Superhydrophobic Materials: Properties & Surfaces

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Overview

1. Basic Concepts

2. A Selection of Surfaces

3. Switching and Superspreading

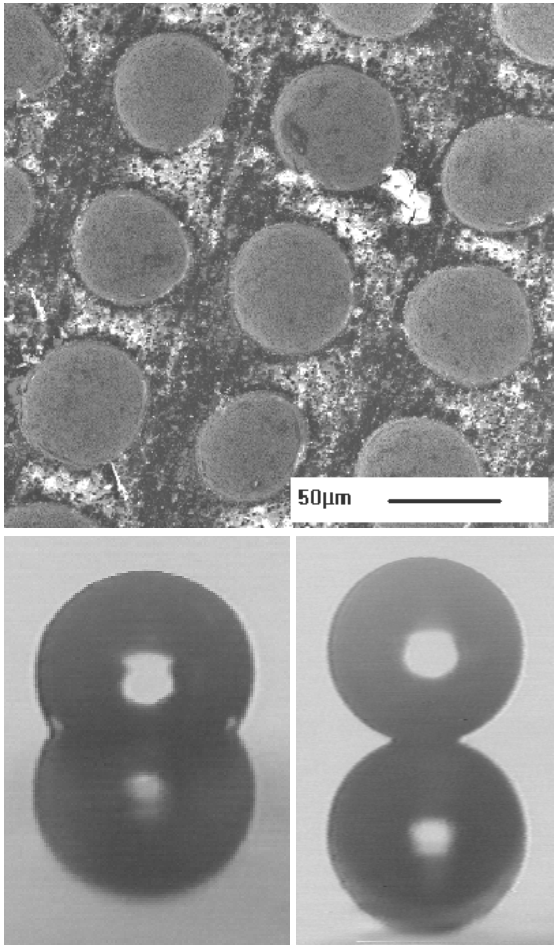
4. Complex Surfaces

5. Porosity and Loose Surfaces

Basic Concepts

Three Examples

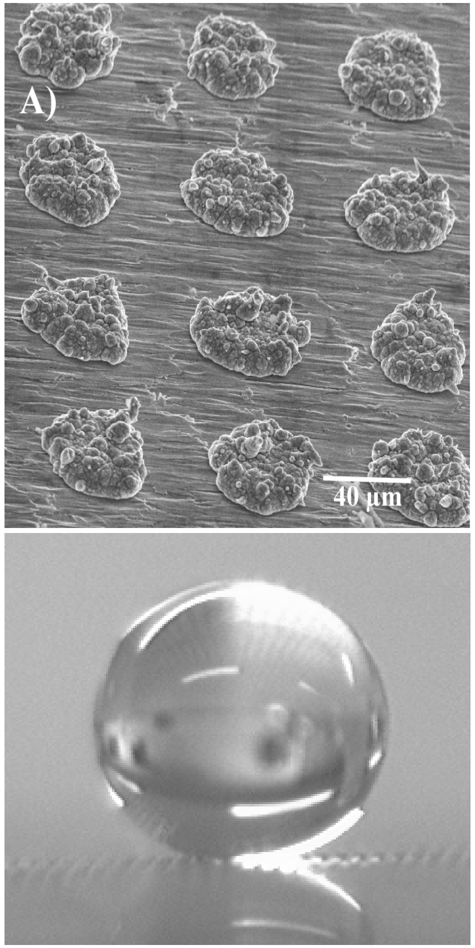
Etched Metal



Flat & hydrophobic

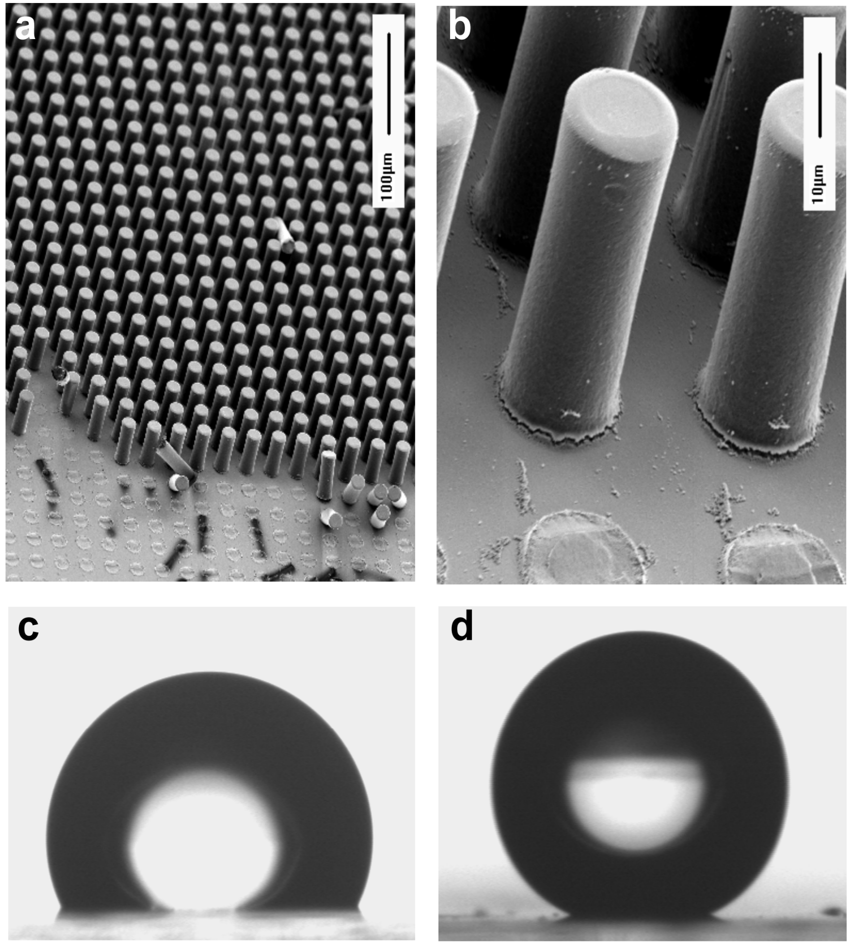
Patterned & hydrophobic

Deposited Metal



Patterned & hydrophobic

Polymer Microposts



Flat & hydrophobic

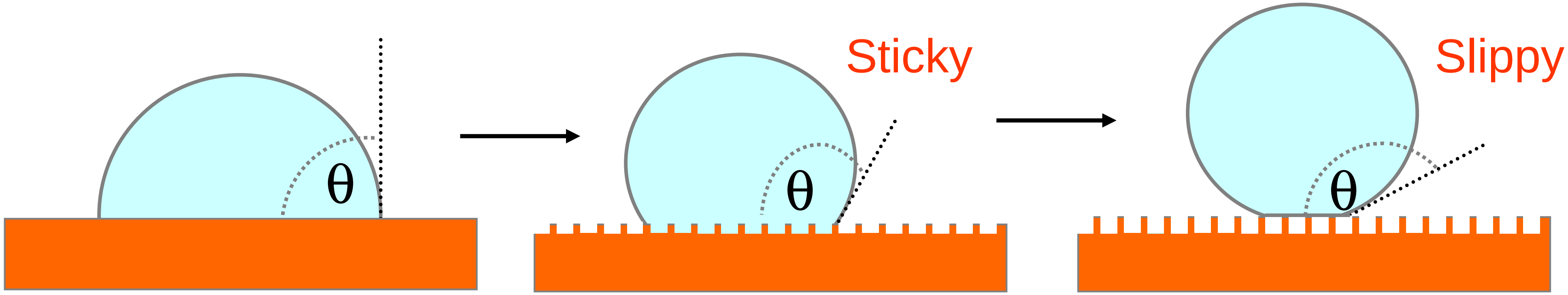
Patterned & hydrophobic

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

Chemistry

Roughness

Chemistry

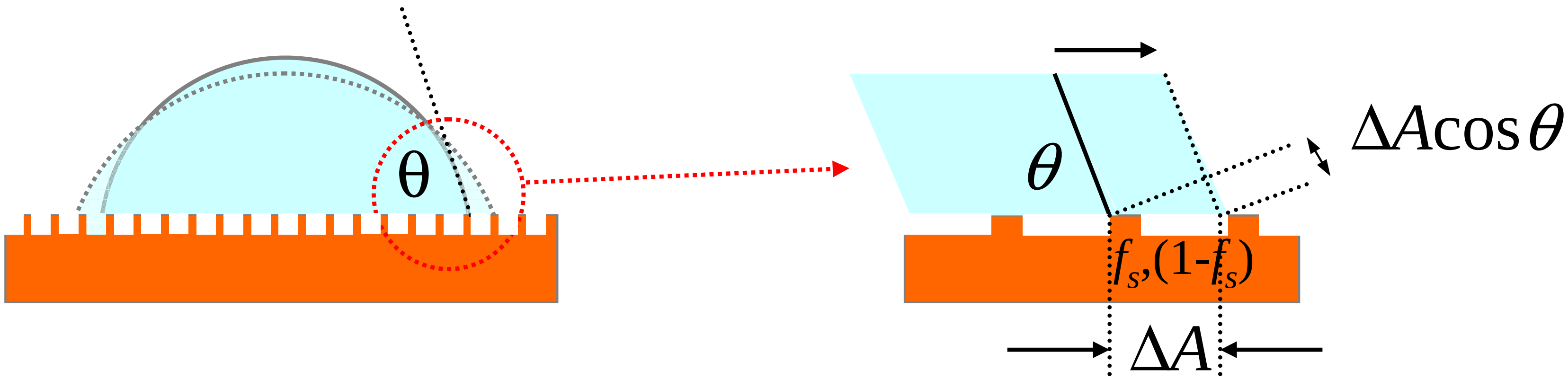
Young’s Law θ_e

Topography

r = true area/planar projection

f_s = solid surface fraction

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

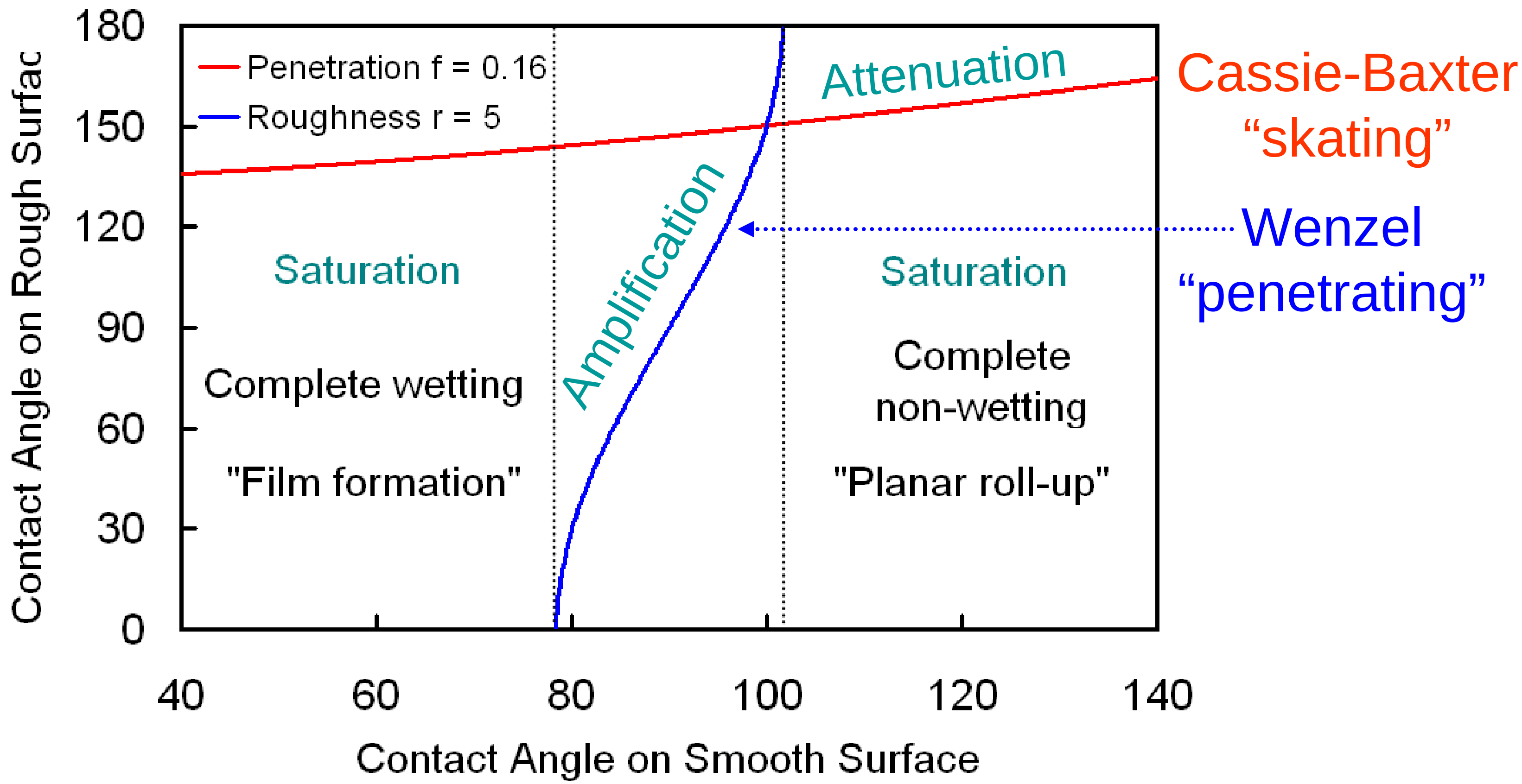
Topography $\Rightarrow$ f_s = solid surface fraction

