NOTTINGHAM TRENT UNIVERSITY

Superhydrophobic Surfaces

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Overview

1. Superhydrophobicity

- Water repellence in nature
- Mechanisms

2. Surfaces & Materials

- SU-8 photolithography
- Etching and electrodeposition
- Sol-gel foams
- Water repellent soil
- Liquid marbles

3. Experiments & Applications

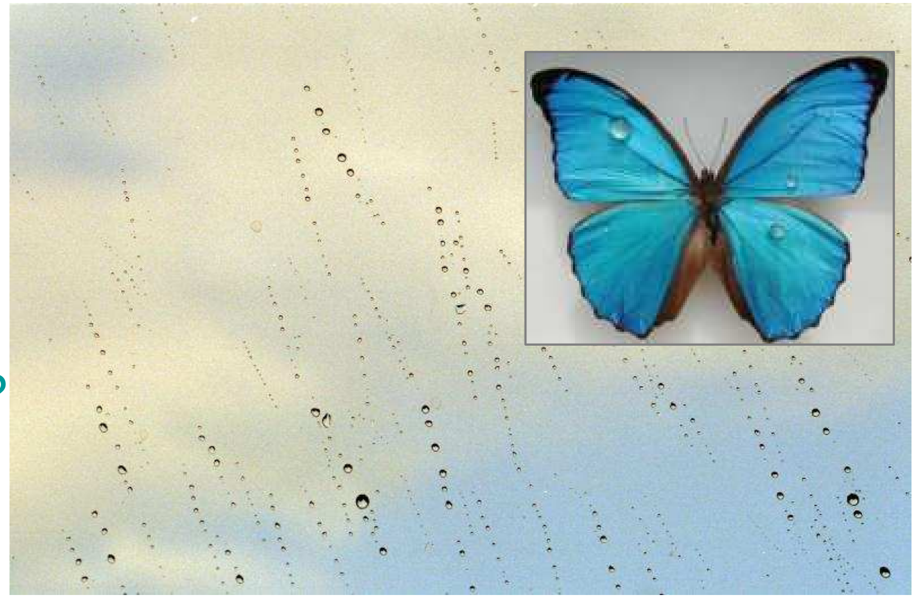
- Double length scale systems
- Superhydrophobic-to-porous transition
- Super-spreading on rough surfaces
- Path definition & self-actuated motion
- Electrowetting of liquid marbles
- A brief survey of other work

Water Repellence in Nature

Sinking and Falling?

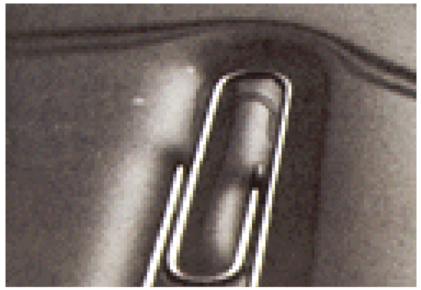
Water-on-Solids

- 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?

