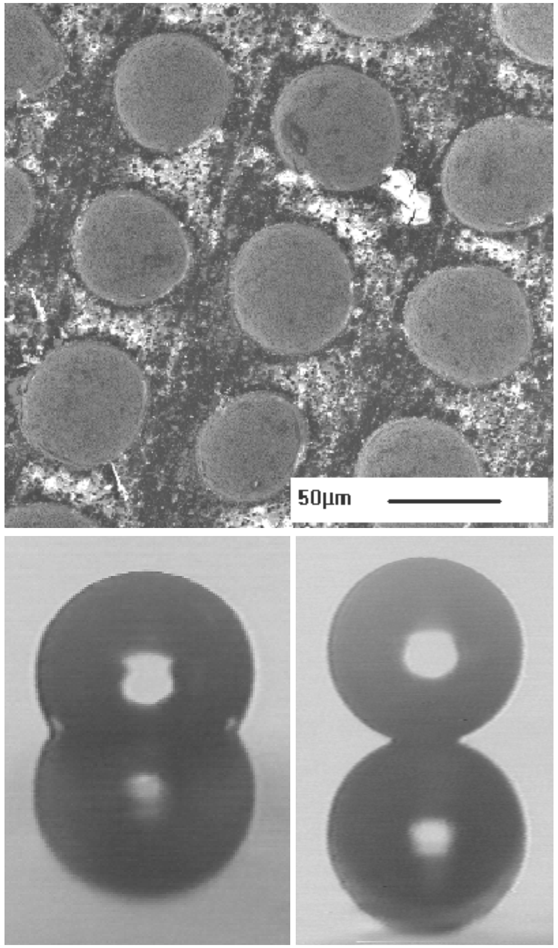


Reference McHale *et al*, Analyst 129 (2004) 284-287; McHale *et al*, Langmuir 20 (2004) 10146-10149

Creating Surfaces

Three Examples

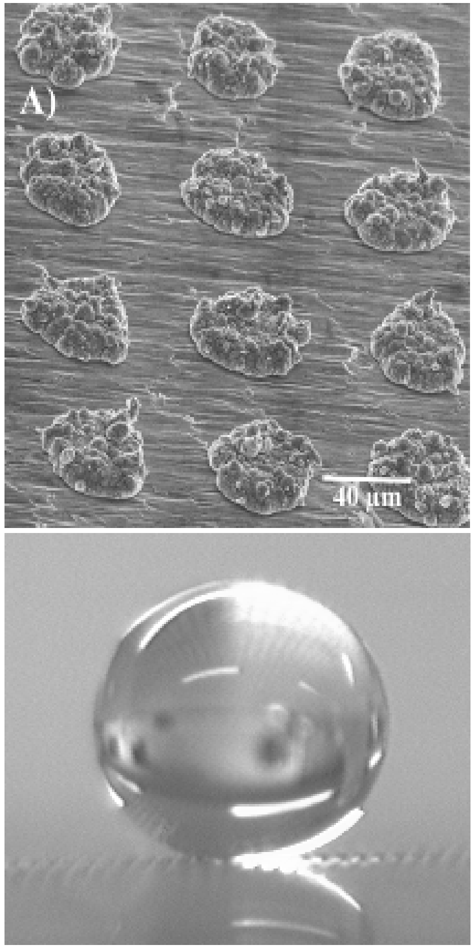
Etched Metal



Flat & hydrophobic

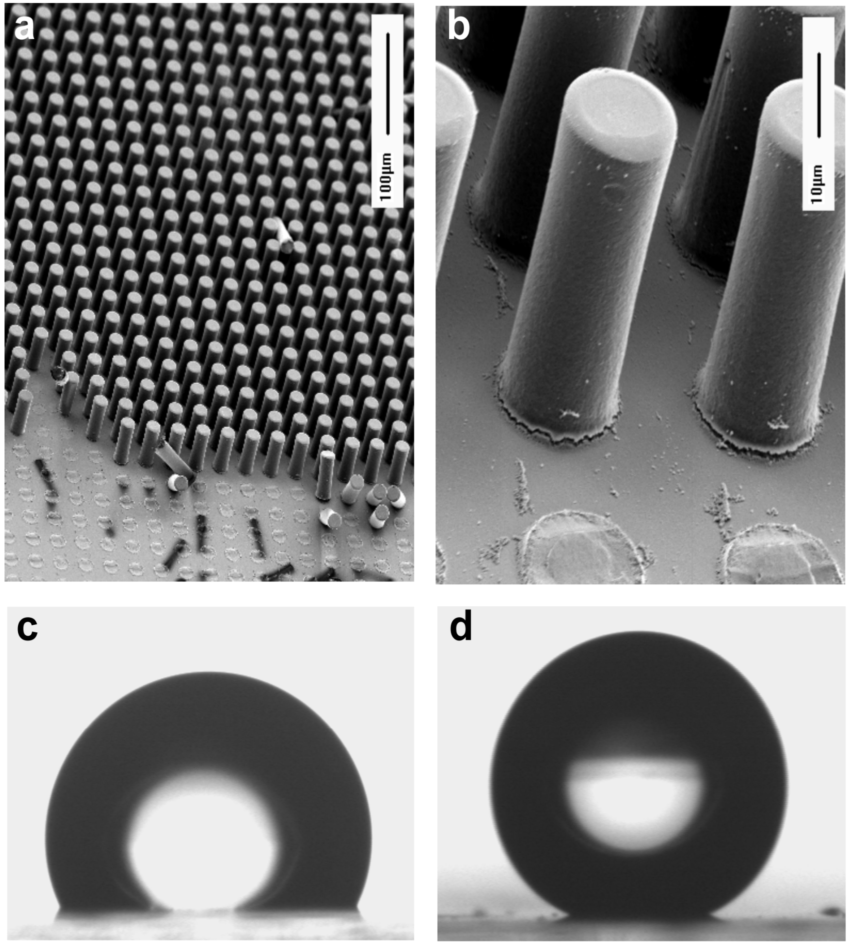
Patterned & hydrophobic

Deposited Metal



Patterned & hydrophobic

Polymer Microposts



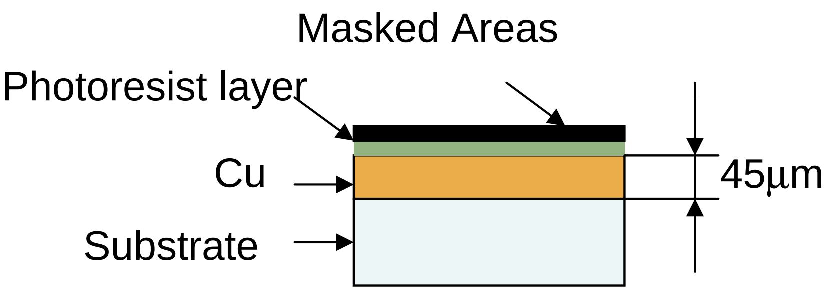
Flat & hydrophobic

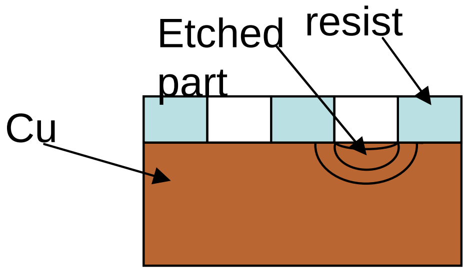
Patterned & hydrophobic

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

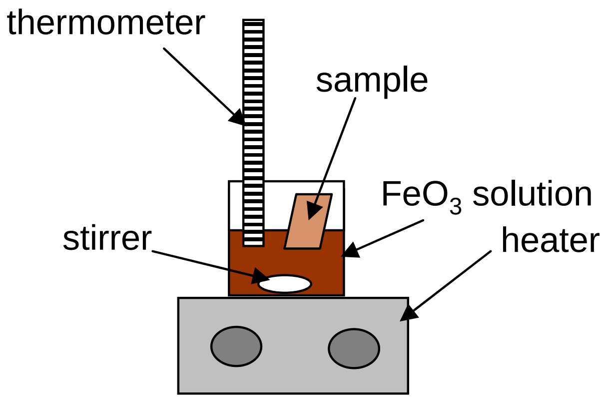
Etching of Copper Surfaces

Etching using PCB Techniques – Simple and Effective

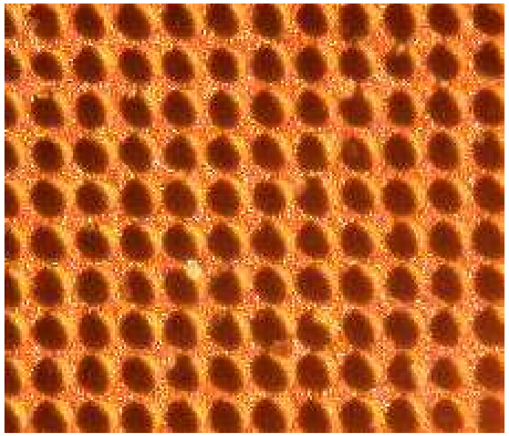




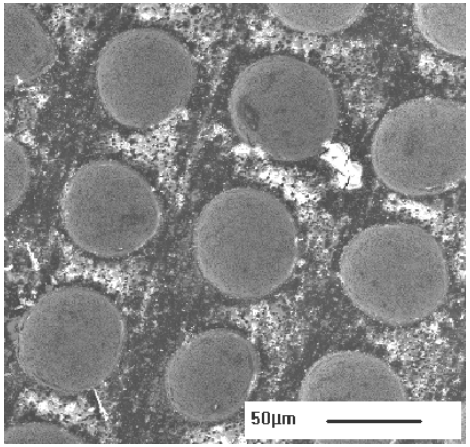
hole growth



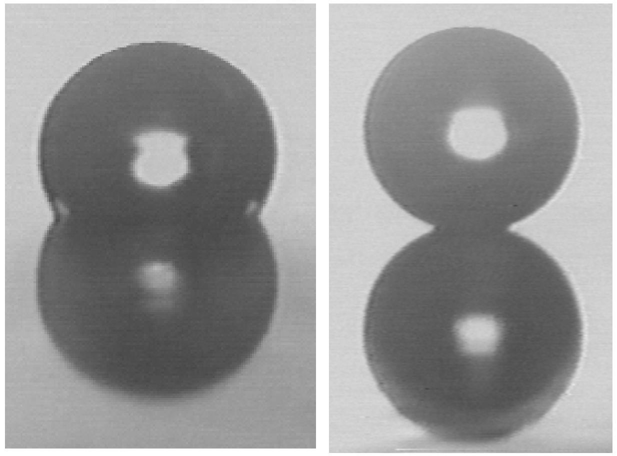
Setup of the copper etching



Copper sample etched through a 30 µm pattern



SEM picture of the pattern of the etched copper surface



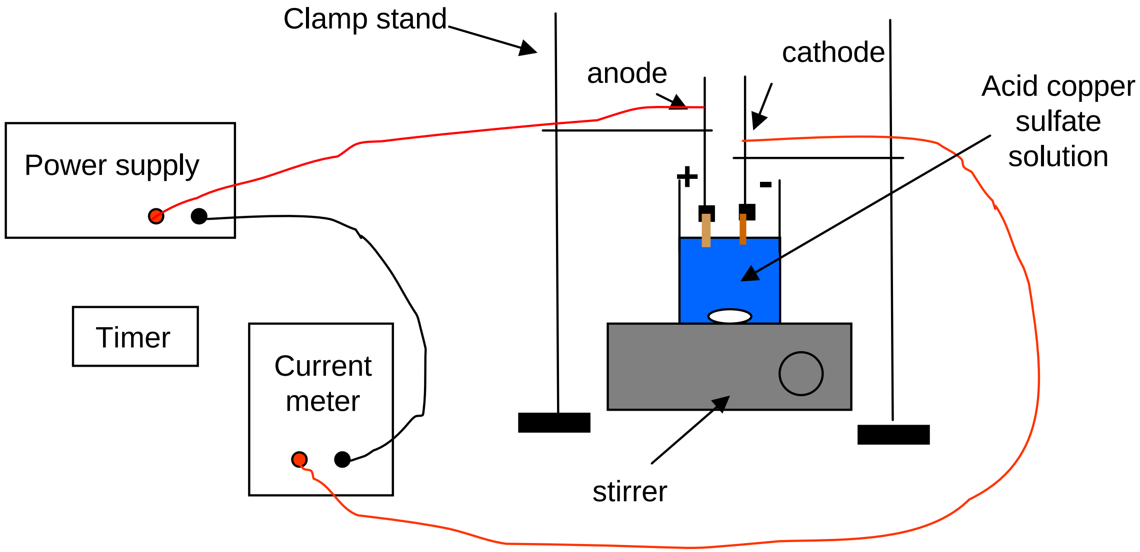
Droplets on hydrophobic flat and hydrophobic etched copper samples