Chemistry $\Rightarrow$ Young's Law θ_e

Air gaps $\Rightarrow$ cos(180º)=-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

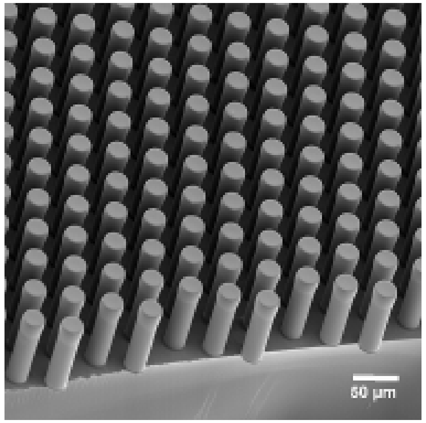
⇒ transition to penetrating

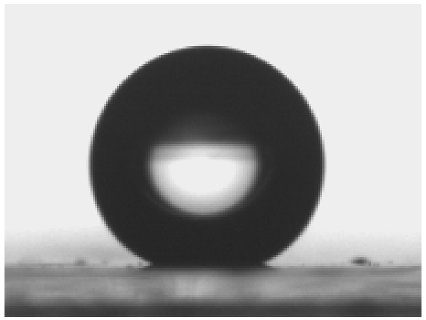
Skating-to-Penetrating Transition

Micro-Structured Surface

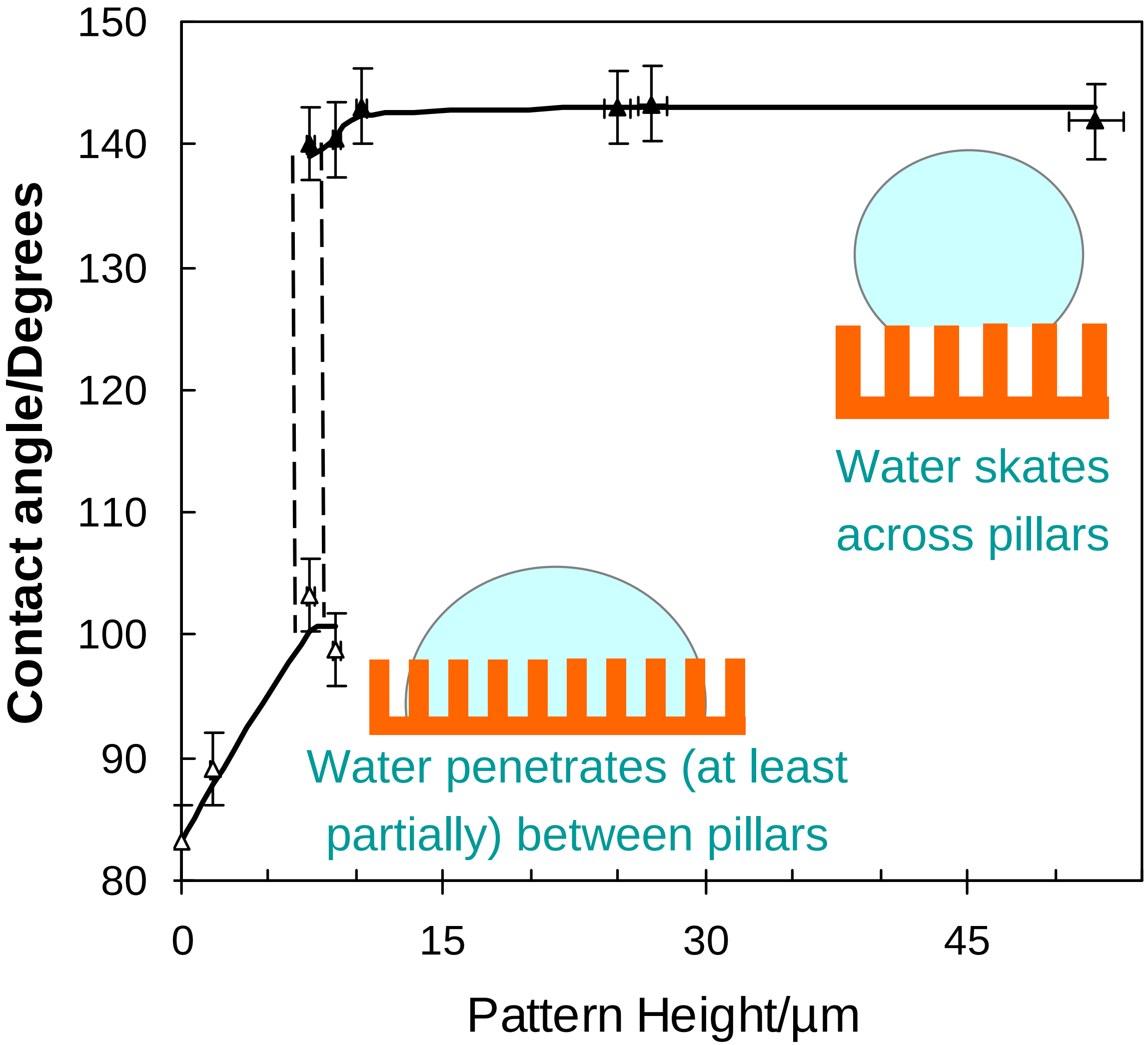
SU-8 pillars 15 µm

Hydrophobic treatment

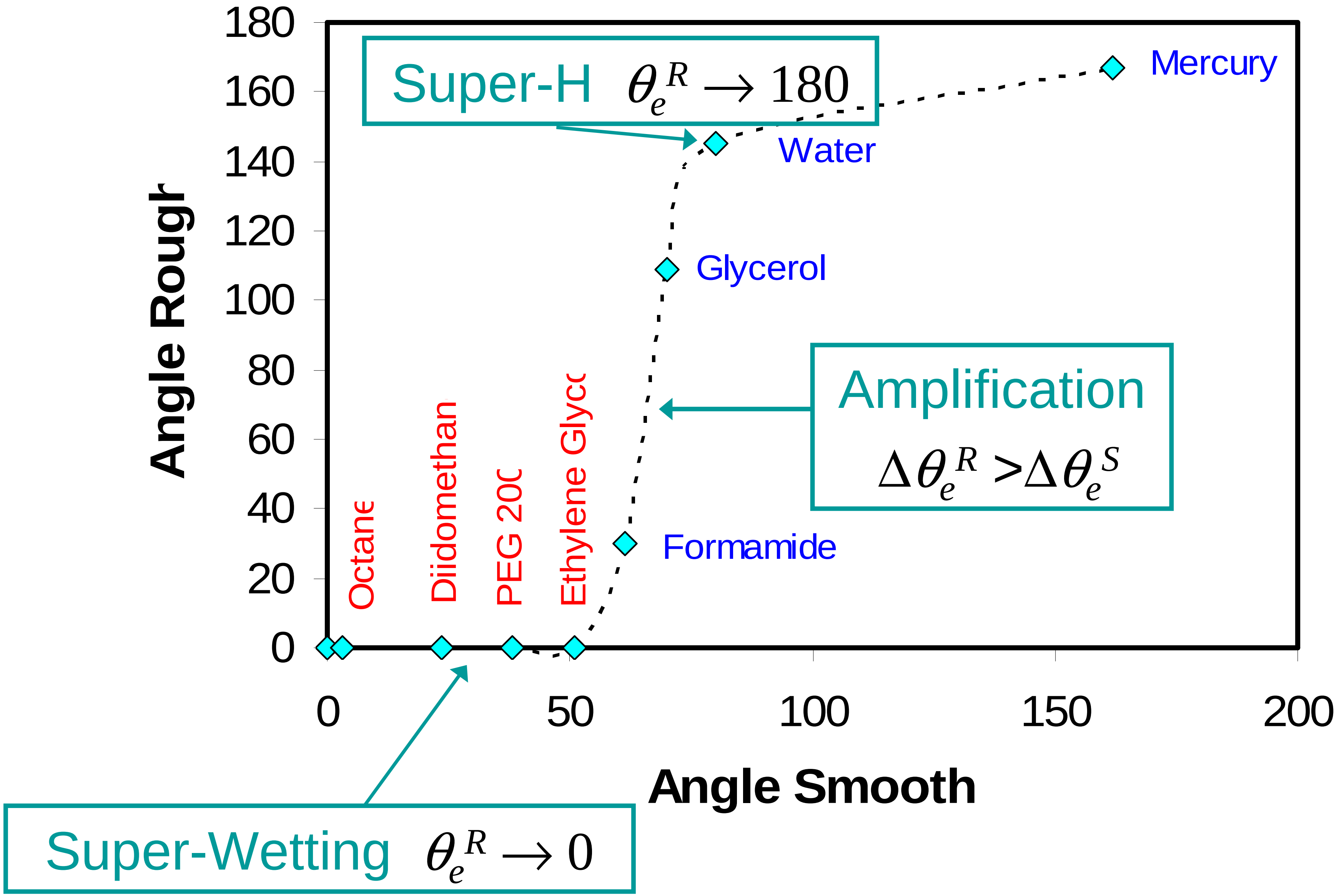




Change of Pillar Height

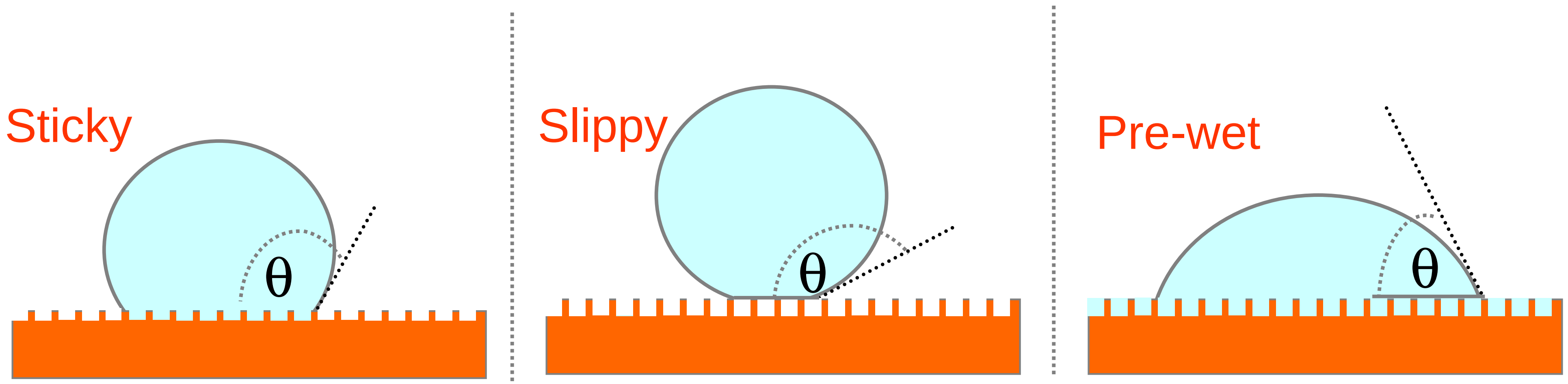


Different Liquids on a SuperH Surface



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

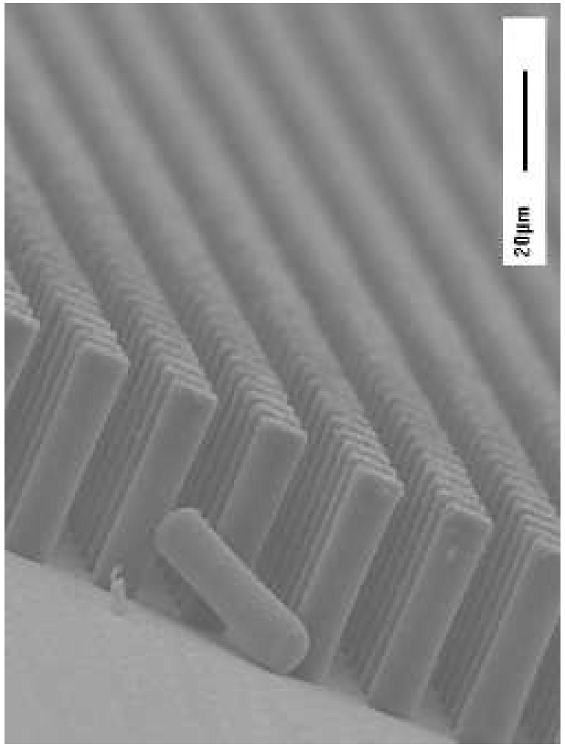
ie. use $\cos(180^o)=-1$ or $\cos(0^o)=+1$ in Cassie-Baxter equation