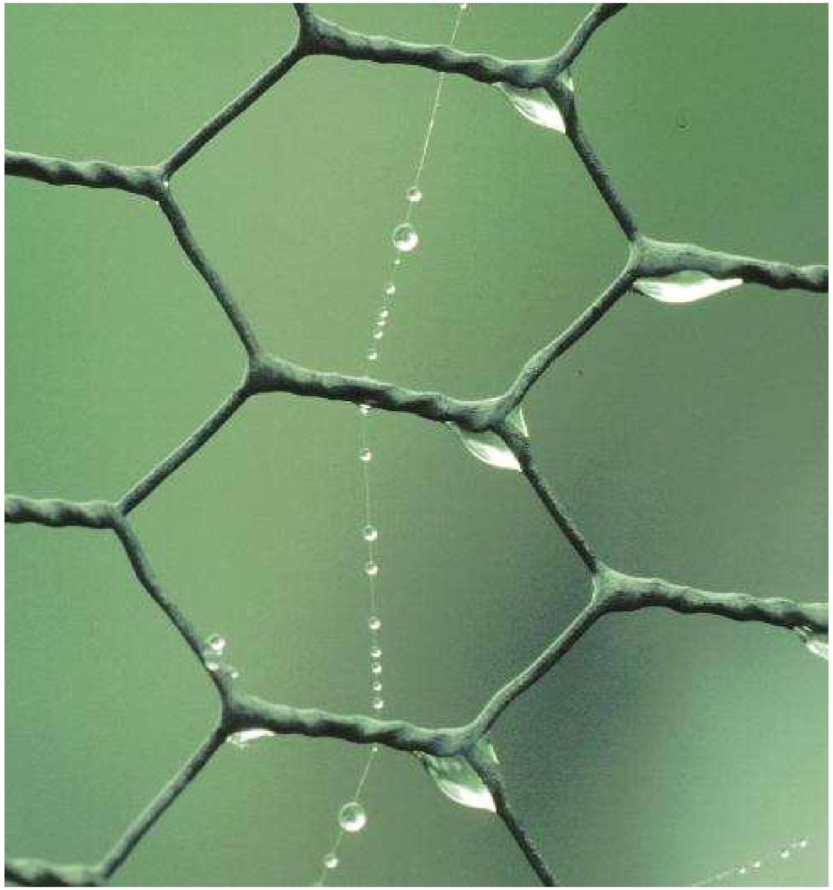
Plants and Leaves

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

Surface Tension

Liquid Surface

- Behaves as if it is in a state of tension
- Tends 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 force scales with length^3

Small sizes $\Rightarrow$ Surface tension wins

- Small means << 2.7 mm for water

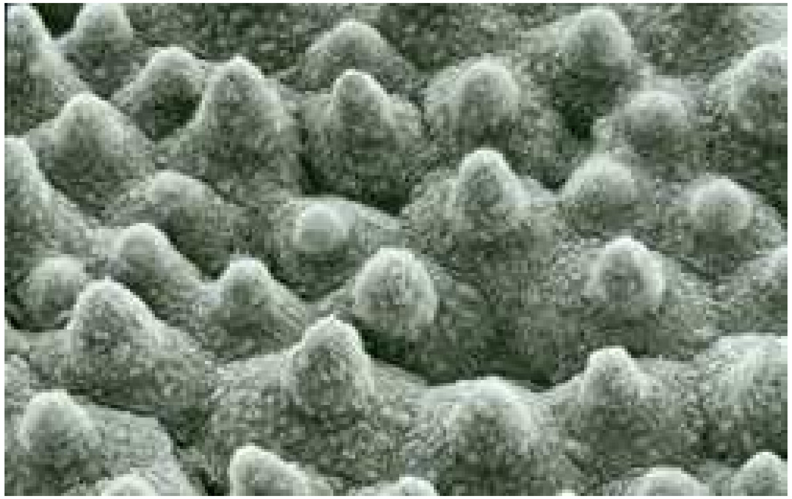
Acknowledgement www.brantacan.co.uk

The Sacred Lotus Leaf

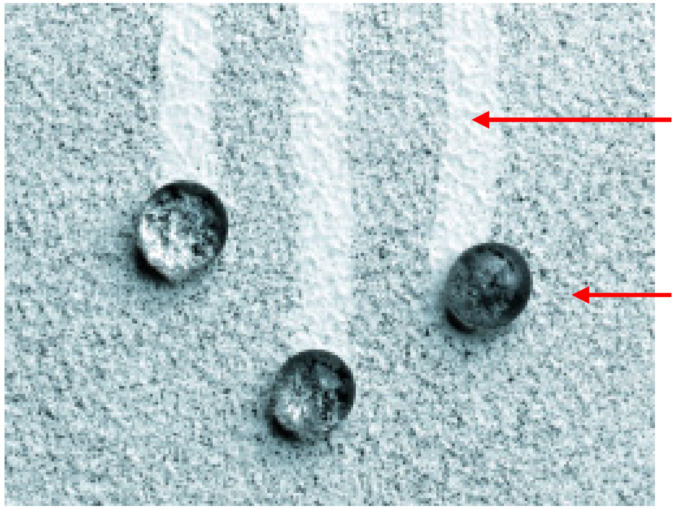
Plants

- 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



A "proto-marble"