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

Electrodeposited Copper Surfaces

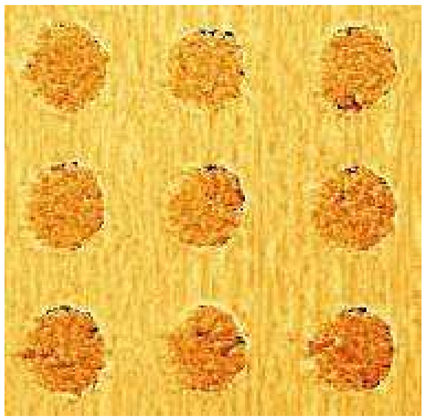
Copper acid bath

- Copper sulphate ($CuSO_4$) and sulphuric acid (H_2SO_4)
- Control current density to create rough to fractally rough
- Mask and grow pillars in Cu on Cu

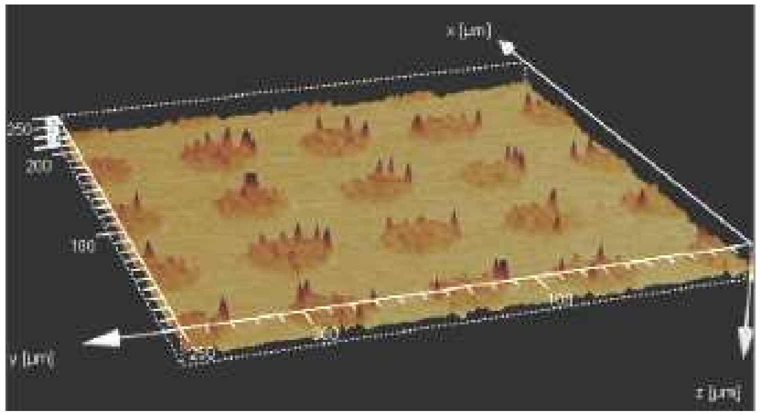


Diffusion limited aggregation

Base Cu electroplated surface



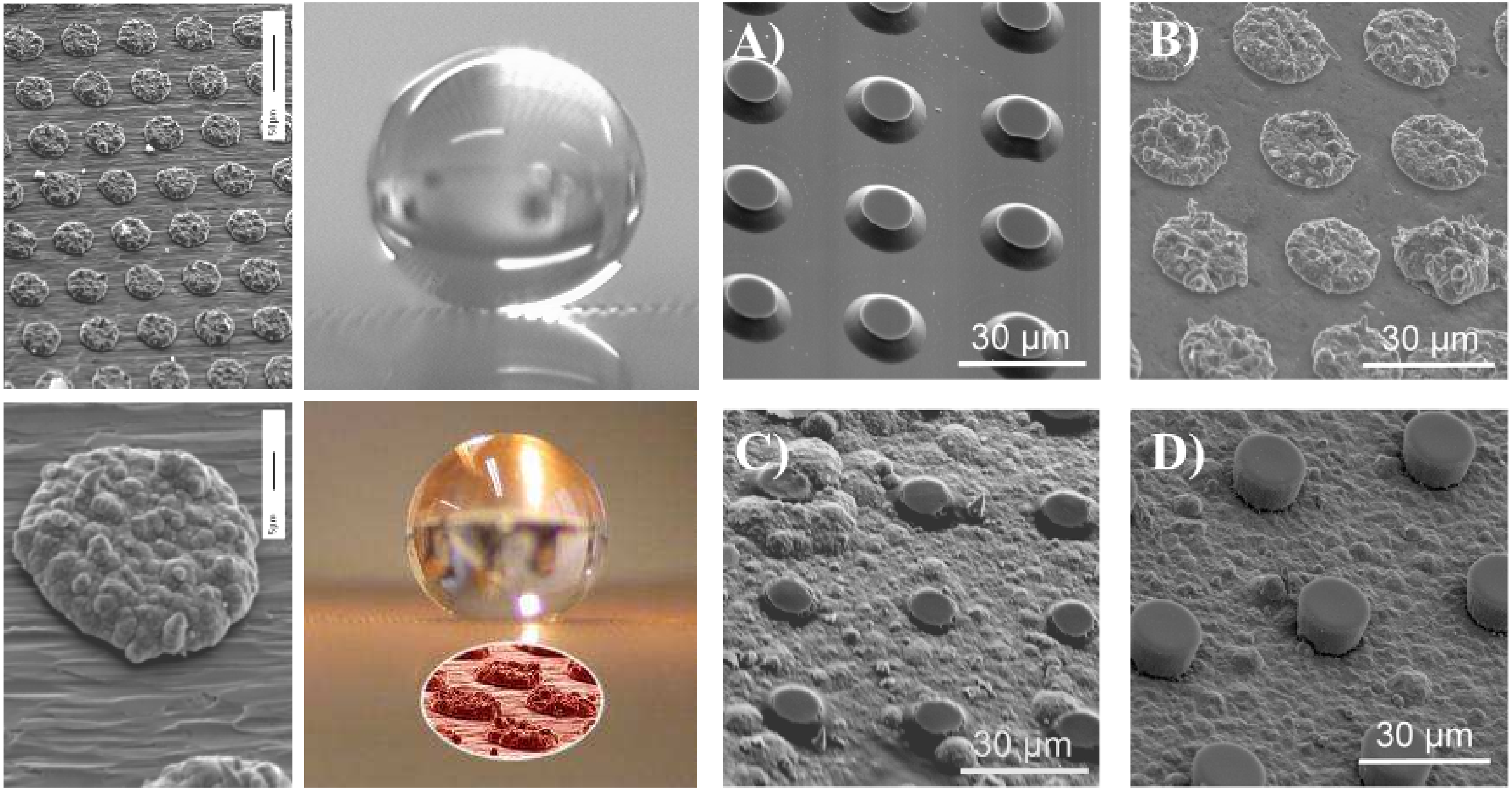
Confocal image of a 30μm textured electroplated Cu



3D view of a electroplated copper sample

Double Length Scale Systems

“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.

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

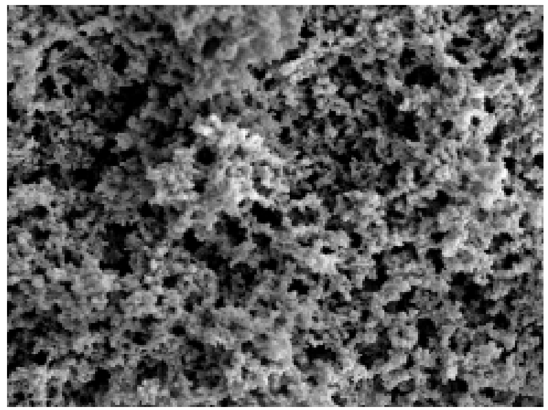
  Intrinsically hydrophobic

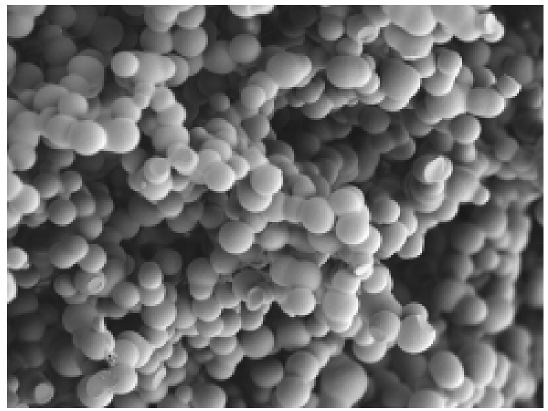
  Abradable (renewable) superhydrophobic surfaces

  Pore size controllable nano- to macro-porous

  Contact angle hysteresis as low as 4^{o}

  Hydrophobic-to-hydrophilic transition by heating



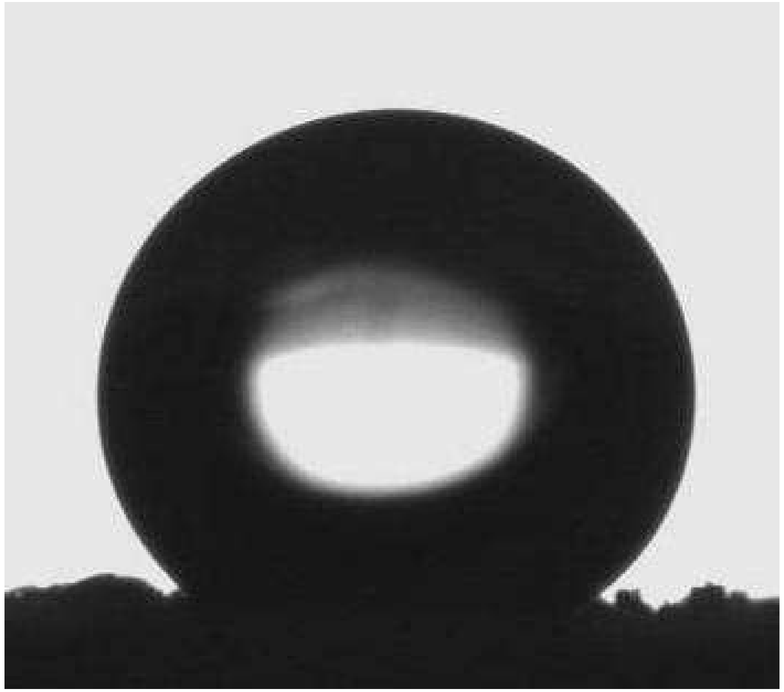


10 μm

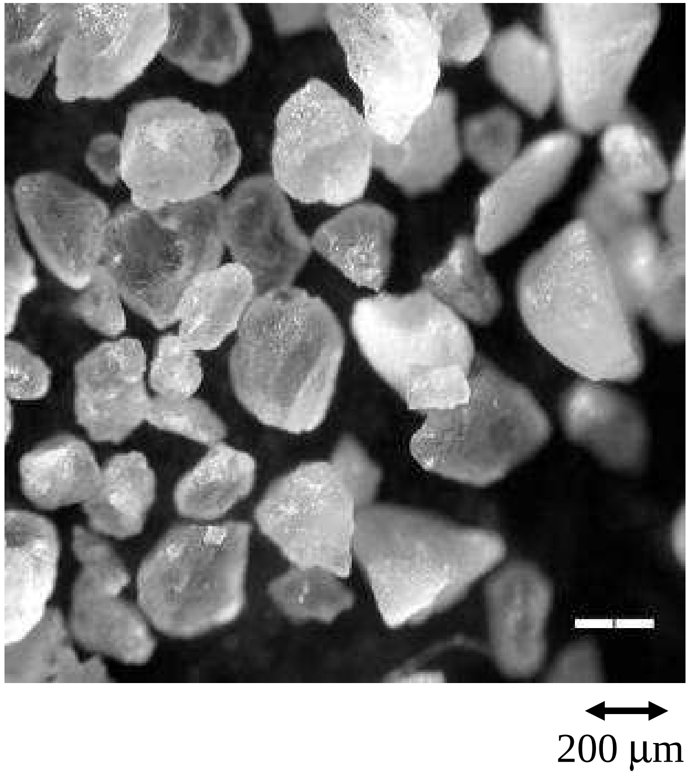
Reference Shirtcliffe *et al*, Langmuir 19 (2003) 5626-5631