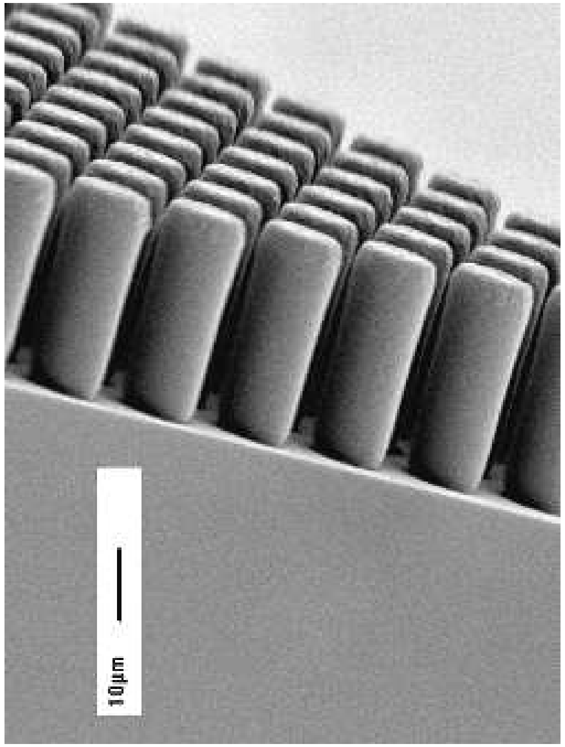
$$\cos\theta_{CB} = f_s \cos\theta_e \pm (1-f_s)$$

A Selection of Surfaces

SU-8 Photoresist Pillars

SEMs of Pillars



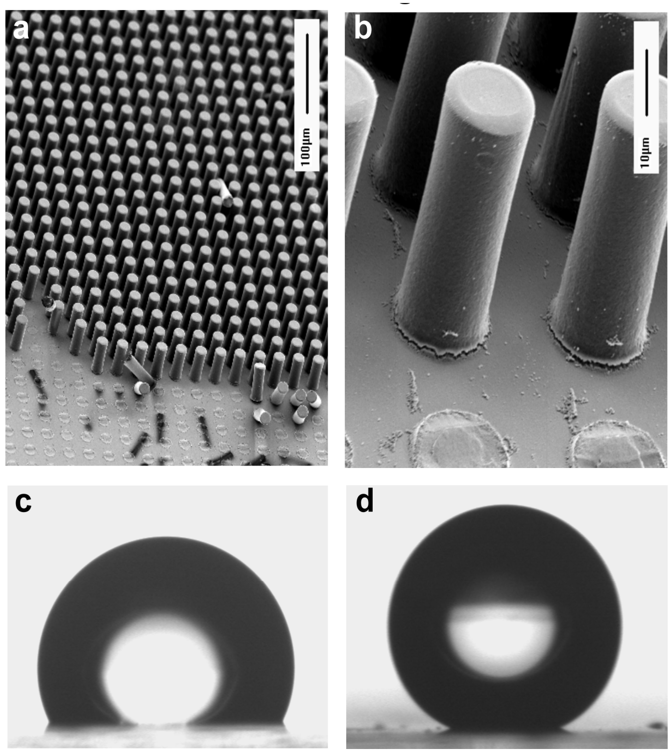


Tall structures to 45-75 µm

smooth and straight walls

Aspect ratios up to ~ 7

Effect on Water



a), b) Pillars *D*=15 µm, *L* = 2*D*

c) Flat and hydrophobic

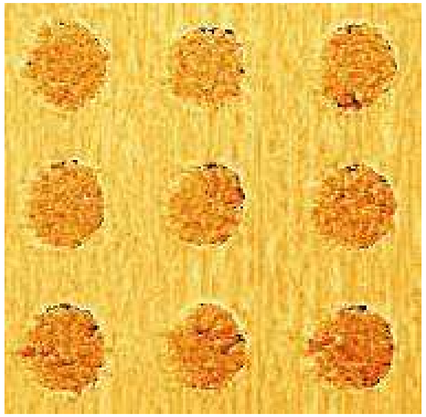
d) Tall and hydrophobic

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

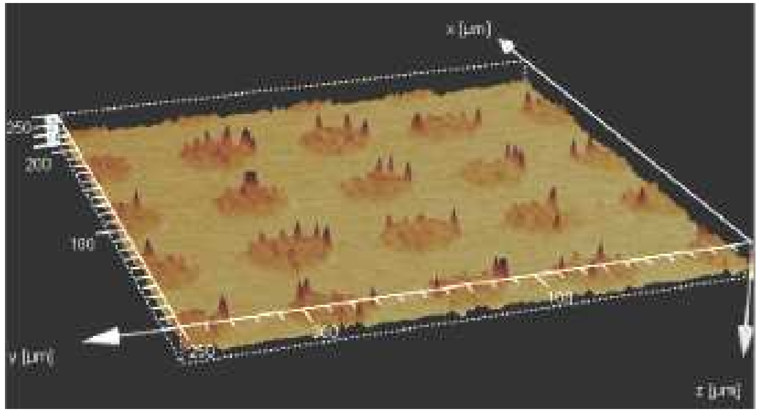
<u>Electrodeposited Surfaces</u>

Diffusion limited aggregation –copper acid bath, fractal roughness

Base Cu electroplated surface

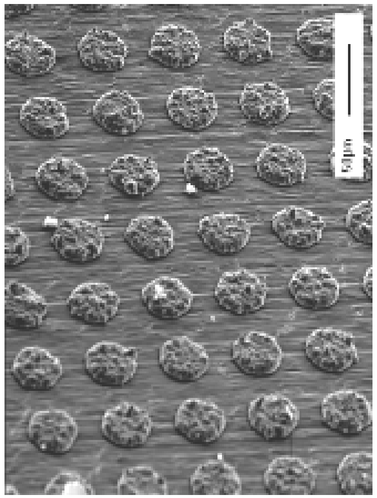


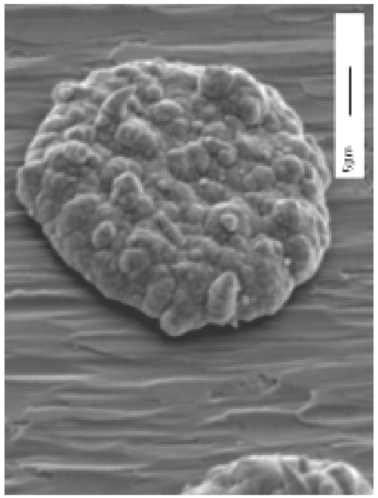
Confocal image of a 30µm textured electroplated Cu

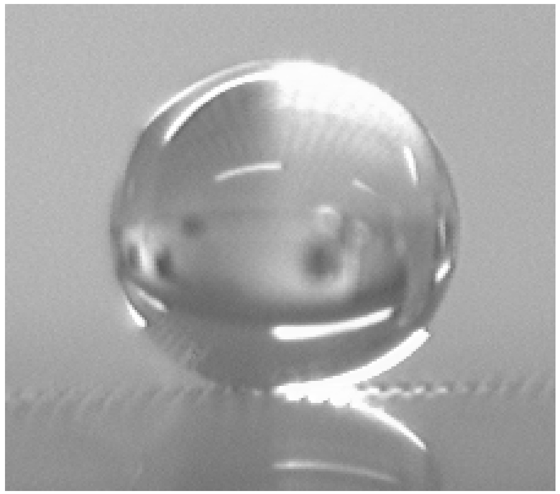


3D view of a electroplated copper sample

"Chocolate Chip Cookies" - Electroplating through a mask



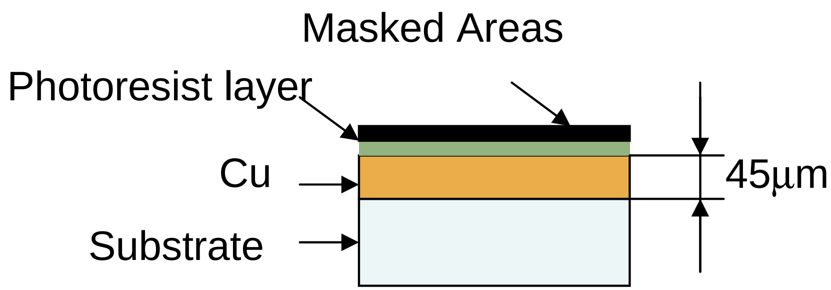


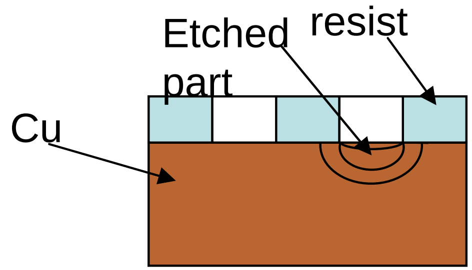


<u>Reference</u> Shirtcliffe *et al*, Adv. Maters. <u>16</u> (2004) 1929-1932; Shirtcliffe *et al*, Langmuir <u>21</u> (2005) 937-943.

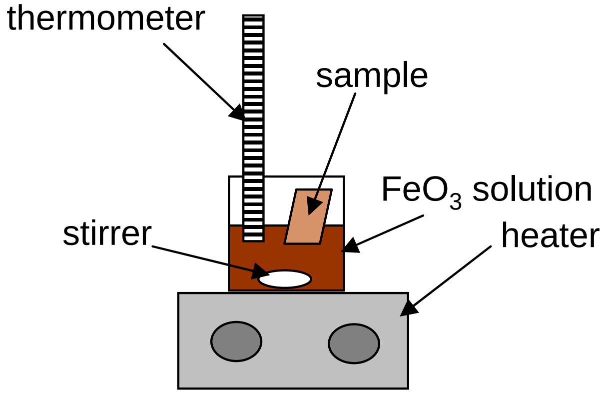
Etched Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

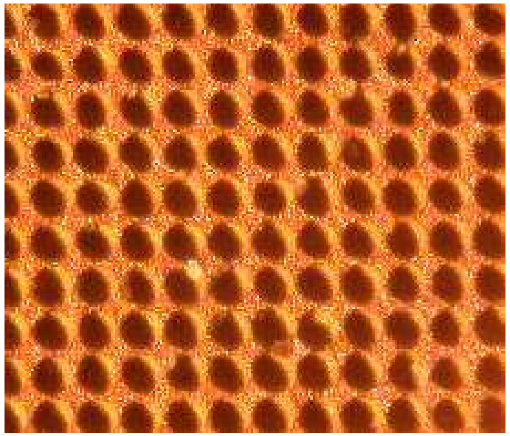




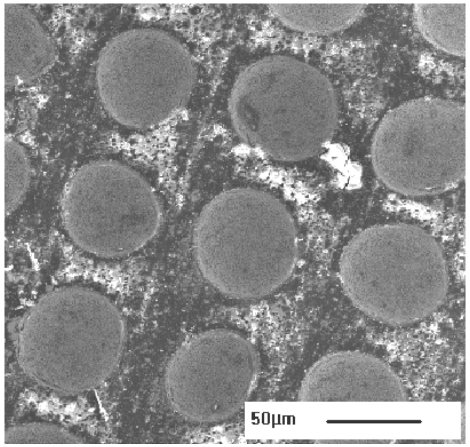
hole growth



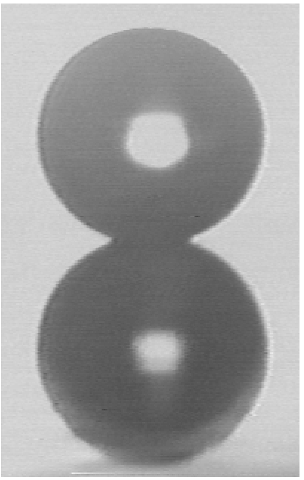
Setup of the copper etching



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

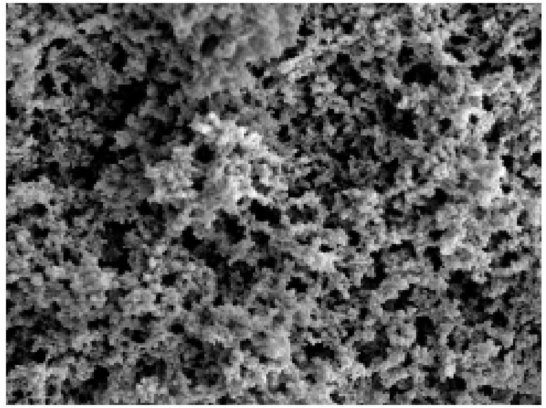
  Usually organosilicon compounds hydrolysed to form intermediates