Self-poisoning surface

Acknowledgement Neinhuis and Barthlott

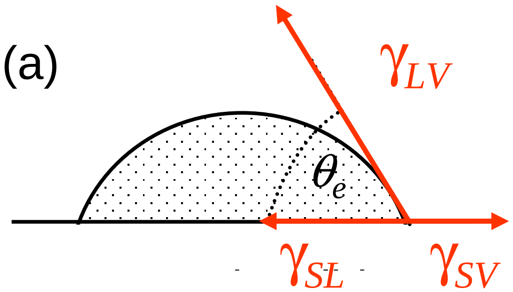
Mechanisms of Superhydrophobicity

Contact Angles & Topography

Smooth Surface

Young's equation summarises the surface chemistry

(a)



Force Balance

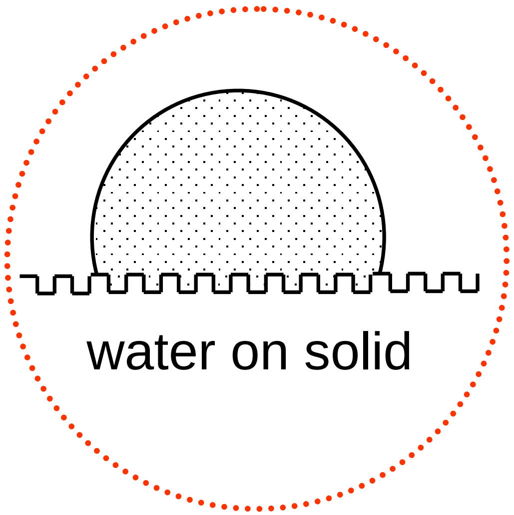
$$\gamma_{SL} + \gamma_{LV} \cos\theta_e = \gamma_{SV}$$

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

Rough/Structured Surfaces - Identical surface chemistry

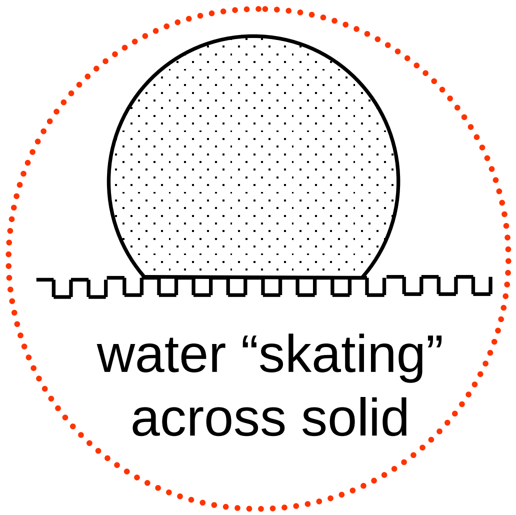
Wenzel

(b)

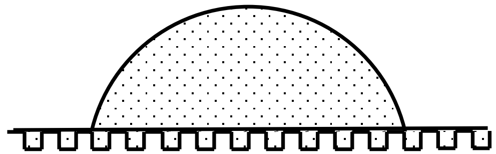


Cassie-Baxter

(c)



(d)



water on
solid-liquid surface

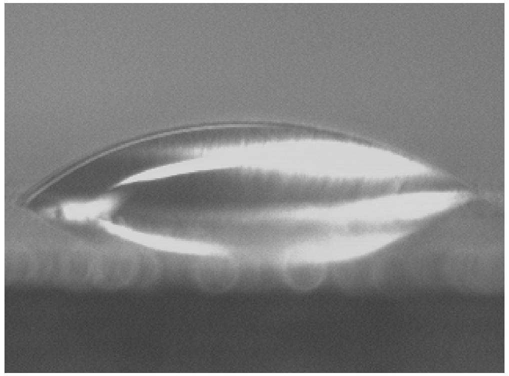
Wenzel ("Sticky")