Super Water-Repellent Sand/Soil

Sand with139^{o}



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)

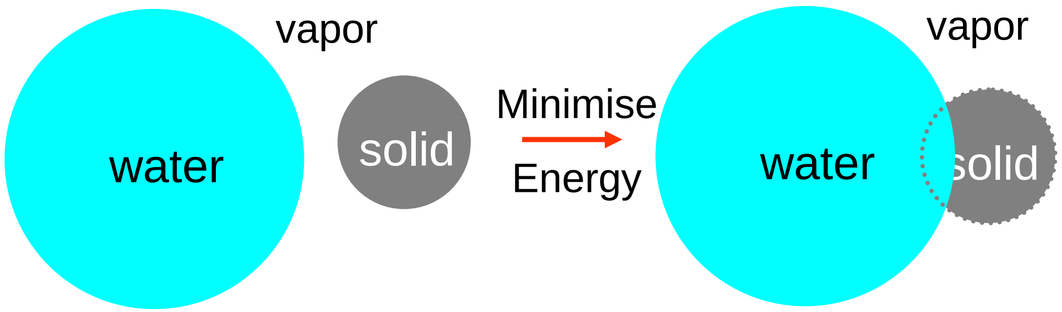
Reference McHale *et al*, Eur. J. Soil Sci. 56 (2005) 445-452; McHale *et al*, Hydrol. Proc. 21 (2007) 2229-2238.

Liquid Marbles

Loose Surfaces

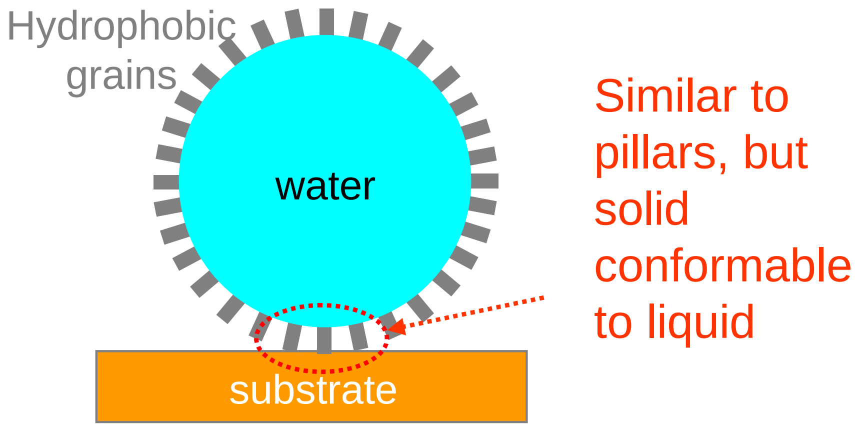
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

Hydrophobic Grains and Water



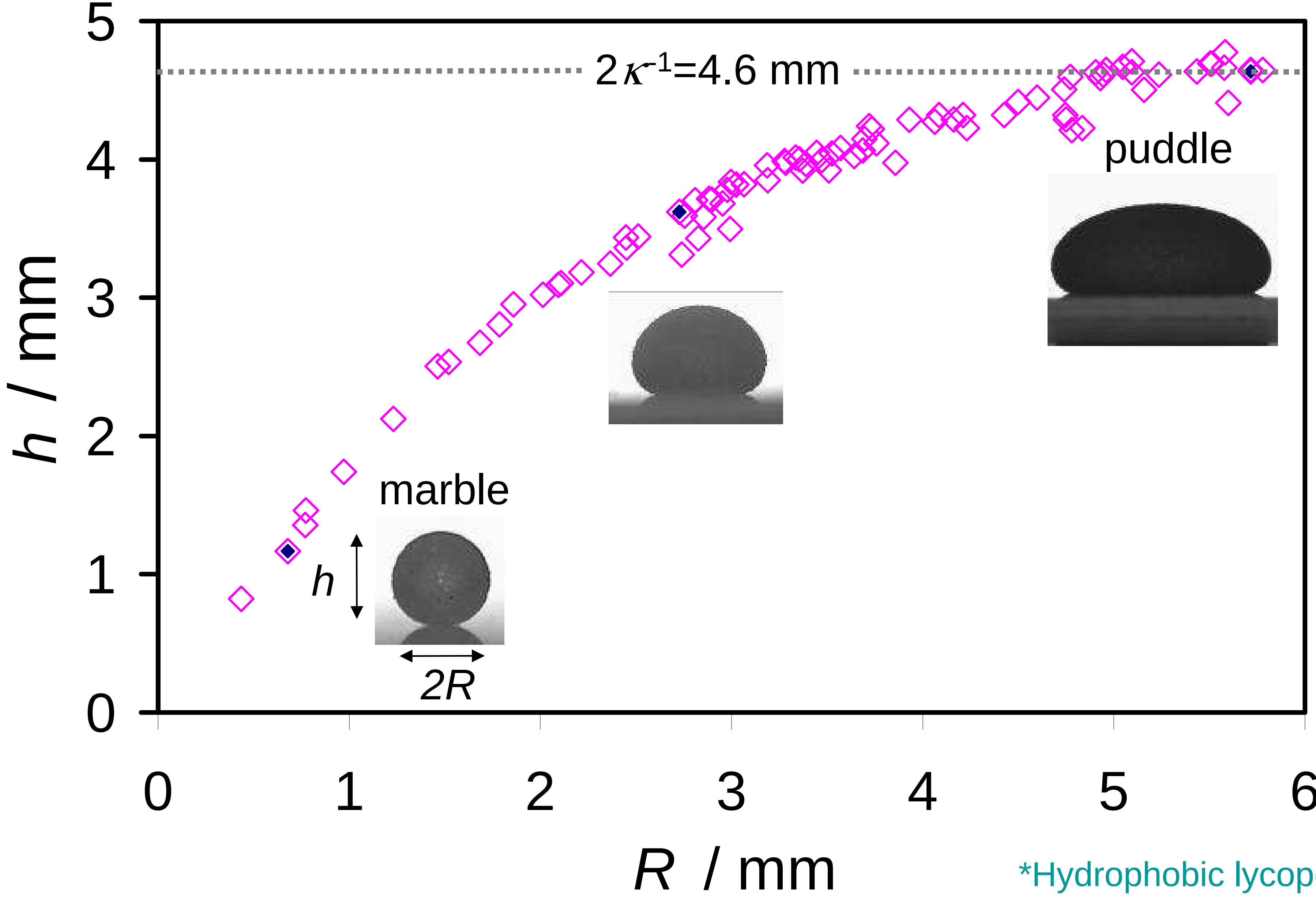
$$\Delta F = -\pi R_g^{\,2} \gamma_{LV} (1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment



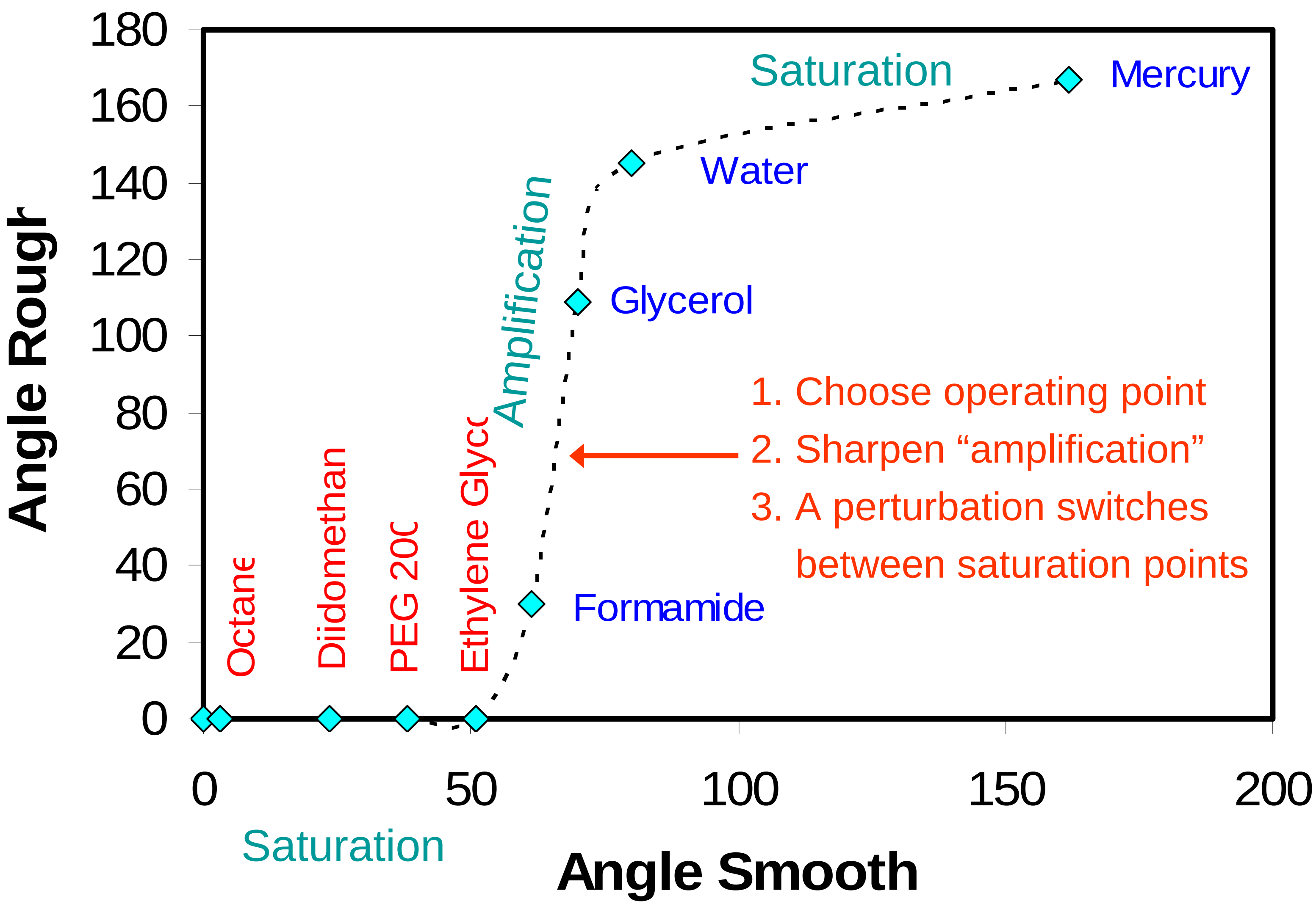
Reference Aussillous, P.; Quéré, D. Nature 411, (2001), 924-927