  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

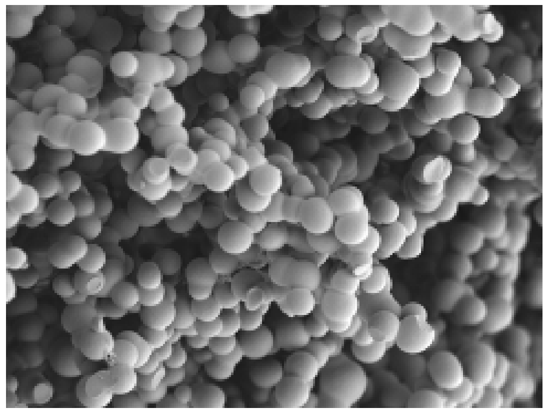
  Intrinsically hydrophobic

  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

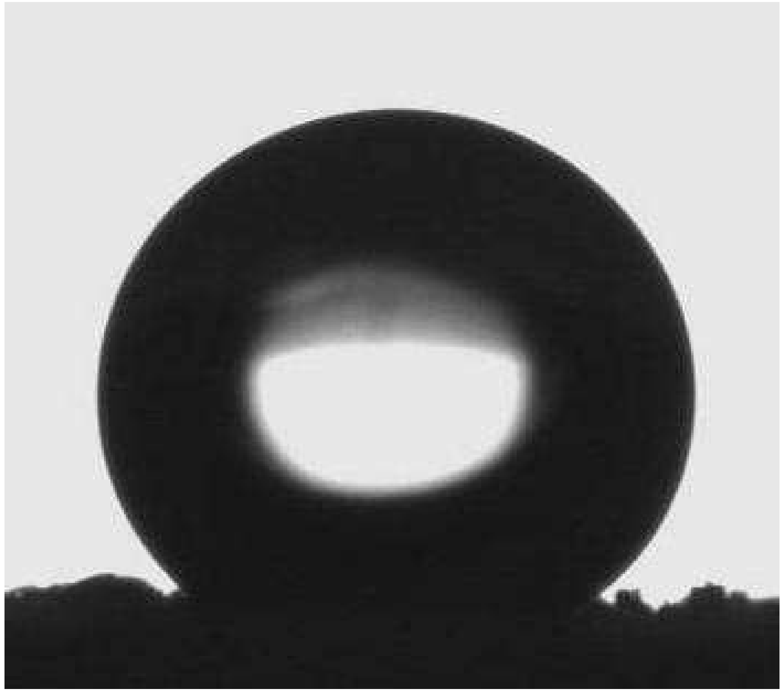


10 µm

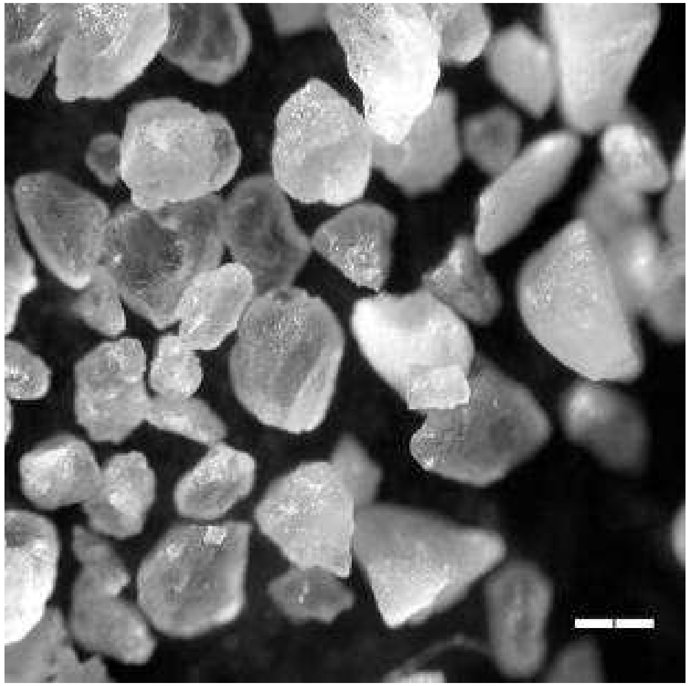
Reference Shirtcliffe *et al*, Langmuir 19 (2003) 5626-5631

Super Water-Repellent Sand/Soil

Sand with139°



Shape and Packing



200 μm

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)

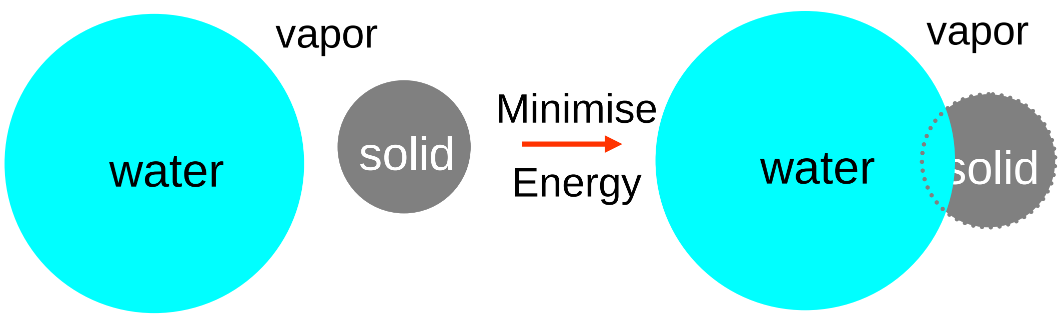
Reference McHale *et al*, Eur. J. Soil Sci. 56 (2005) 445-452; McHale *et al*, Hydrological Processes (2007).

Liquid Marbles

Loose Surfaces

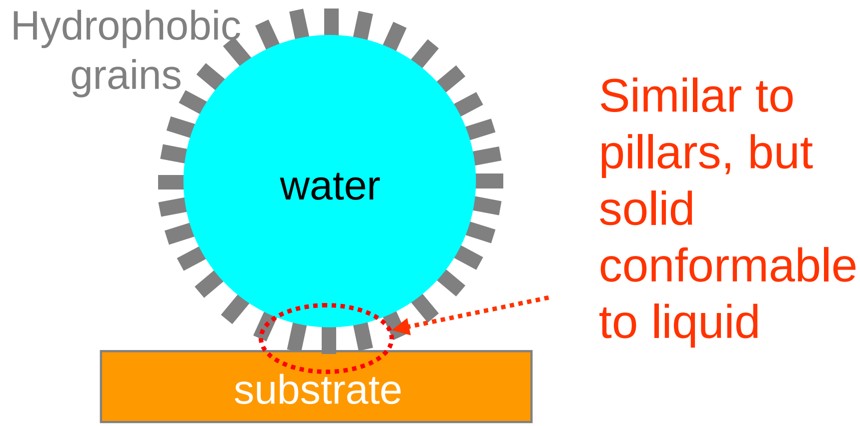
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

Hydrophobic Grains and Water



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

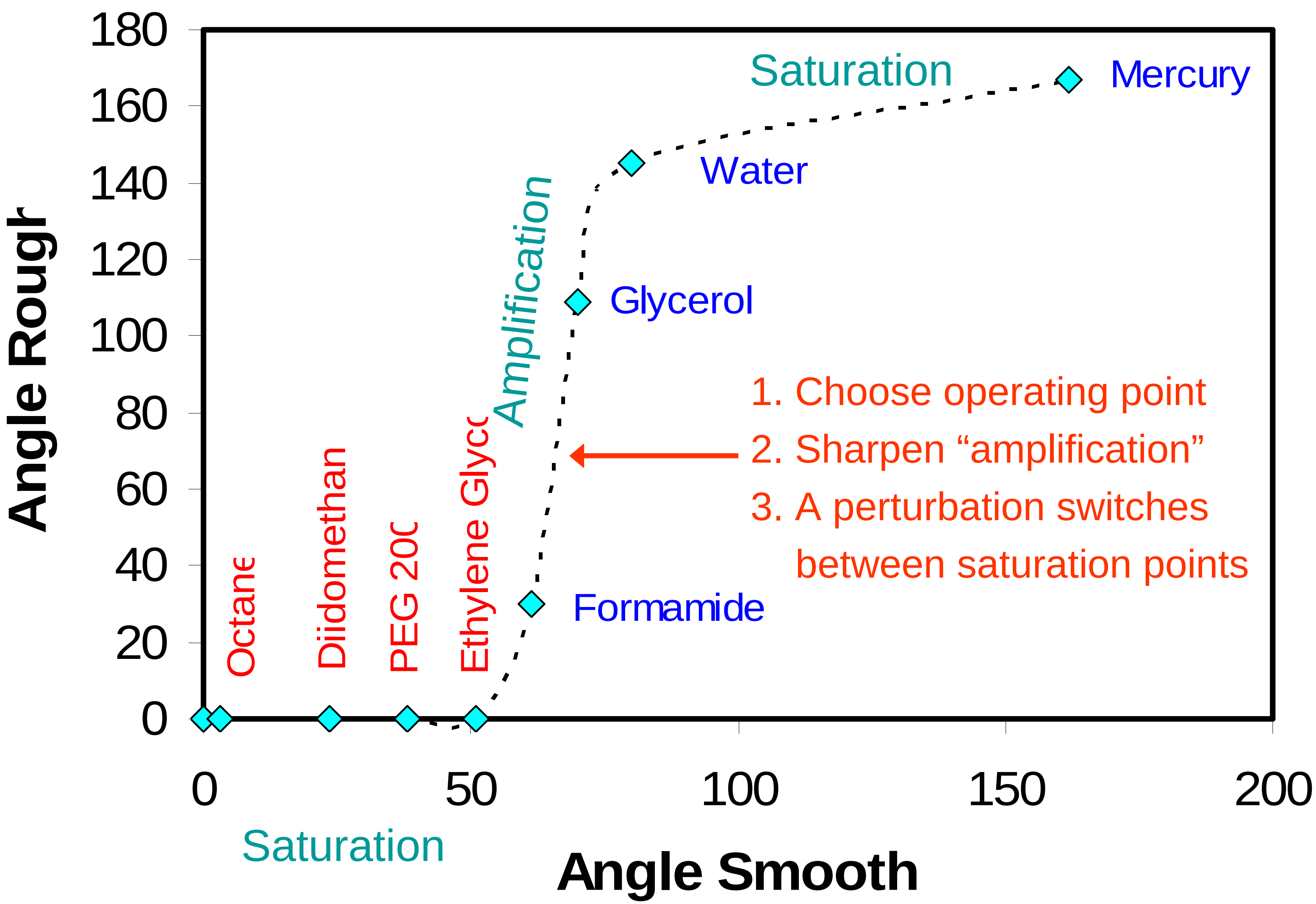
Energy is always reduced on grain attachment