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

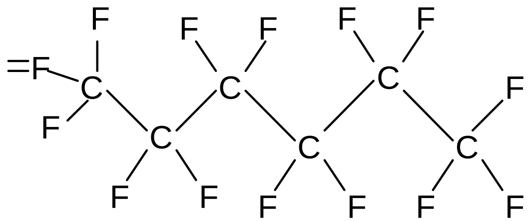
Cassie-Baxter ("Slippy")

$$\cos\theta_{CB} = f\cos\theta_e + (1 - f)\cos(180^0)$$

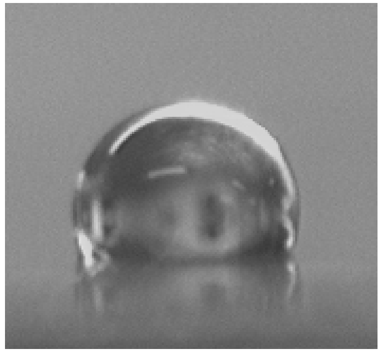
Superhydrophobic Surfaces



Simple Cu surface

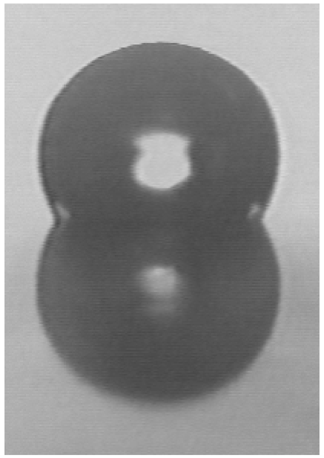


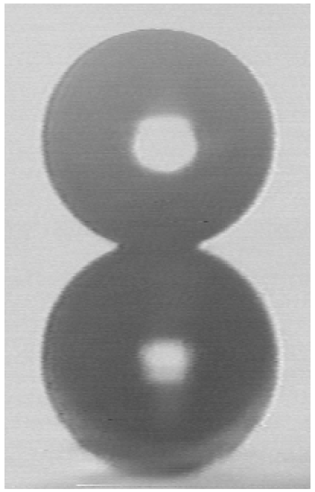
Grangers' molecular chain



Hydrophobic surface

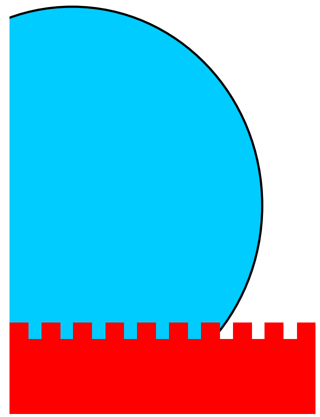
Water Drop (~ 2 mm)