Perfect Non-Wetting Marbles*



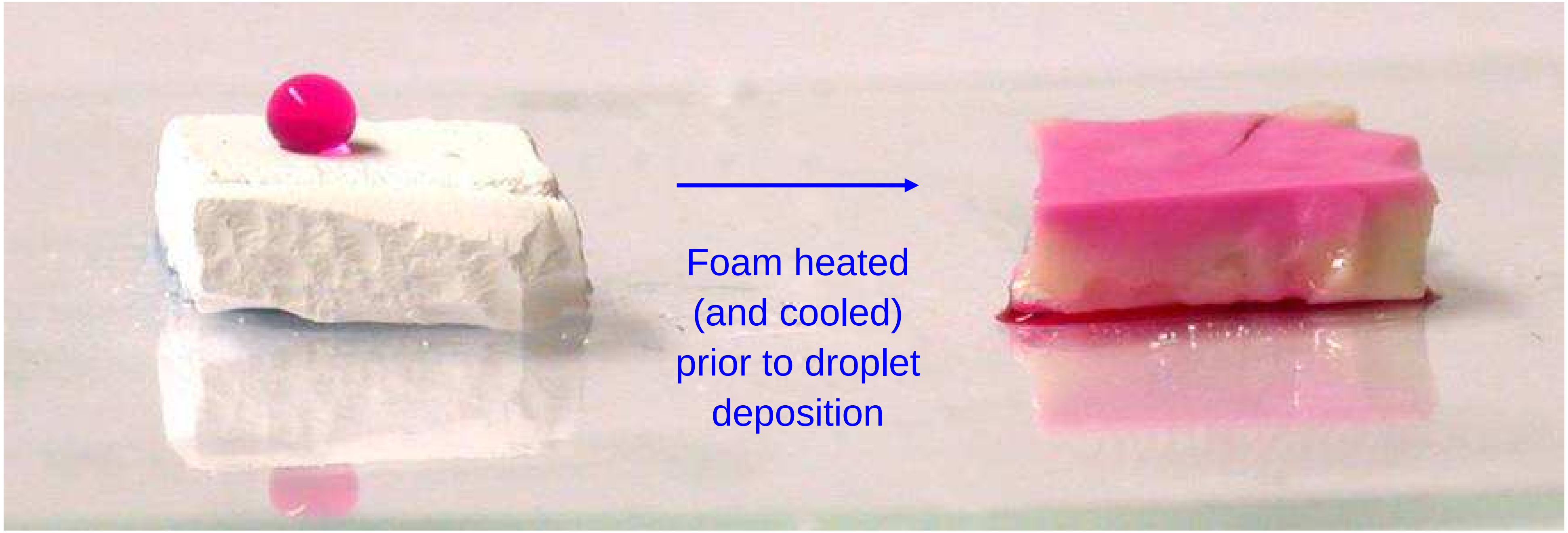
*Hydrophobic lycopodium

“Digital” Switching - Recall



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

Sol-Gel Foams – Switching from S/H



- 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.

Liquids in Motion

Infiltration into Bead Packs and Sand

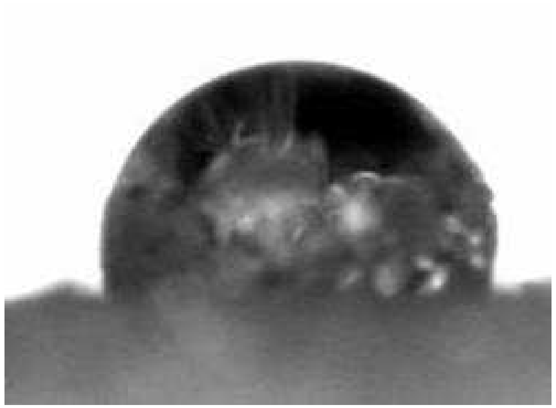
Fluorocarbon Bead Packs

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

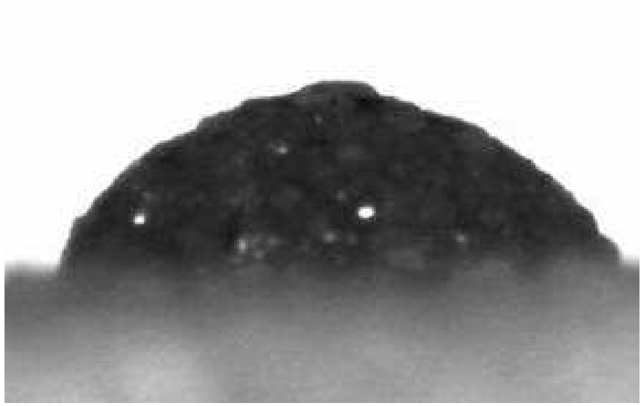
Liquid	***θ on fluorocarbon coated glass slides / °±4***
Octane	72°
Heptane	65°
Hexane	61°
Pentane	52°

Fluorocarbon Coated Sand

Penetration occurs for hexane



Octane (72°)

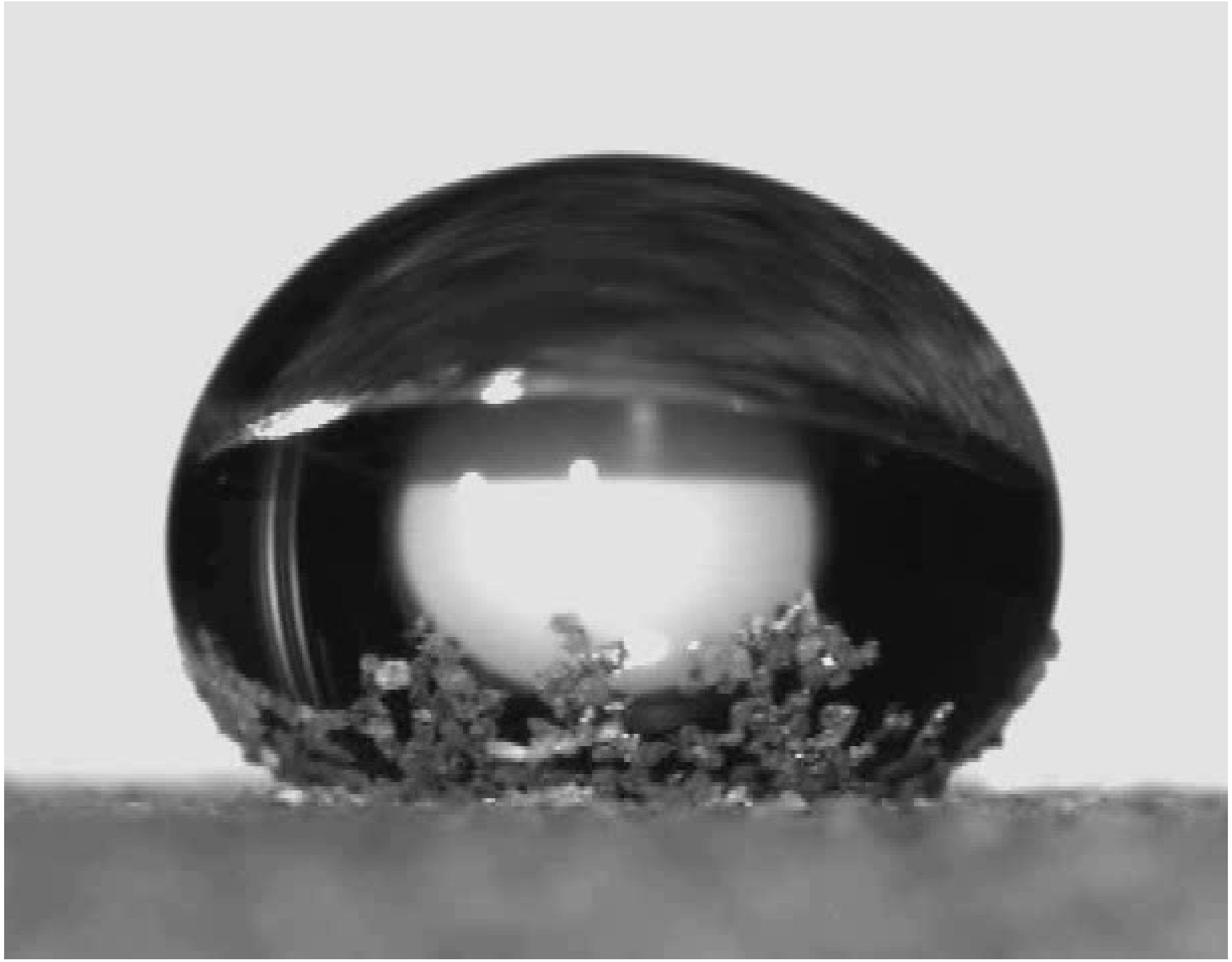


Heptane (65°)