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

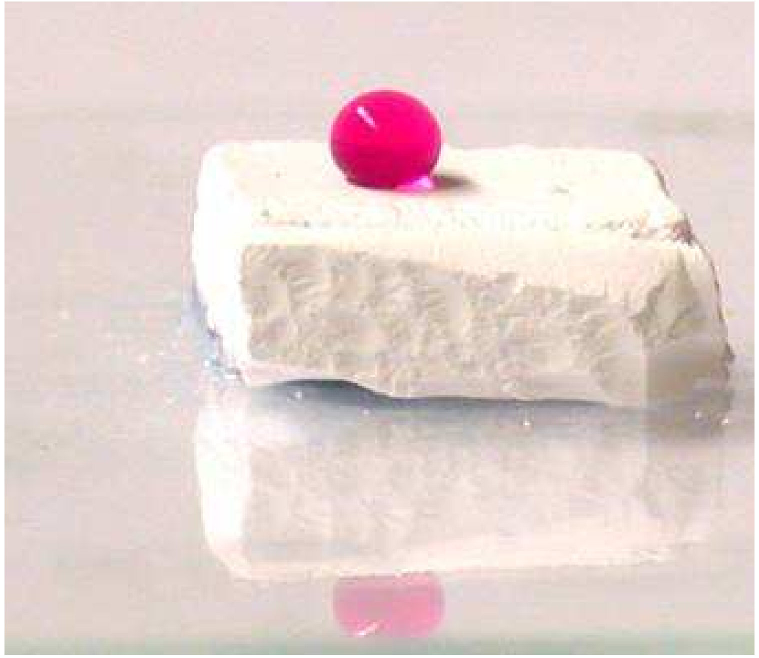
Switching and Super-spreading

“Digital” Switching - Recall



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

Sol-Gel Foams – Switching from S/H

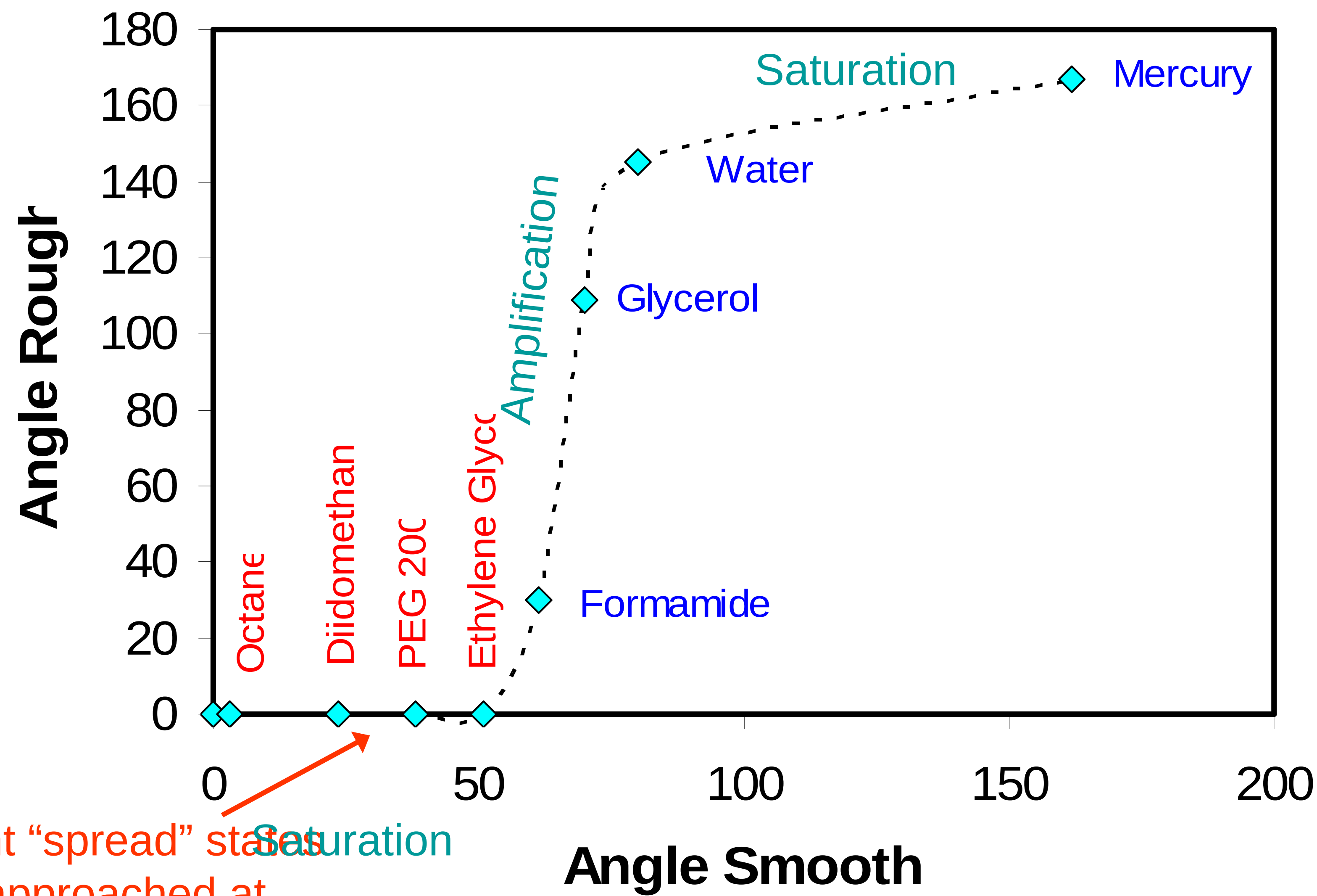


Foam heated (and cooled) prior to droplet deposition

- 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



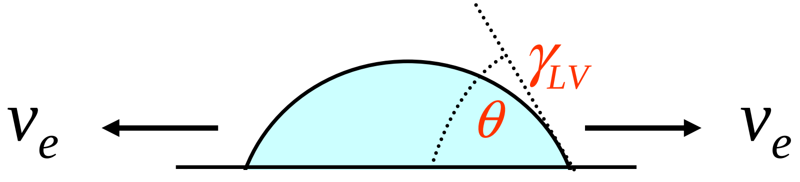
Different “spread” states are approached at different rates

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 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

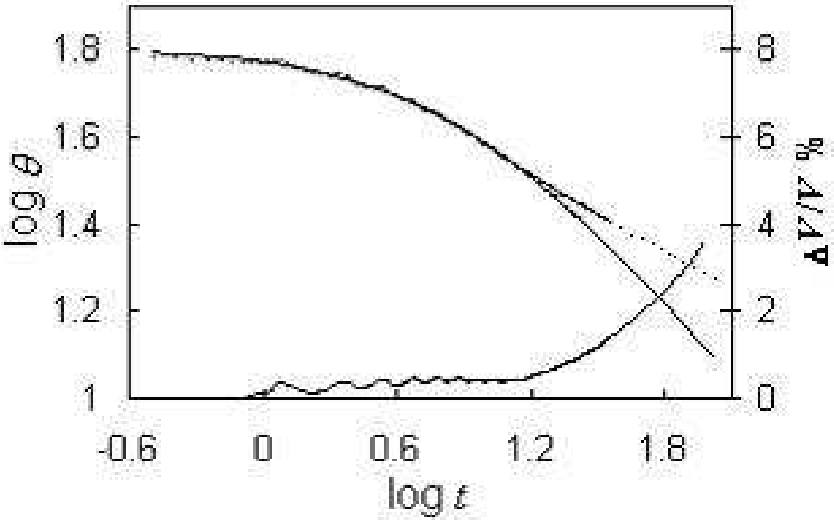
Weak roughness (or surface texture) modifies edge speed:

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

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

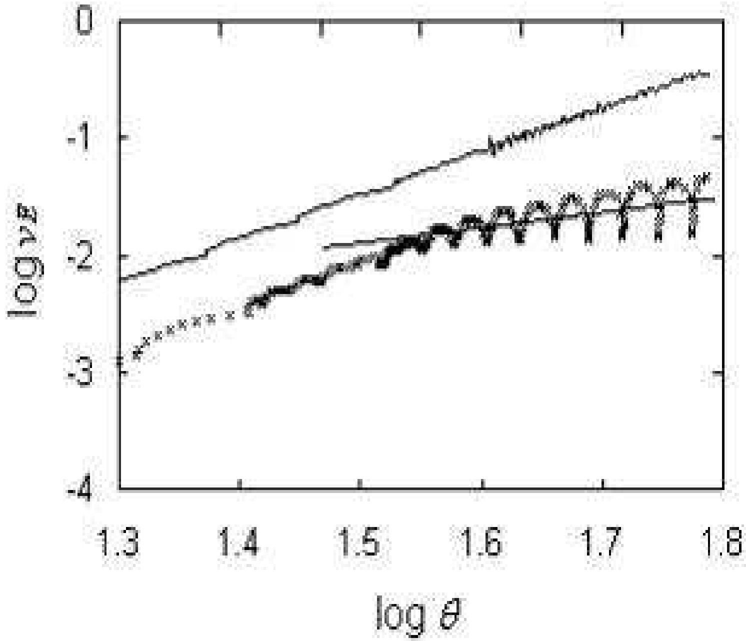
Superspreading of PDMS on Pillars

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



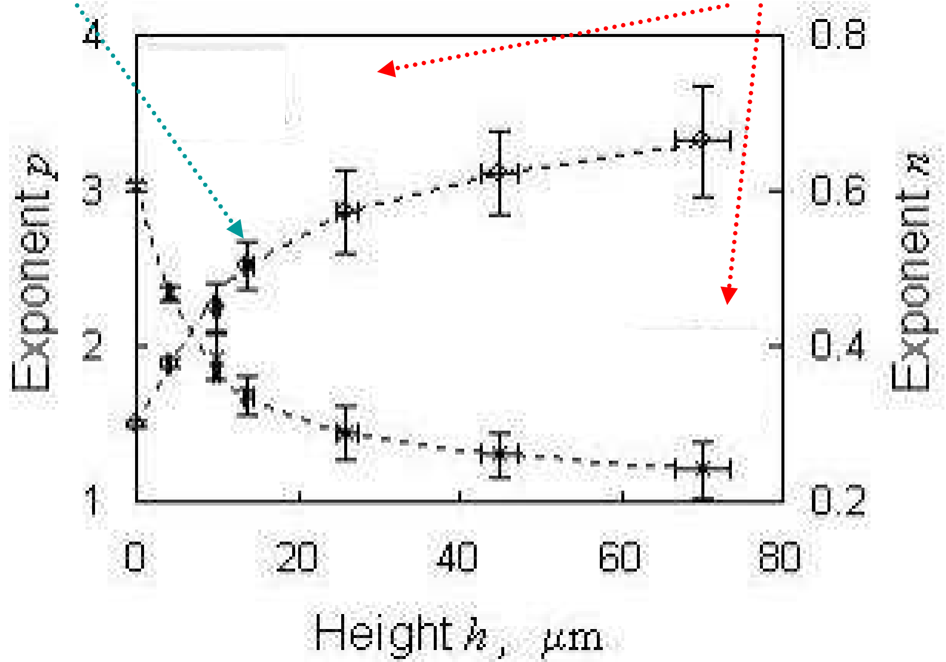
$$v_E \propto v^* \theta^p$$

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



Effect of substrate on PDMS

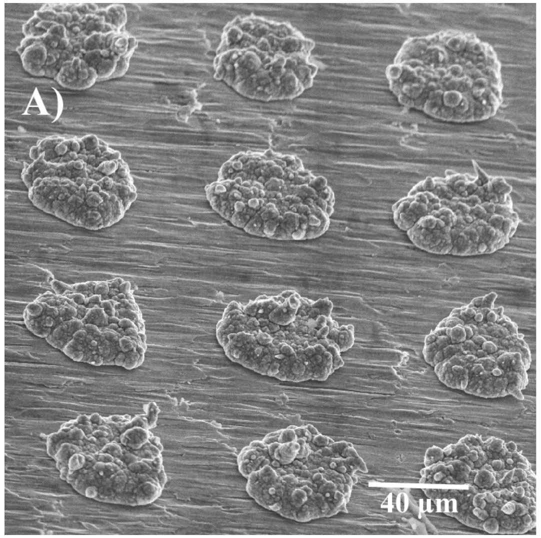
Effect of substrate on water

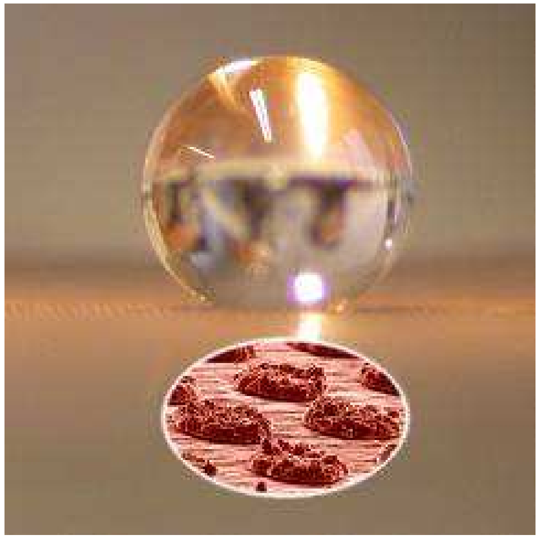


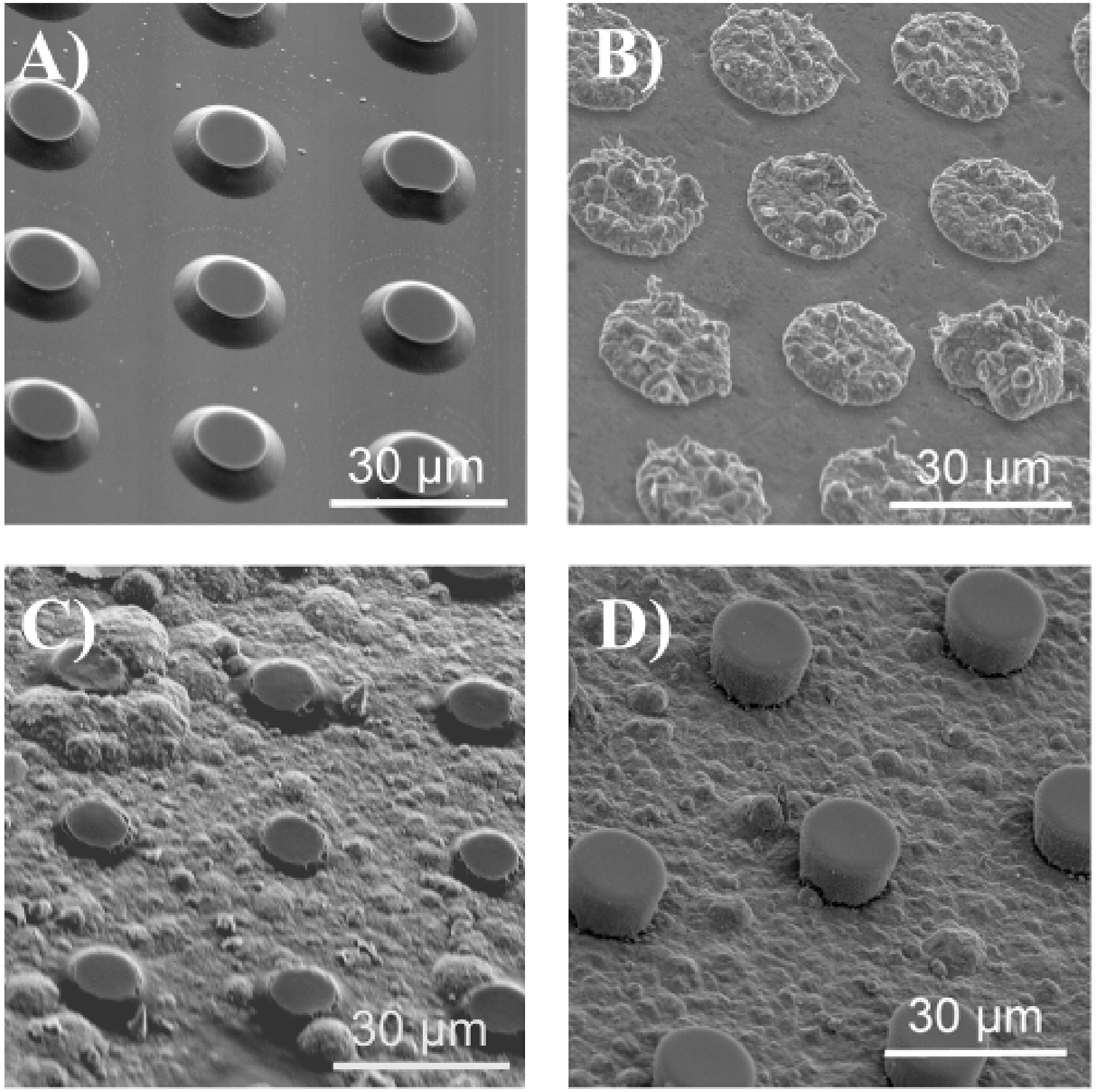
References McHale, *et al*, Phys. Rev. Lett. 93, (2004) article 036102.