Two Forms of Contact Angle Enhancement

Wenzel's Equation



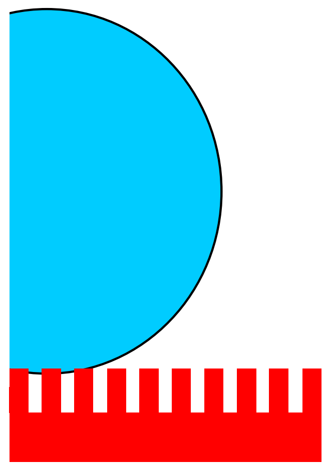
- Based on roughness, *r*

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

- Super-H with large hysteresis,

  i.e. "Sticky" surface

Cassie-Baxter Equation



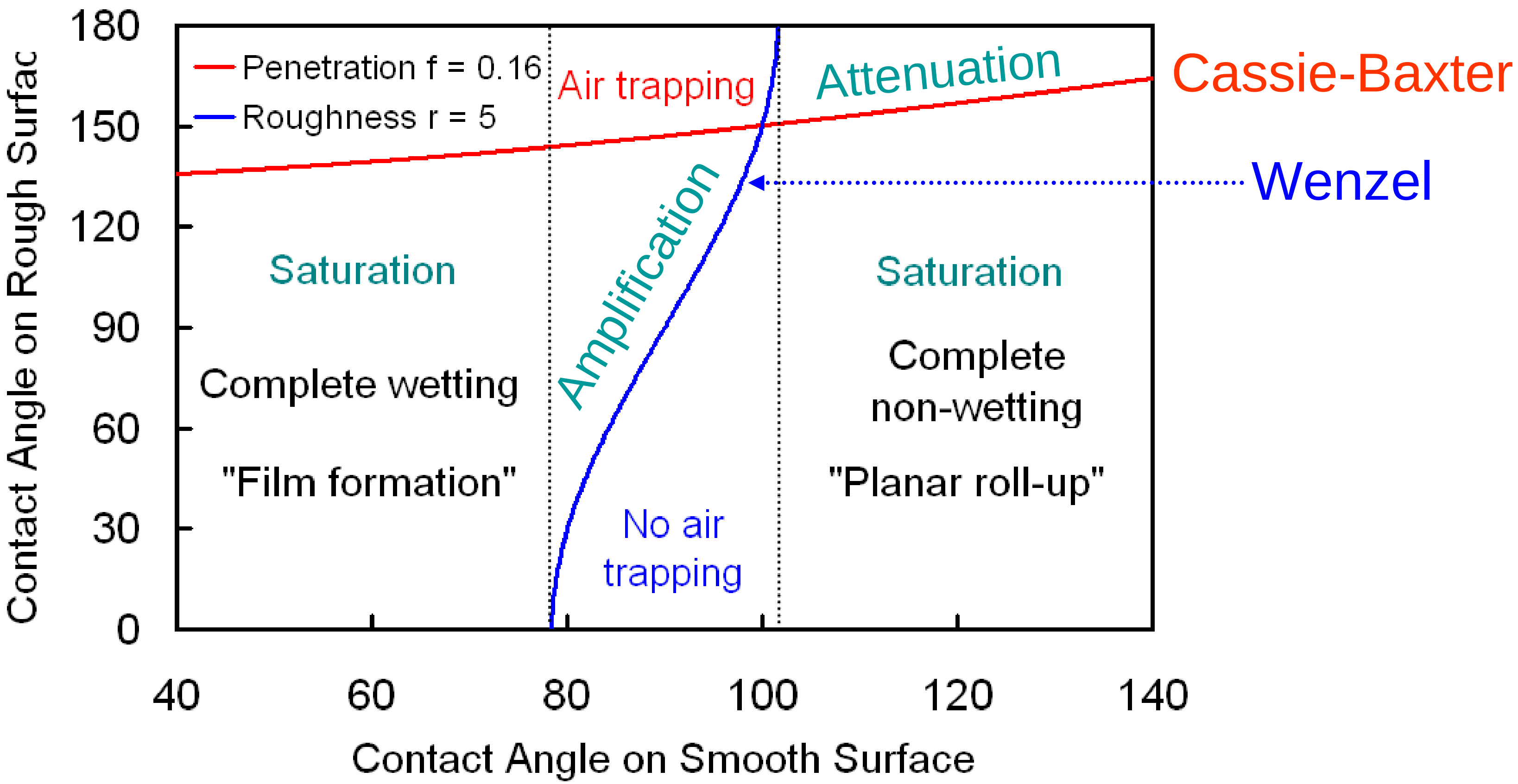
- Based on composite air-solid surface, *f*

$$\cos\theta_e^C = f\cos\theta_e^S + (1 - f)\cos(180)$$

- Low hysteresis: "Slippy" rather than "sticky" surface

Reference McHale *et al*, Langmuir 20 (2004) 10146-10149.

Effect of Topography - Theory



Roughness/Topography

θ_e^s > threshold

⇒ enhances hydrophobicity

θ_e^s < threshold

⇒ enhances film formation

Superhydrophobic

Air "trapping" ("Skating case")