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

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

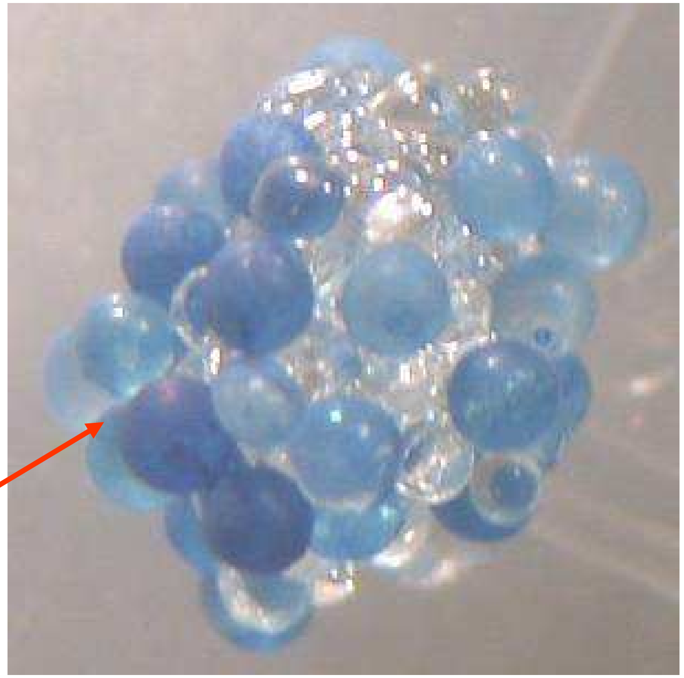
Ejection: Surface–into-Liquid

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

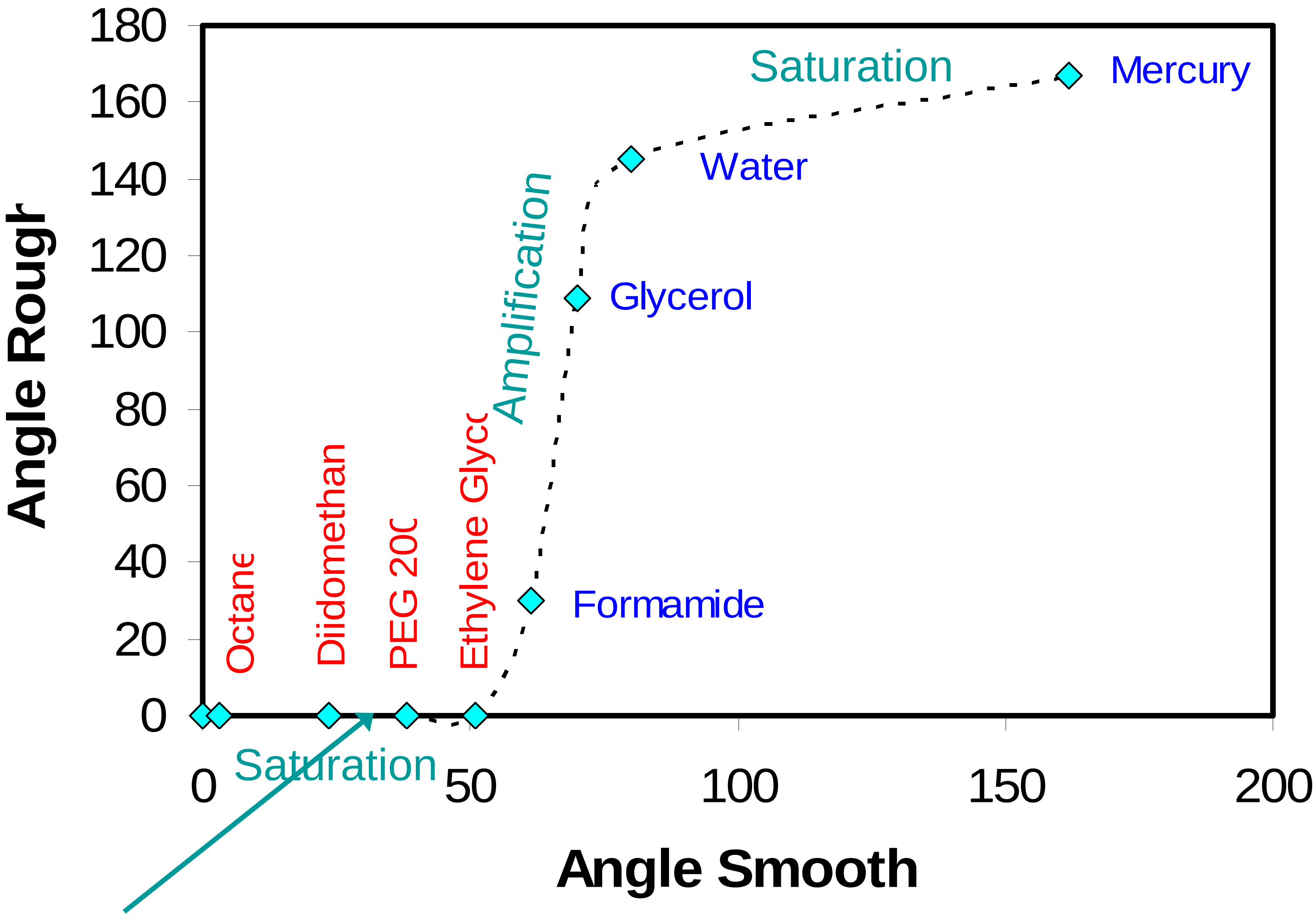
Experimental Test

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



“Superspreading” - Recall



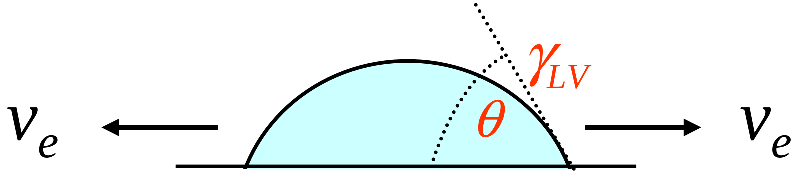
Different “spread” states are approached at different rates and liquids are “pulled” into (i.e. hemi-wicked) the surface structure (⇒ self-cleaning superhydrophobic surfaces can also self-contaminate when exposed to oils).

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

Super-spreading and "*Driving Forces*"

Drop spreads radially until contact angle reaches equlibrium

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



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

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

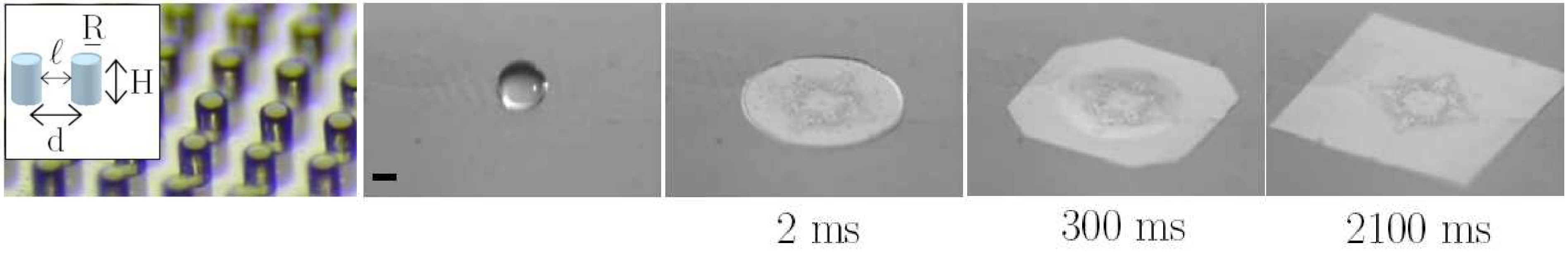
Prediction – Verified Experimentally

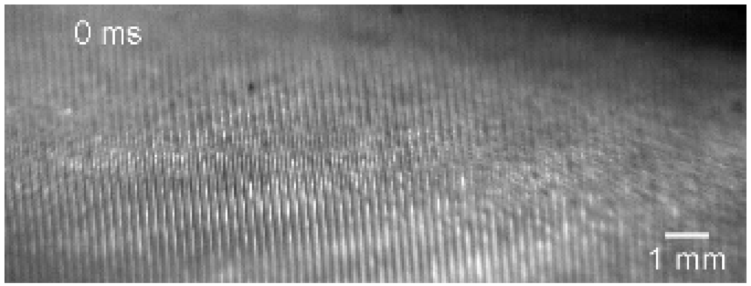
Weak roughness (or surface texture) modifies spreading speed:

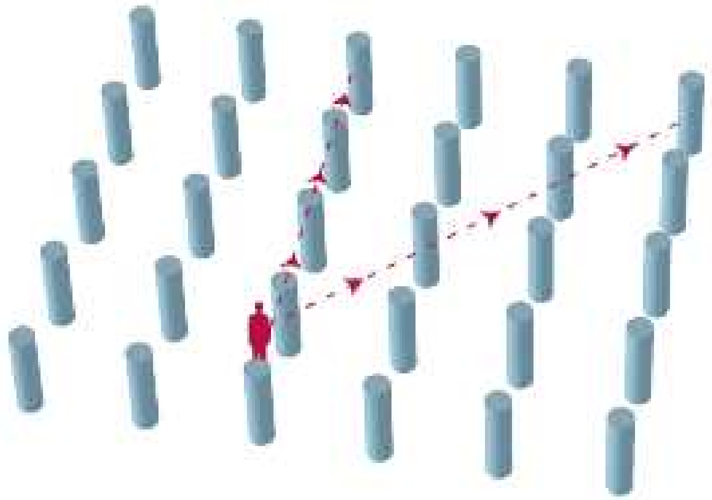
$v_E \propto \theta(\theta^2 - \theta_e^2)$ changes towards $v_E \propto \theta$

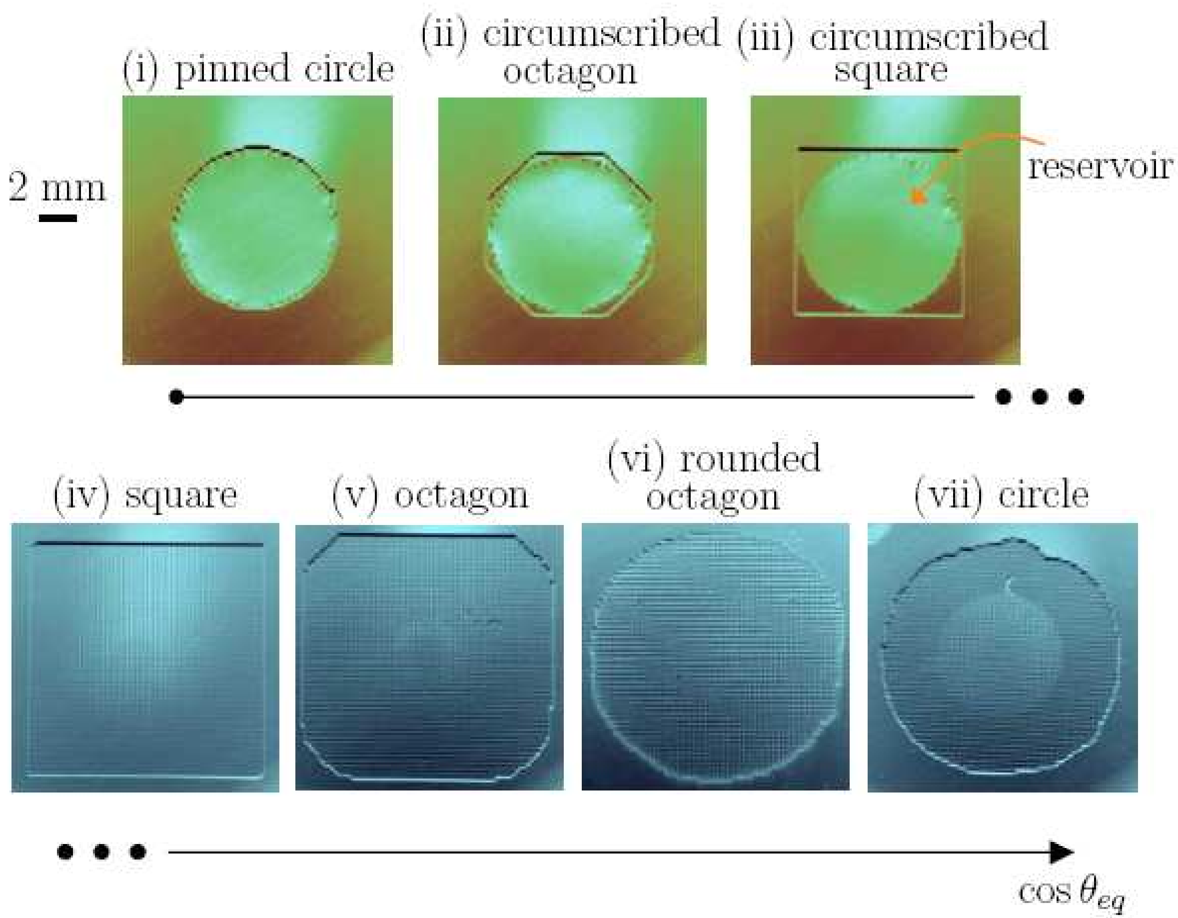
Reference McHale and Newton, Colloids & Surfaces, A206 (2002) 193-201.

Superspreading - Hemi-Wicking







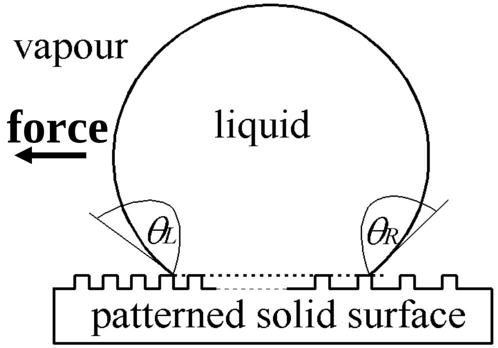


Reference Courbin *et al*, Nature Materials. 6 (2007) 661-664; McHale, 6 (2007) 627-638.

Patterns in Superhydrophobicity

Driving Force

Droplet experiences different contact angles ⇒ driving force

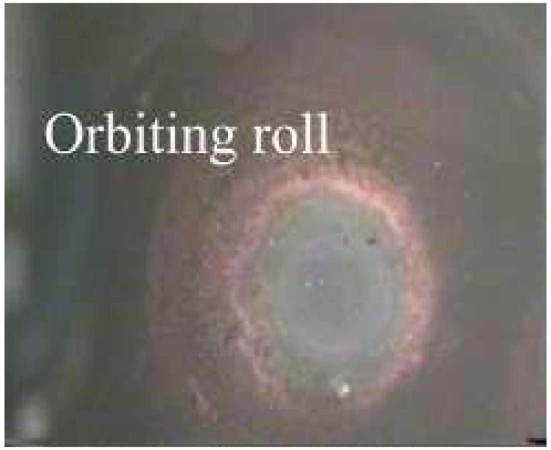


$$Force \propto \gamma_{LV}(\cos\theta_R - \cos\theta_L)$$

Need to overcome contact angle hysteresis

Self-Actuated Motion

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

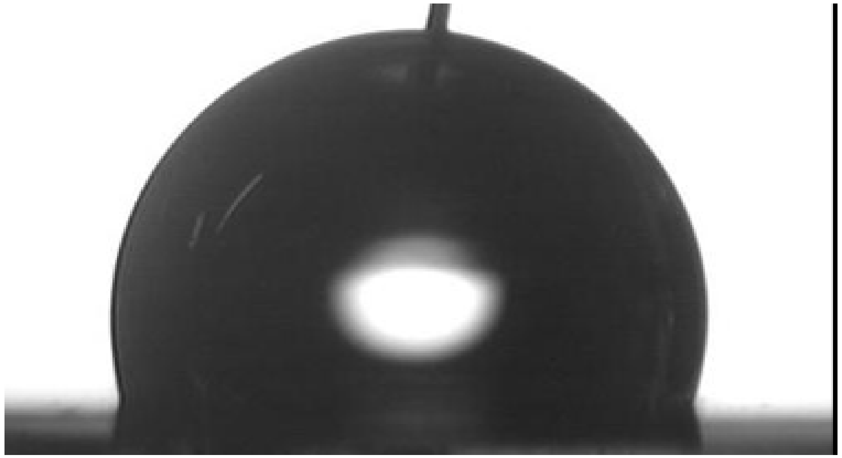


Reference   Quéré *et al* (unpublished); McHale *et al*, Analyst 129 (2004) 284-287; McHale, Langmuir 23 (2007) 8200-8205.