Complex Surfaces

Double Length Scale Systems





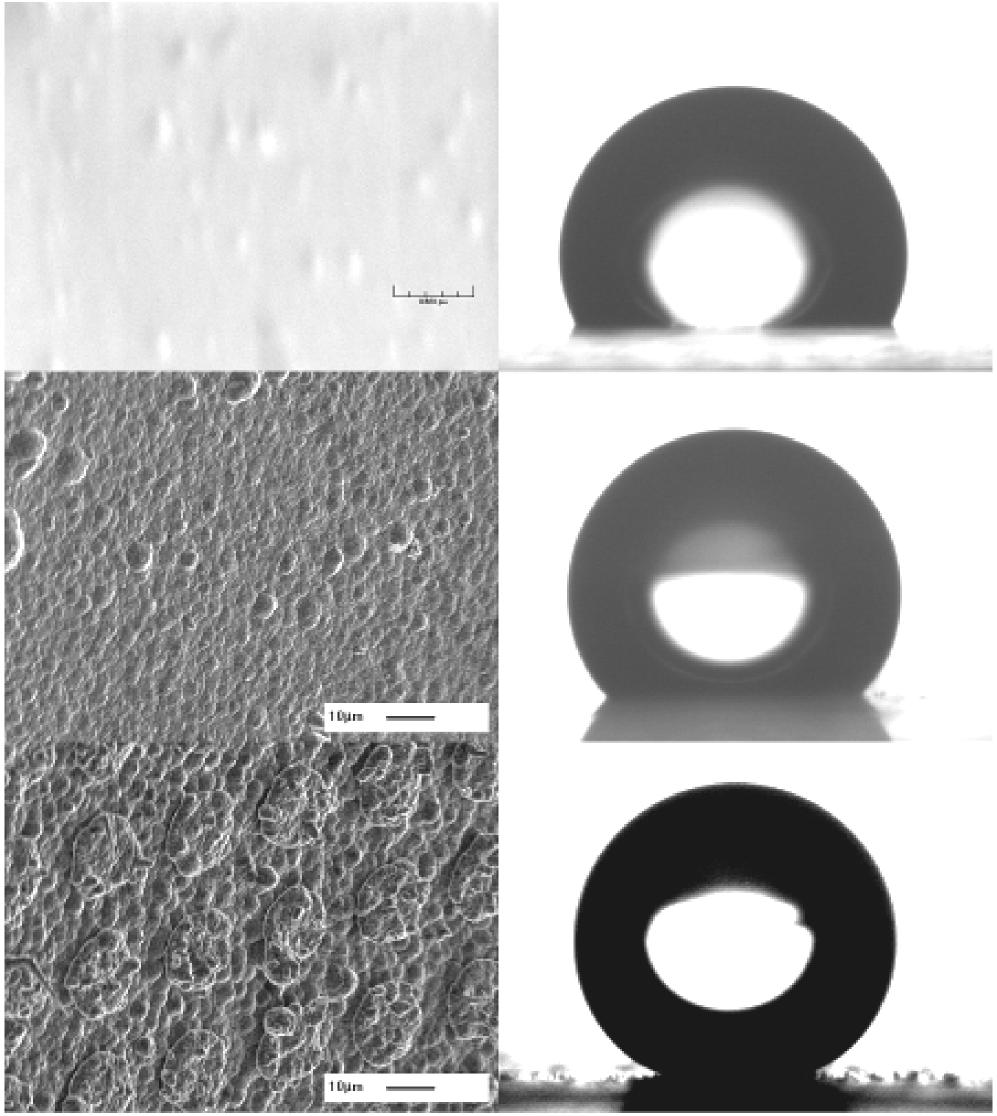


Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932 (Theory is in the supplementary information).

Combining Slight Roughness and Texture

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

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

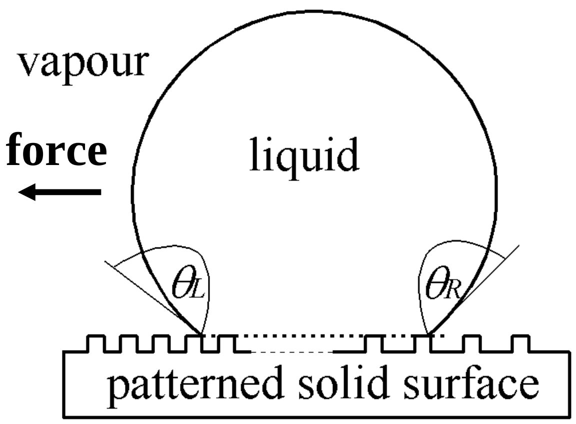
Make contact angle depend on position and surface chemistry $\theta(x, \theta_e^s)$

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 $\Rightarrow$ driving force



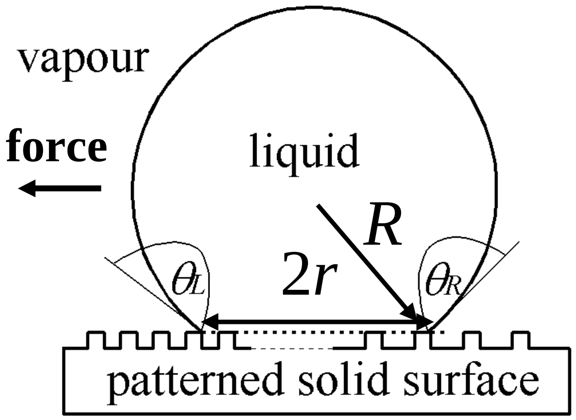
$$Force \propto \gamma_{LV}(\cos\theta_R - \cos\theta_L)$$
$$\propto \gamma_{LV}(f_R - f_L)(\cos\theta_e^s + 1)$$

Need to overcome contact angle hysteresis

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

Conditions for Motion

Spherical Cap



Assume small contact area:

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

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

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

Defect Based Hysteresis Force

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

Drive Condition

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

More superhydrophobic (f_{ave}) — Larger droplets (R)

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

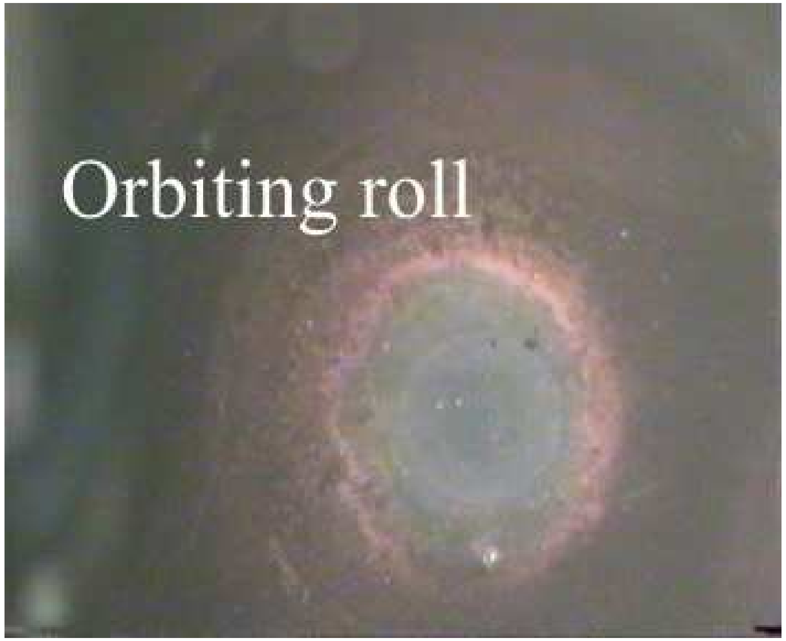
Self-Actuated Motion

Radial Gradient in Contact Angle

Electrodeposited copper – Diffusion limited aggregation

Fractal–like to overcome contact angle hysteresis

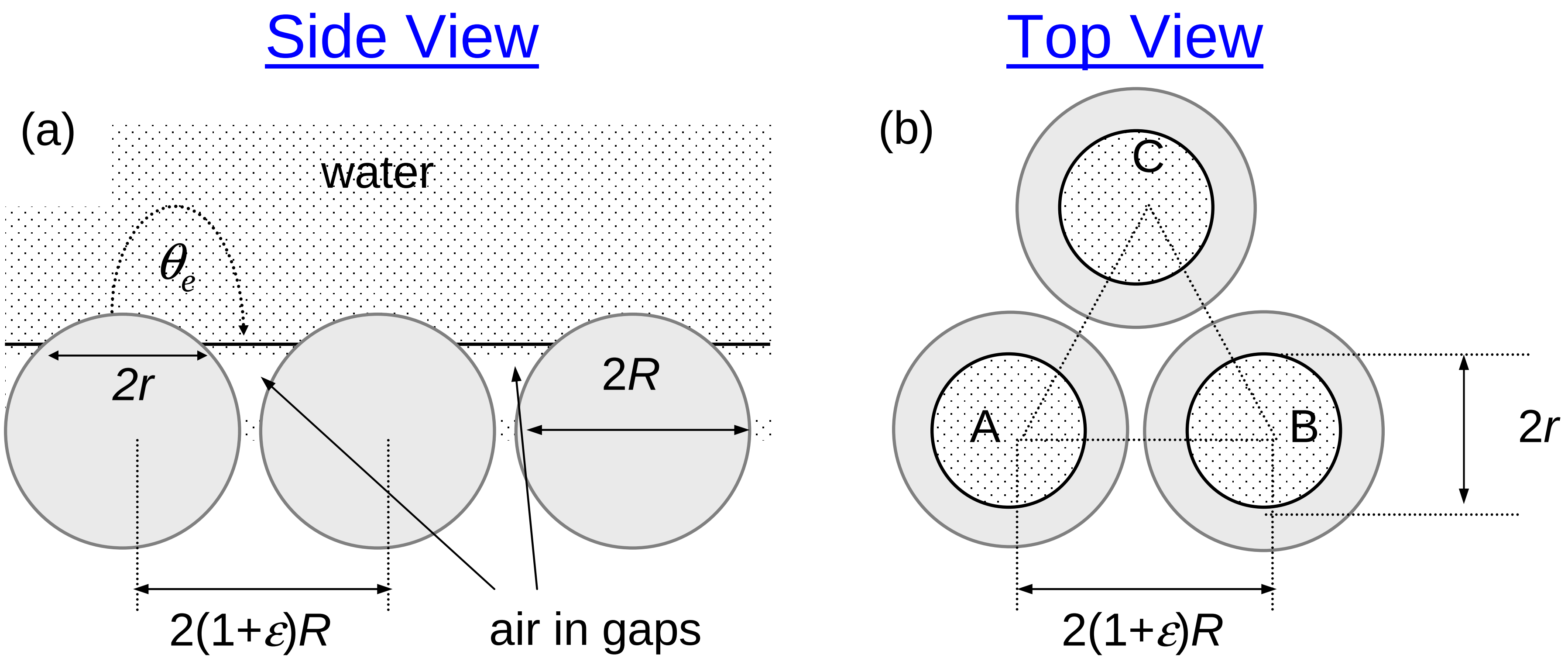
Radial gradient $\theta(r)$=110°$\rightarrow$ 160°



Reference McHale *et al*, to be submitted.

Wetting to Porosity

Simple Model of Soil



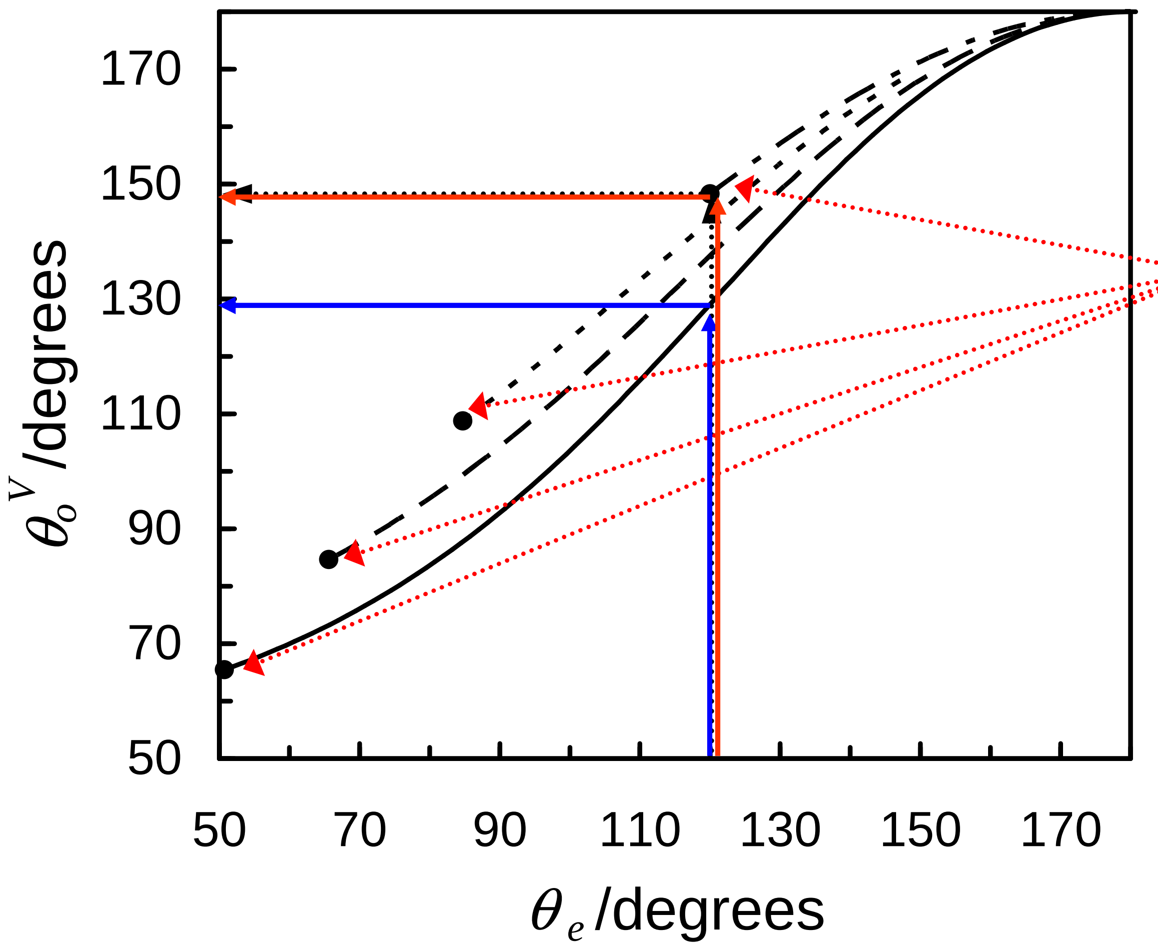
Assumptions

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.