Electrowetting and Superhydrophobicity

Electrowetting-on-Dielectric

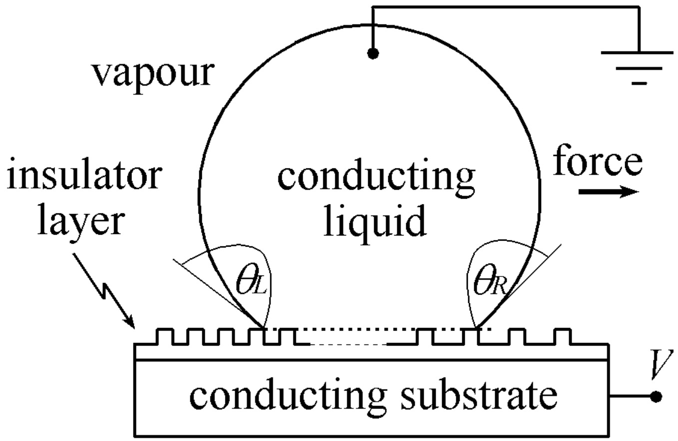
- Conducting liquid on electrical insulator on conducting substrate
- Applying voltage electrically charges solid-liquid interface (i.e. a Capacitive effect)
- Droplet spreads and contact angle reduces



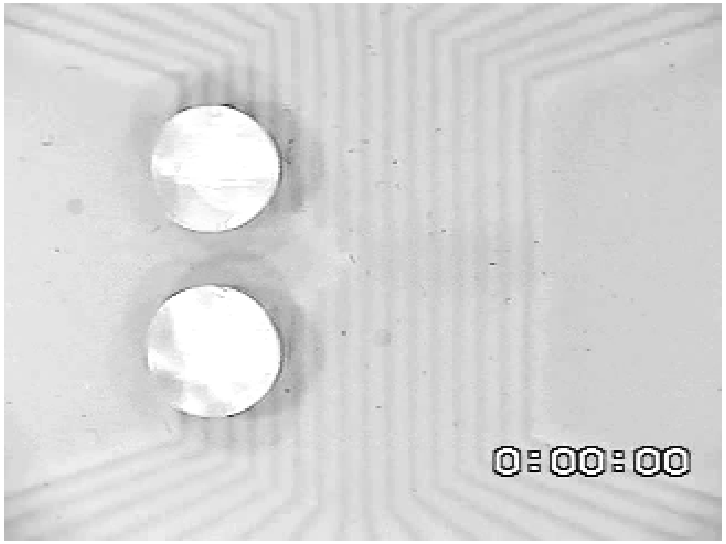
$$\cos\theta_e(V) = \cos\theta_e(0) + CV^2/2\gamma_{LV}$$

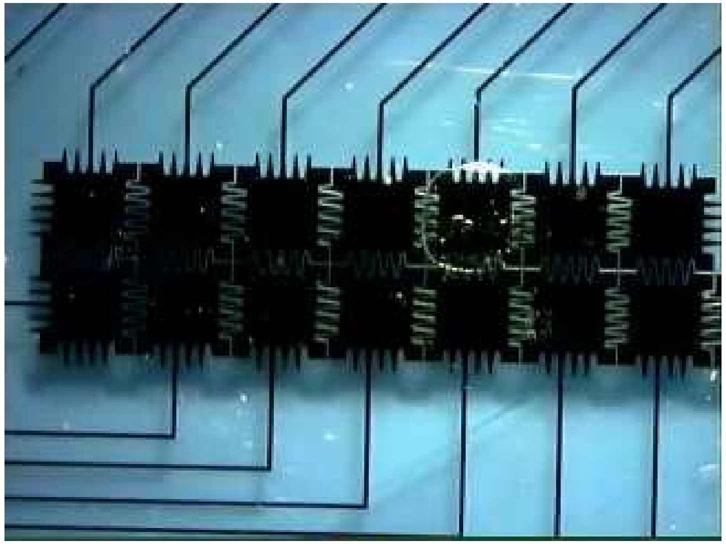
Driving Force

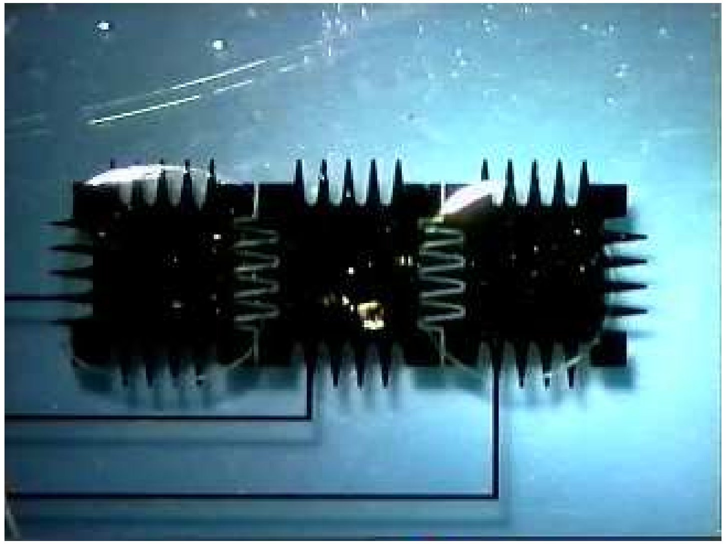
- Difference in angles on opposite sides of drop generates a driving force
- e.g. superhydrophobic surface drop moves once hysteresis overcome

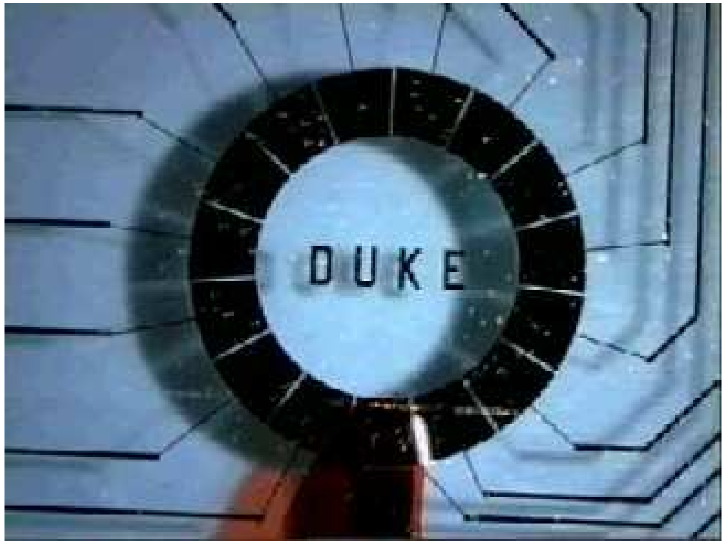


Droplet Microfluidics (VTT and Nanolytics)









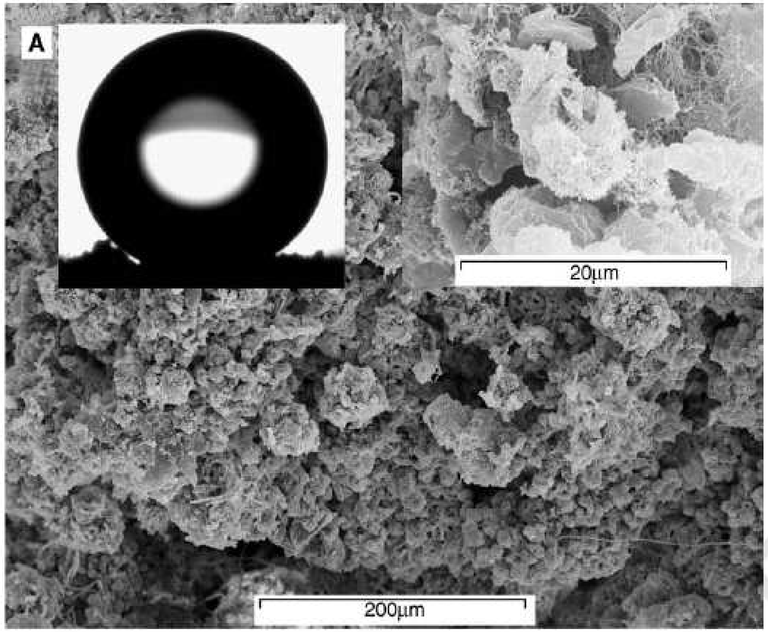
Motion induced by electrowetting (voltage actuation)

Role of superhydrophobicity – reduce force needed for motion

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

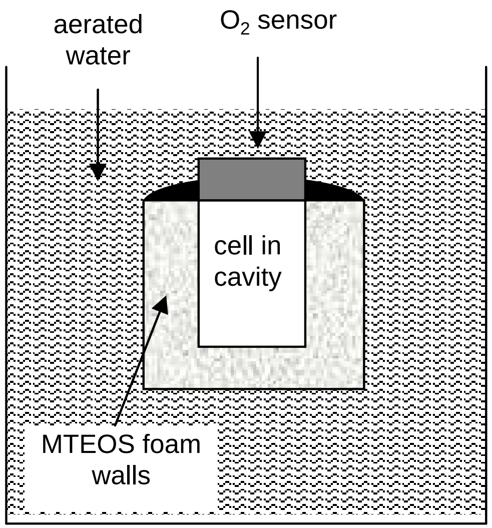
Resistance to acid rain?

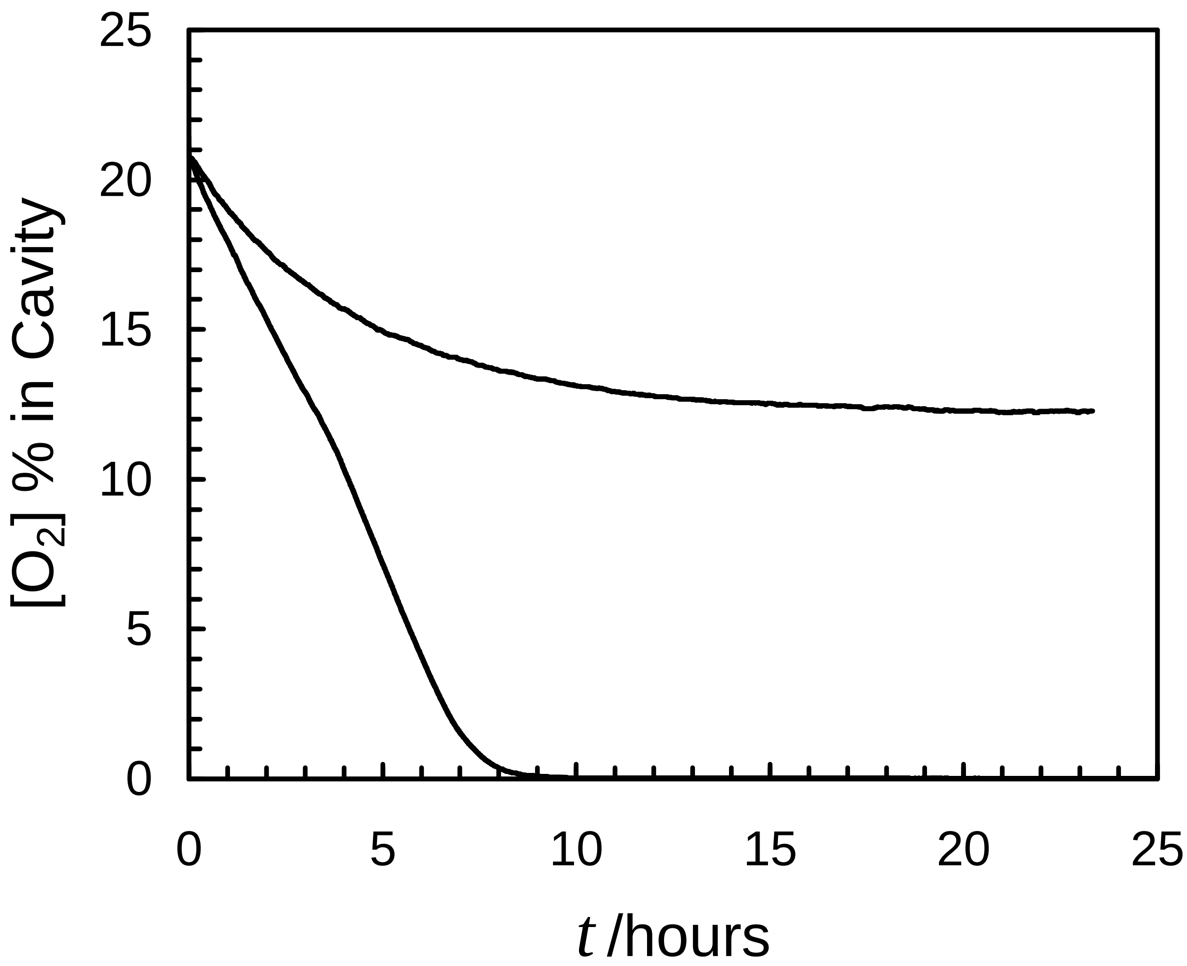
Reference Shirtcliffe *et al.*, J. Plant. Phys. 163 (2006) 1193-1197.

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

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

EPSRC
Engineering and Physical Sciences Research Council

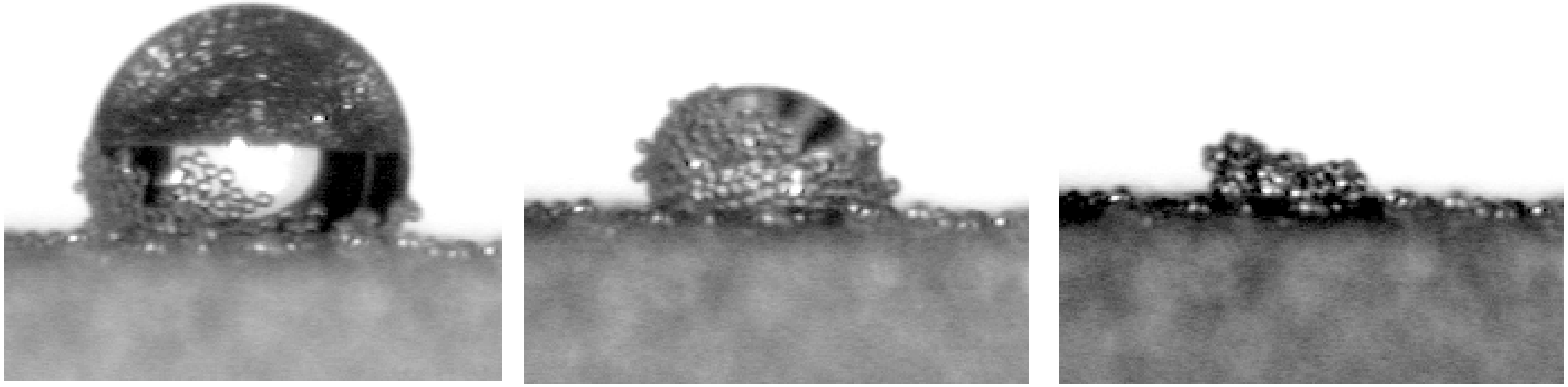
NOTTINGHAM TRENT UNIVERSITY

NATURAL ENVIRONMENT RESEARCH COUNCIL

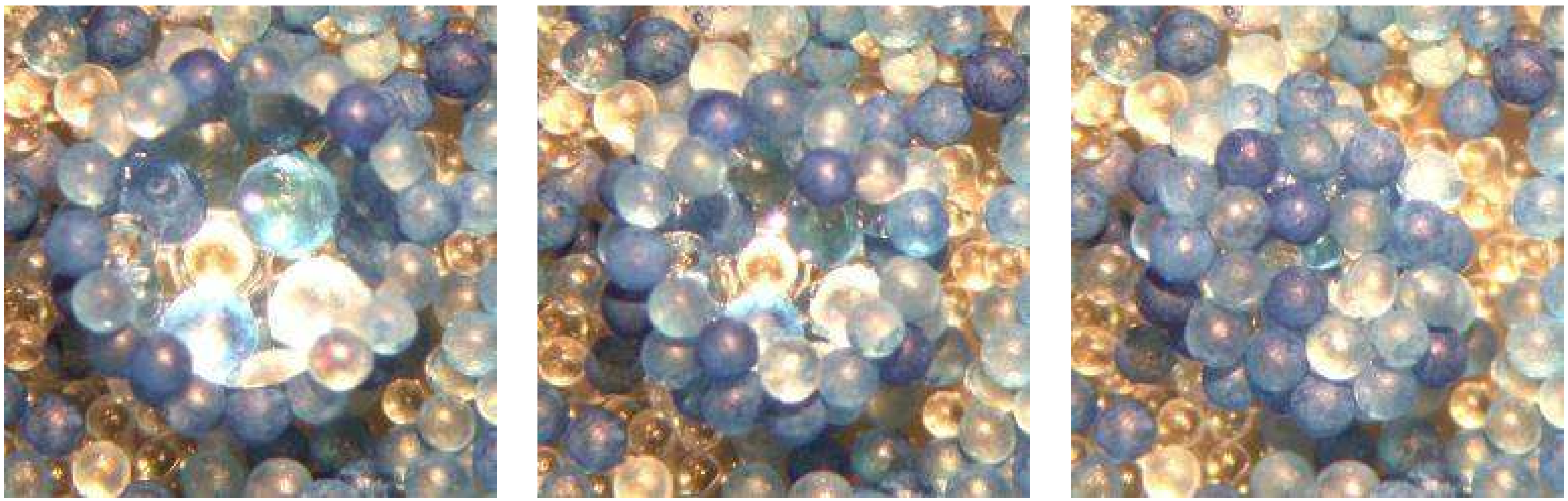
Appendices

Hydrophobic Granular Self Sorting

Water droplet digging during drying

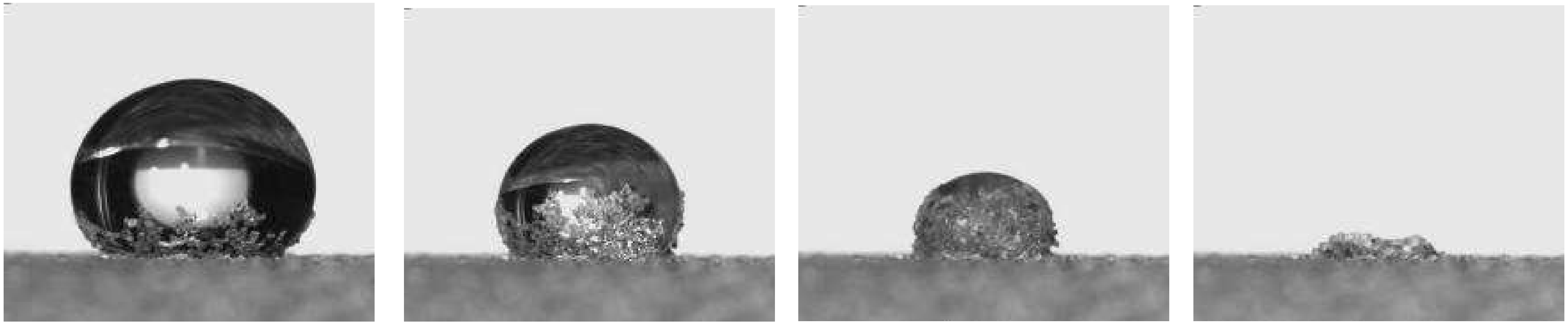


Mixed hydrophobic (blue)/hydrophilic (clear)