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

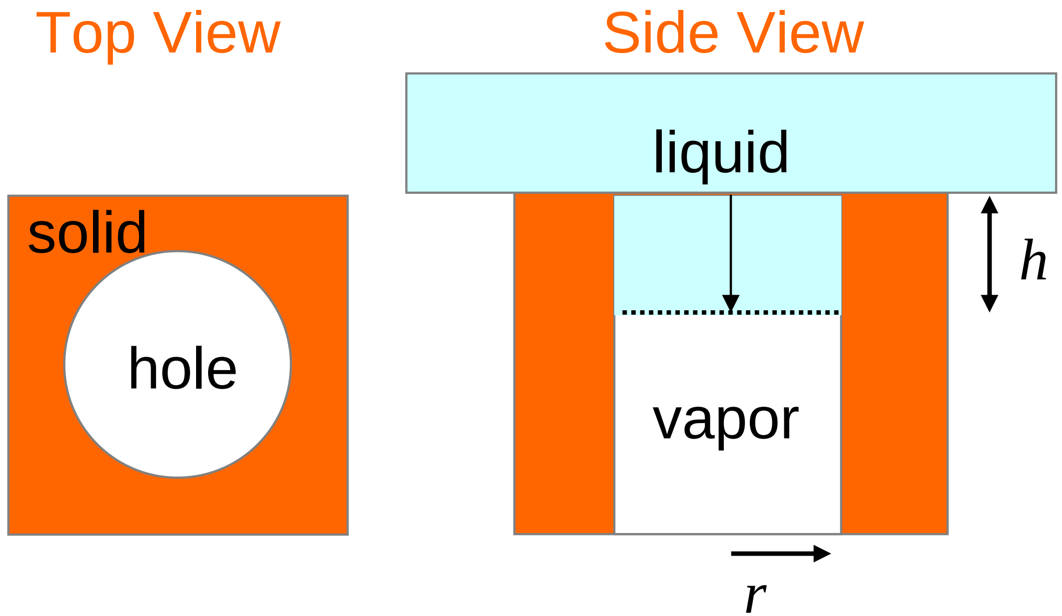
Separation when bead pushes up through hole is $\varepsilon_{max} = \sqrt{3} - 1 = 0.732$

Reference McHale *et al*, Hydrological Processes (2007).

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



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

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

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

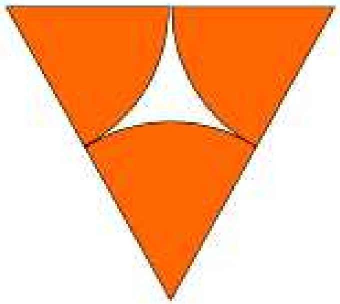
But soil is not a set of parallel pipes

Transition from Wetting to Porosity

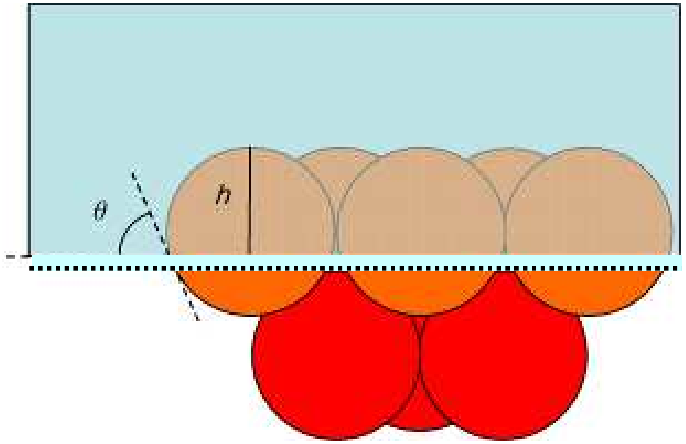
Assumptions

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

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

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

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

4. Critical contact angle, θ_c, when h_c reached

θ_c=50.73°

*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

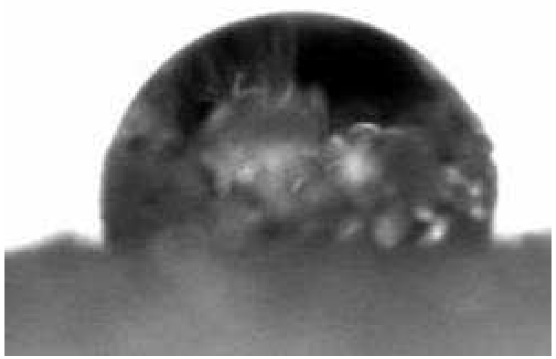
Fluorocarbon Bead Packs

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°

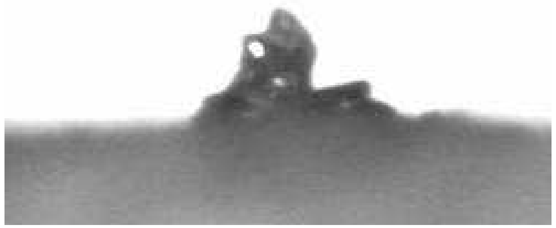
Fluorocarbon Coated Sand

Penetration occurs for hexane



Octane (72°)

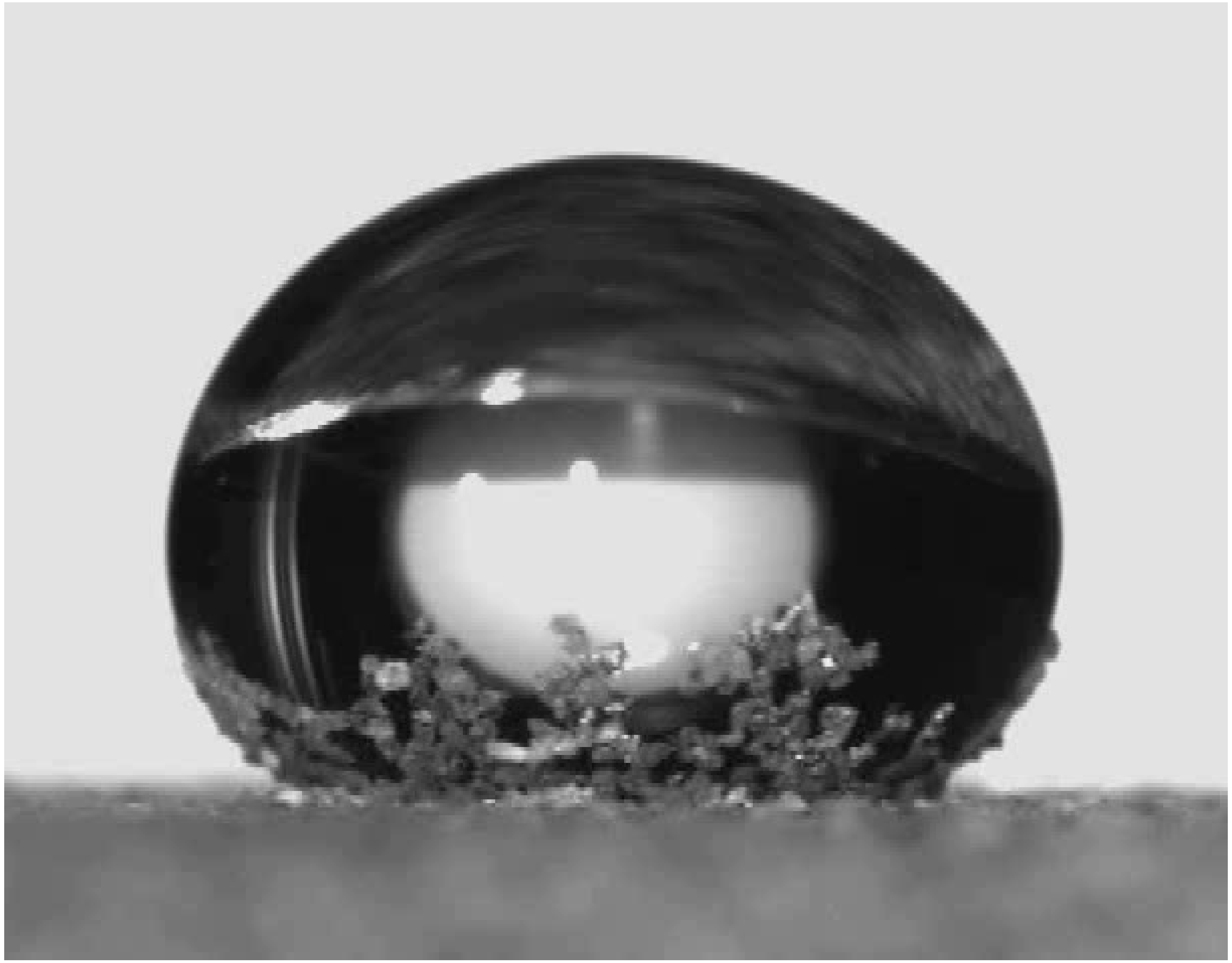
Heptane (65°)



Hexane (61°)

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

Water Droplet Evaporation on Hydrophobic Sand



Reference Shirtcliffe *et al.*, APL 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° should win and remain at the interface

Ejection: Surface–into-Air

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

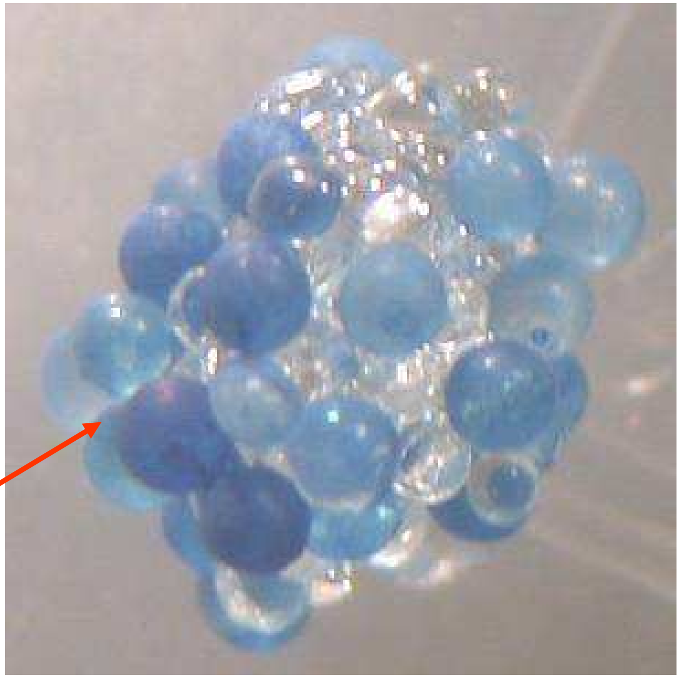
Ejection: Surface–into-Liquid

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

Experimental Test

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

After evaporation blue particles are on outside of clump



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 90^o

   (e.g. 51^o-65^o)

3. Fixed versus Loose Solid Structures

   Grains can re-arrange – droplets become liquid marbles

   Evaporation drives self-coating and grain sorting

The End

Acknowledgements

Funding Bodies

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

  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, Herbertson, Roach and Shirtcliffe), Other staff at NTU (Dr Newton, Prof. Perry & Pyatt), and external collaborators

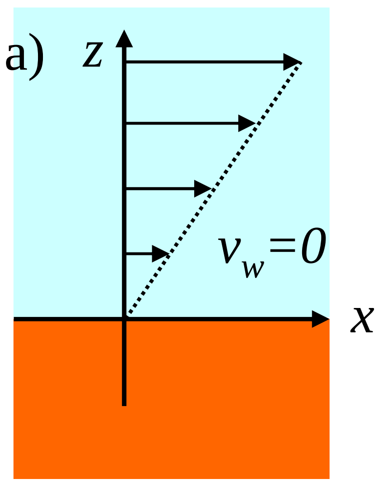
EPSRC Engineering and Physical Sciences Research Council