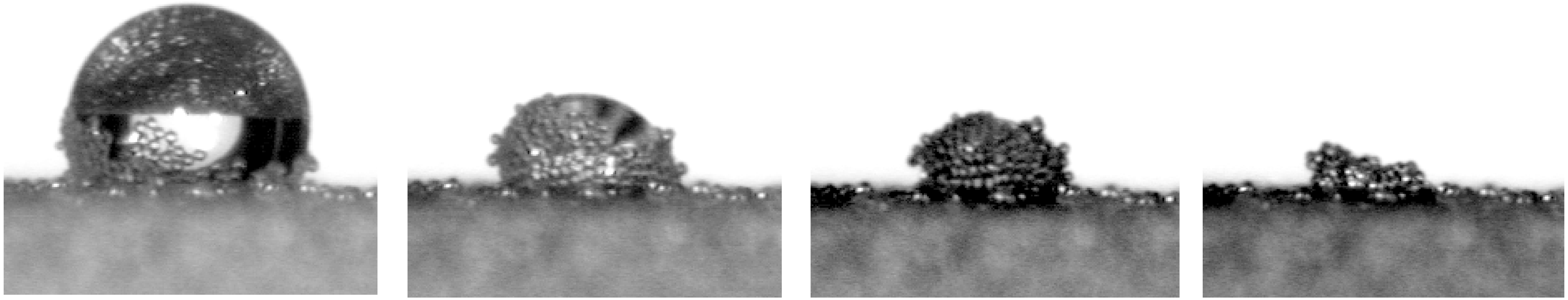


Evaporatively Driven Coating

Water on Hydrophobic Sand

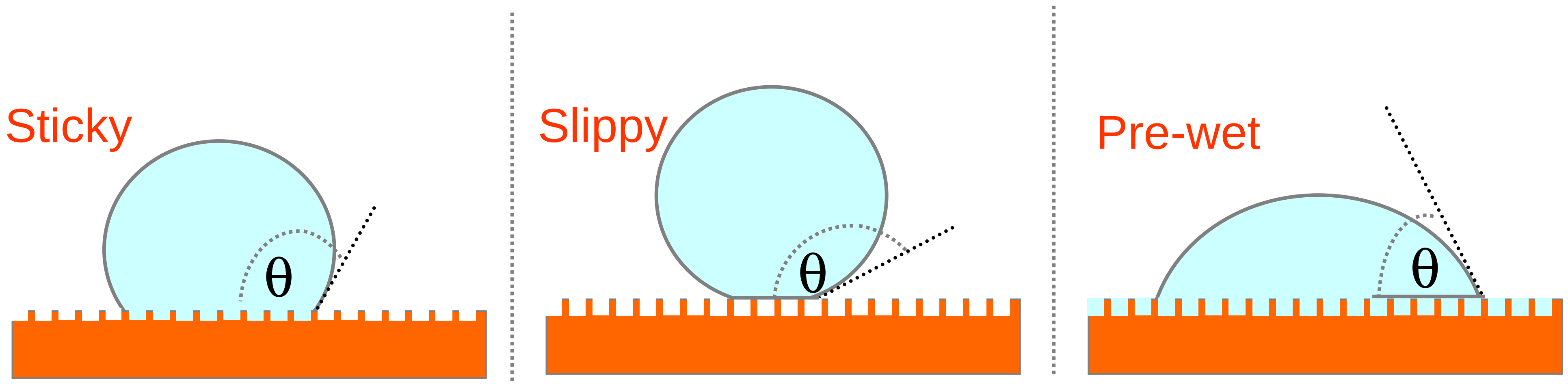


Water on Hydrophobic 75 µm Silica Beads



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

Pre-existing Wetness



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

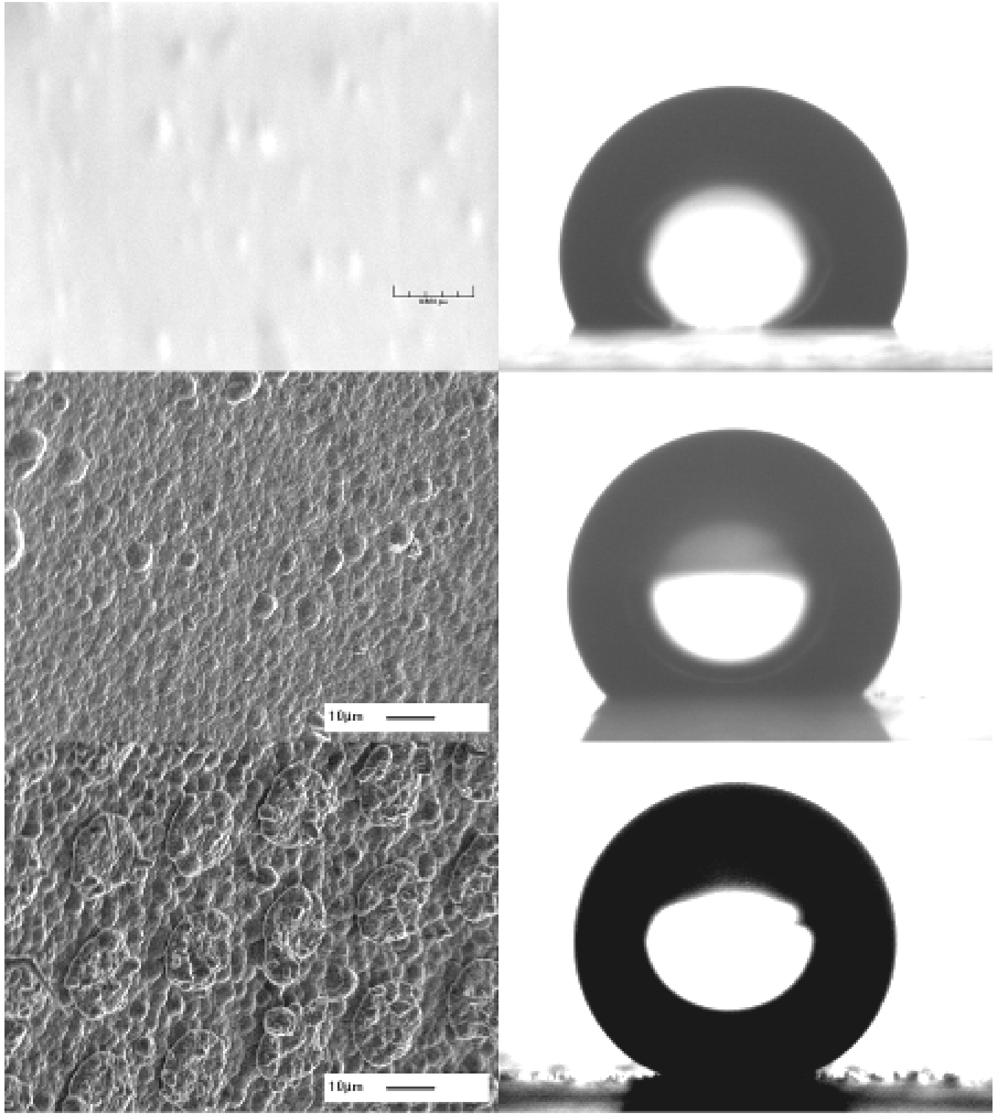
ie. use $\cos(180^o)=-1$ or $\cos(0^o)=+1$ in Cassie-Baxter equation

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

Combining Slight Roughness and Texture

- Smooth and Hydrophobised 115º
- Slightly Rough and Hydrophobised 136º
- Slightly Rough, Textured and Hydrophobised 160º

Two length scales is extremely effective



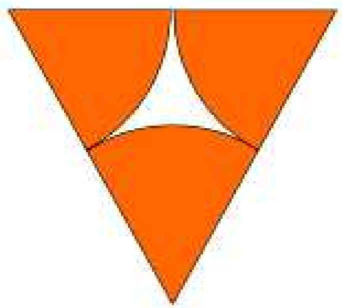
Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932 (Theory is in the supplementary information).

Transition from Wetting to Porosity

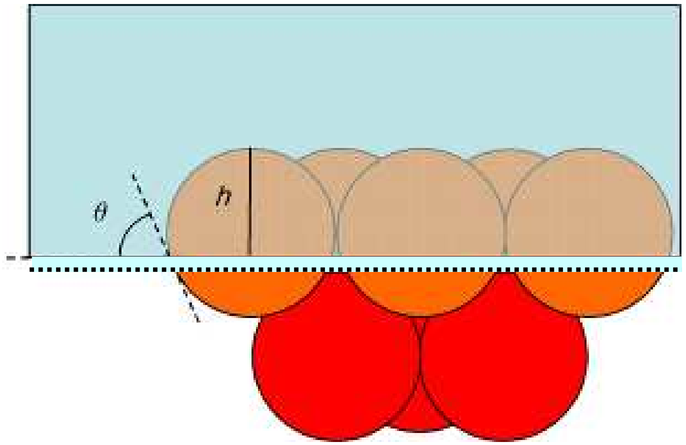
Assumptions

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

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

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

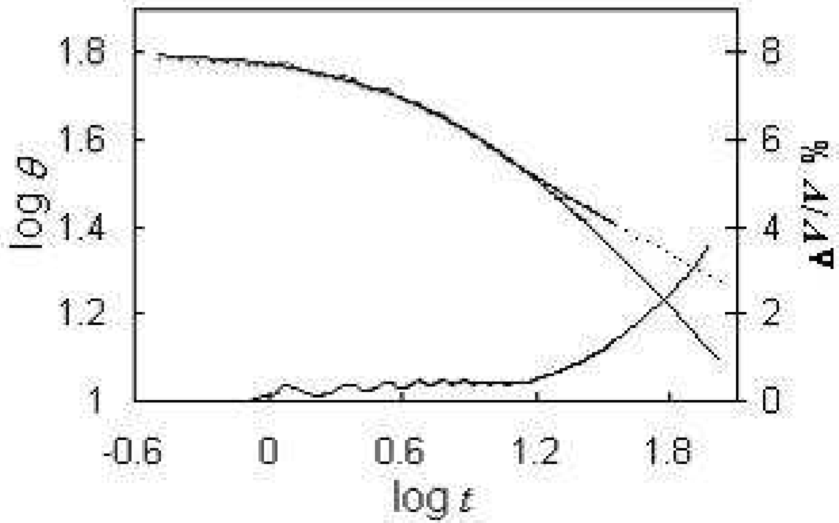
$\theta_c = 50.73^o$

*Consistent with experiments**

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

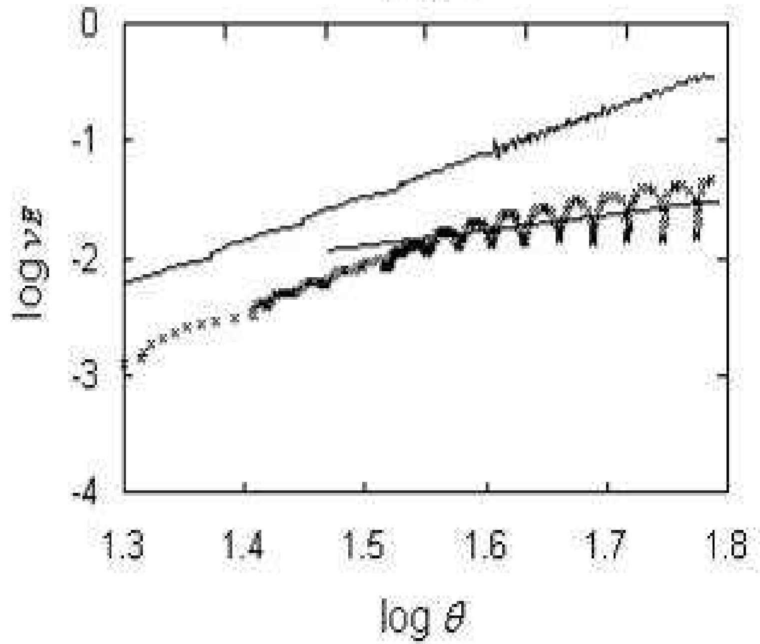
Superspreading of PDMS on Pillars

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



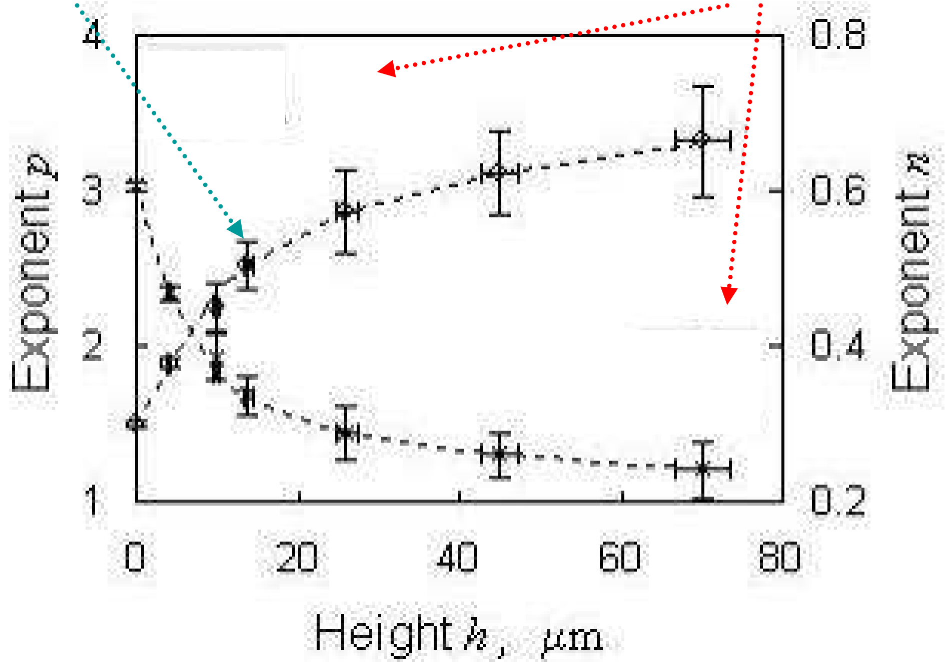
$$v_E \propto v^* \theta^p$$

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



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.

Two Forms of Superhydrophobicity

Wenzel's Equation

- Based on roughness, *r*

$$\cos\theta_e^W = r\cos\theta_e^S$$

Consequences

- Causes larger/smaller contact angles when θ_e^s > or < 90º
- Creates a "Sticky" surface – drops don't easily move

Cassie-Baxter Equation

- Based on composite air-solid surface, f_s (Lotus effect)

$$\cos\theta_e^C = -1 + f_S(\cos\theta_e^S + 1)$$

Consequences

- Easier to get 150+º than with Wenzel
- Creates a "Slippy" surface – drops easily move