NOTTINGHAM TRENT UNIVERSITY

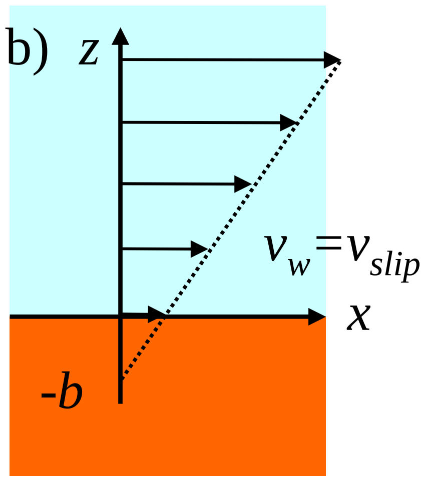
NATURAL ENVIRONMENT RESEARCH COUNCIL

Slip by Simple Newtonian Liquids

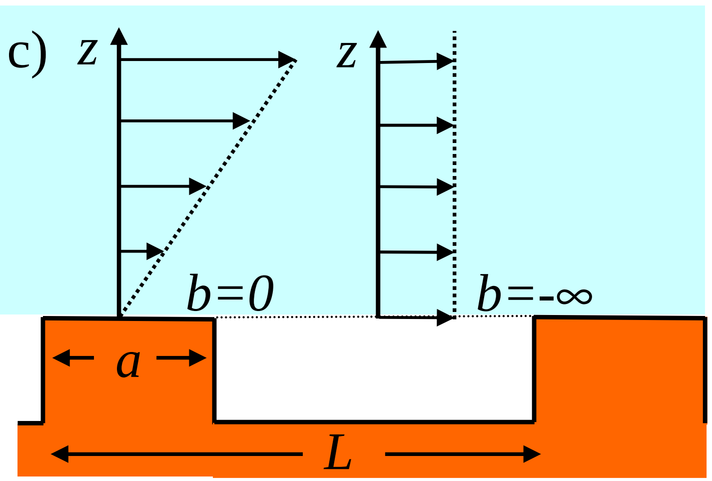
No Slip



Slip



Mixed

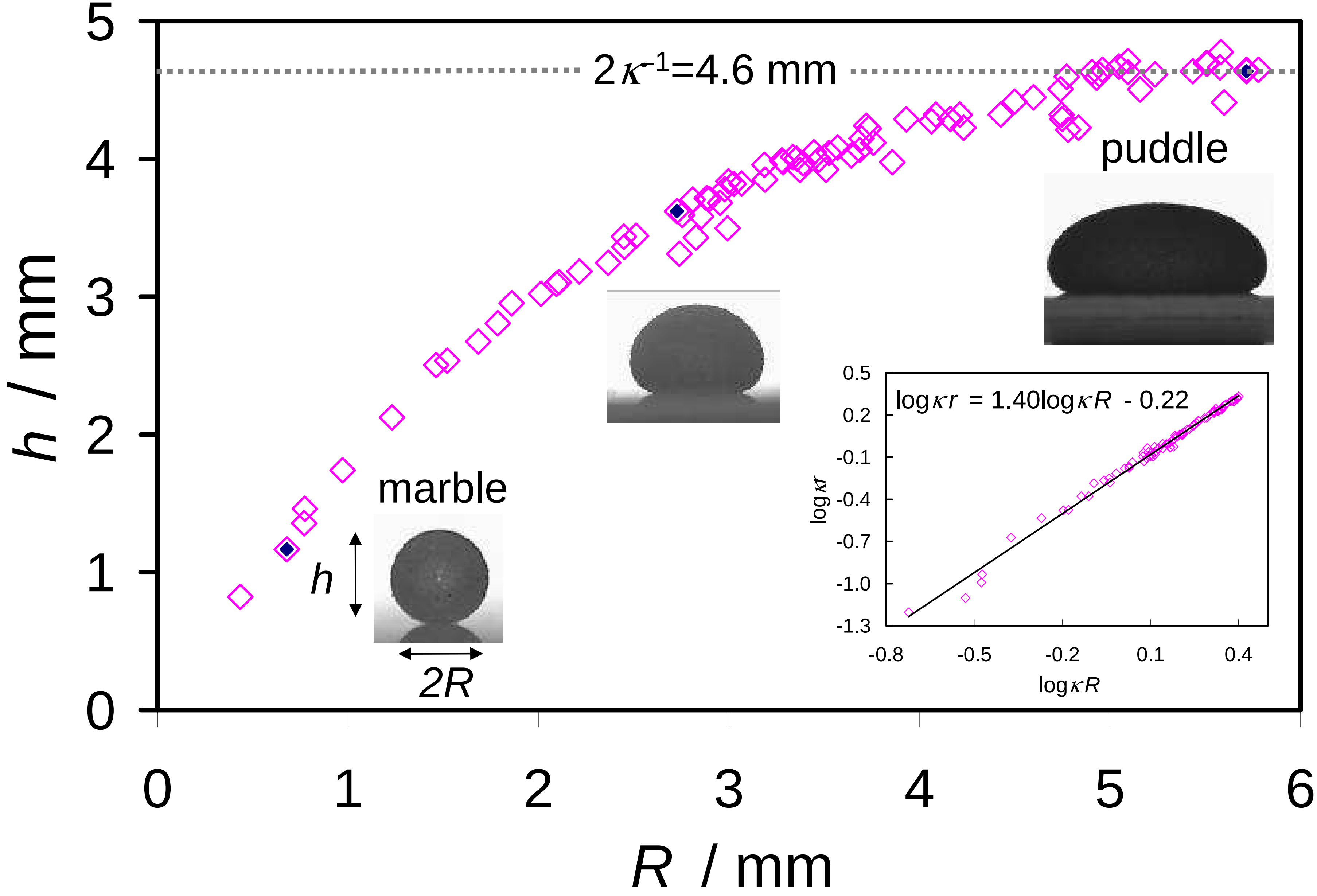


Experimental Evidence – Steady Flow

1. Theory[1,2] supported by simulations suggests $b = L\, f(\varphi_s)/2\pi$
2. Micro-PIV experiments detailing flow profiles[3] (h=1-7 μm ⇒ 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)

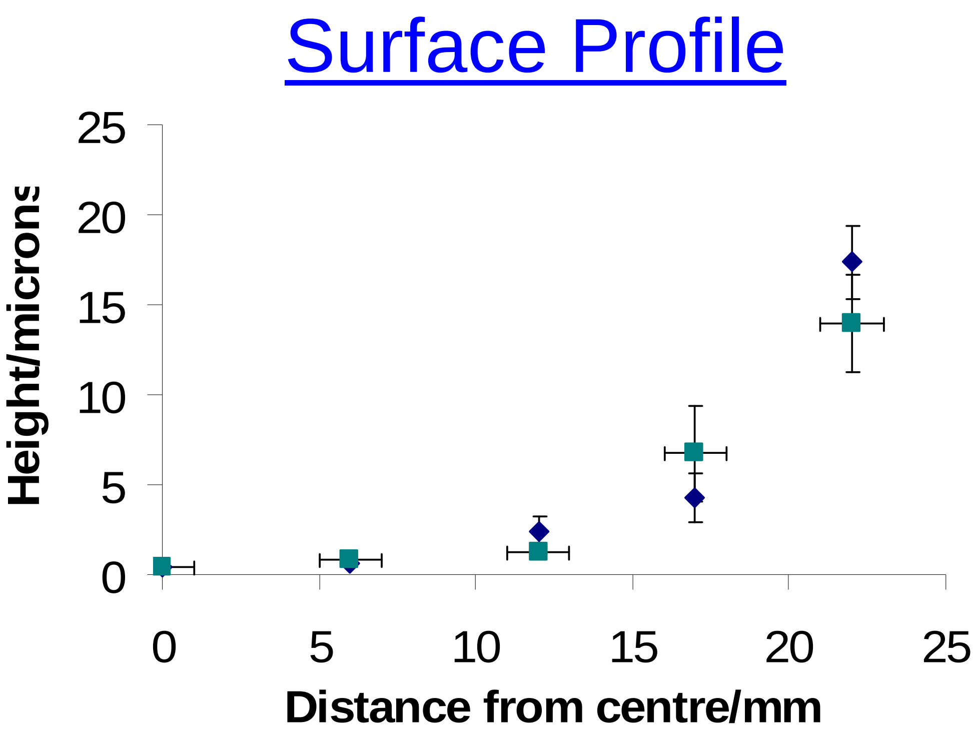


Surface Profile

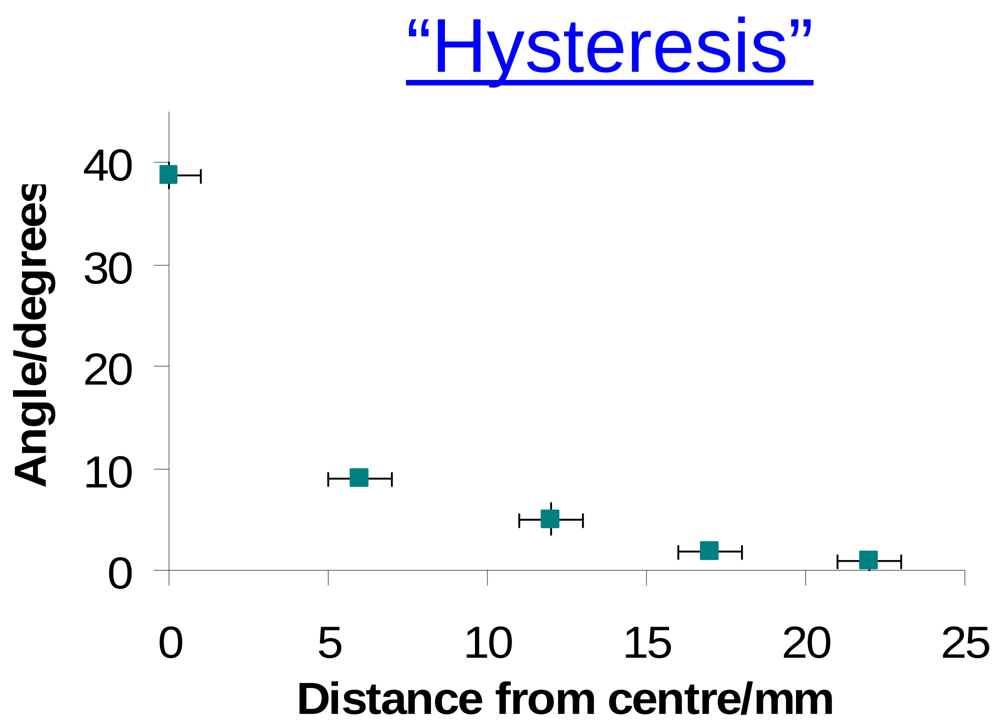
Mechanism for Motion

Small slope on extremely low hysteresis surface?

Truly contact angle driven?



Multiple profiles have been taken along different radial lines

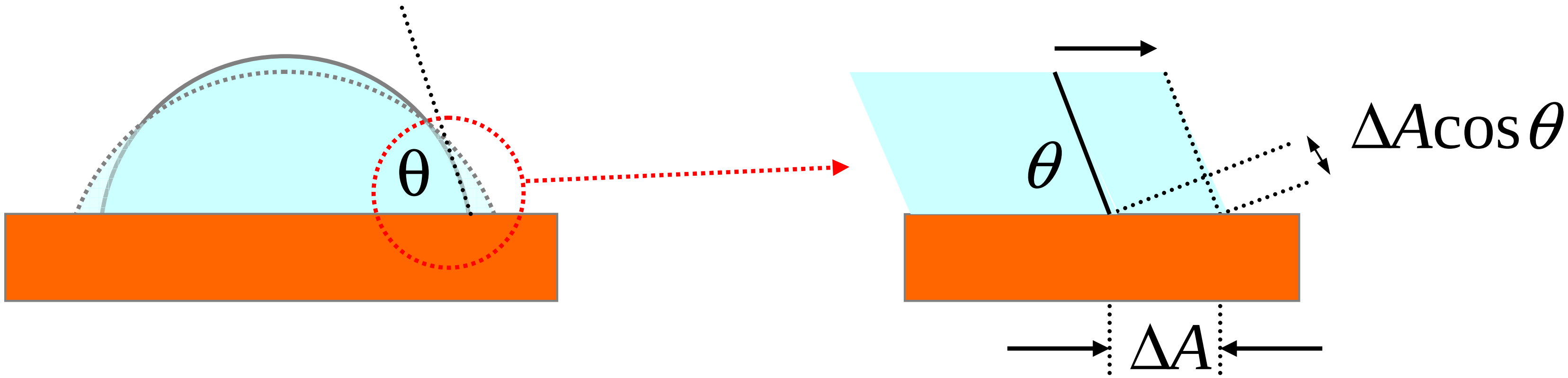


Using radial view and tilt table tangential to radius

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

(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)

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

Equilibrium is when $\Delta F = 0$ $\Rightarrow$

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

Young's Law