⇒ most existing examples

Pressure

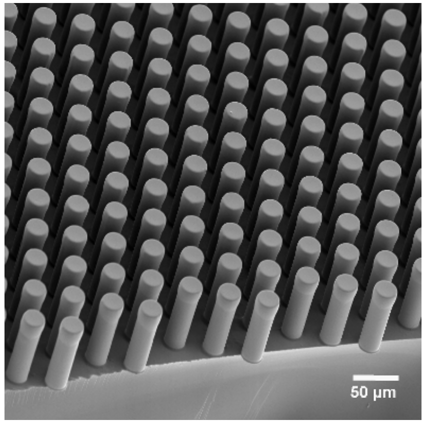
⇒ air "trapping" disappears

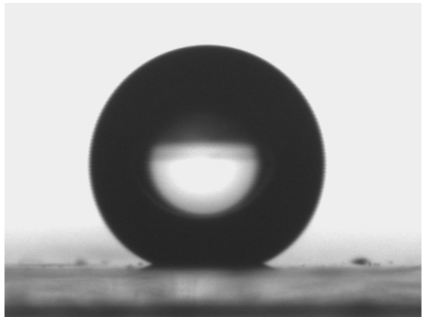
Skating-to-Penetrating Transition

Micro-Structured Surface

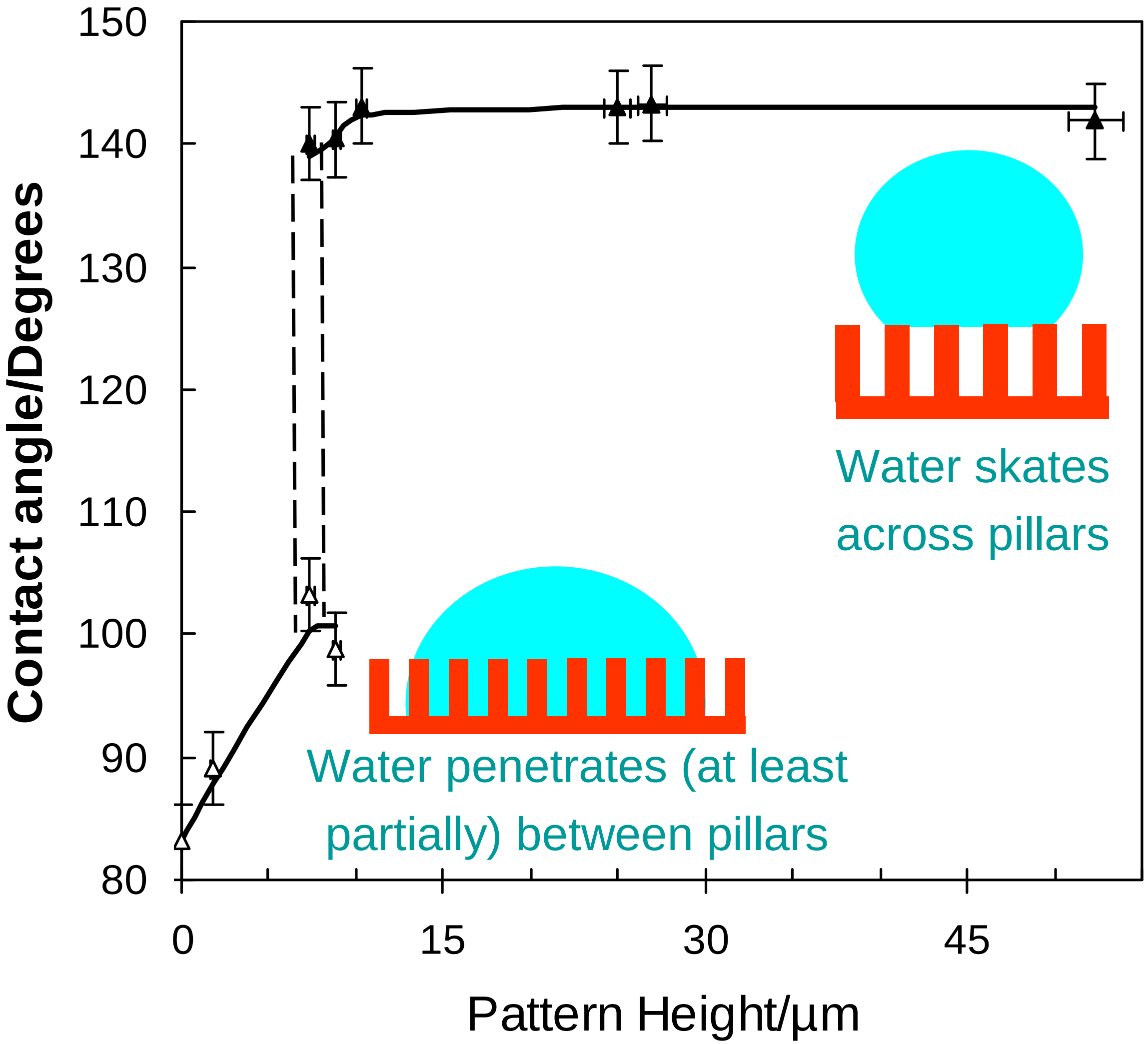
SU-8 pillars 15 µm

Hydrophobic treatment

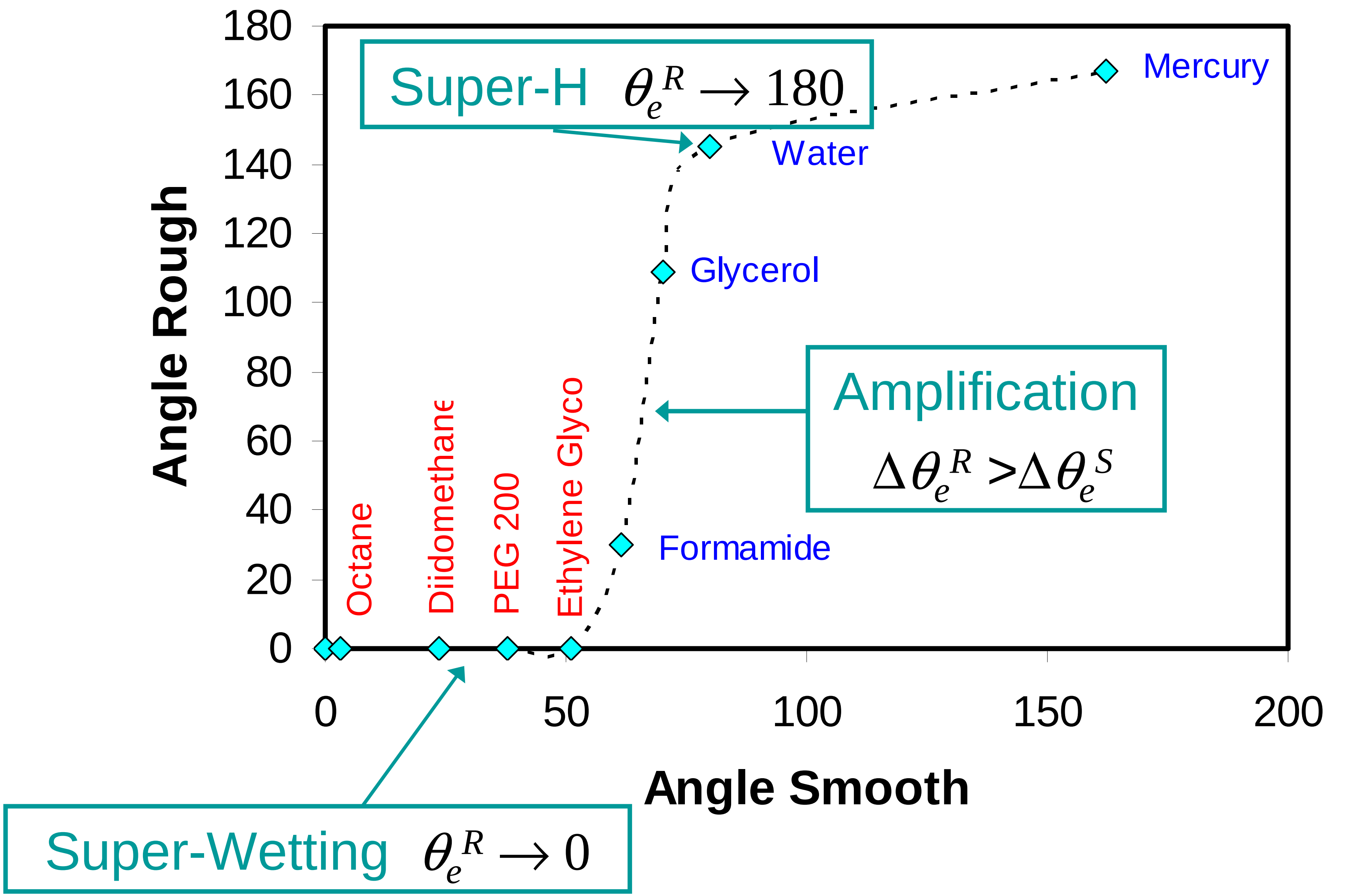




Change of Pillar Height



Different Liquids on a SuperH Surface

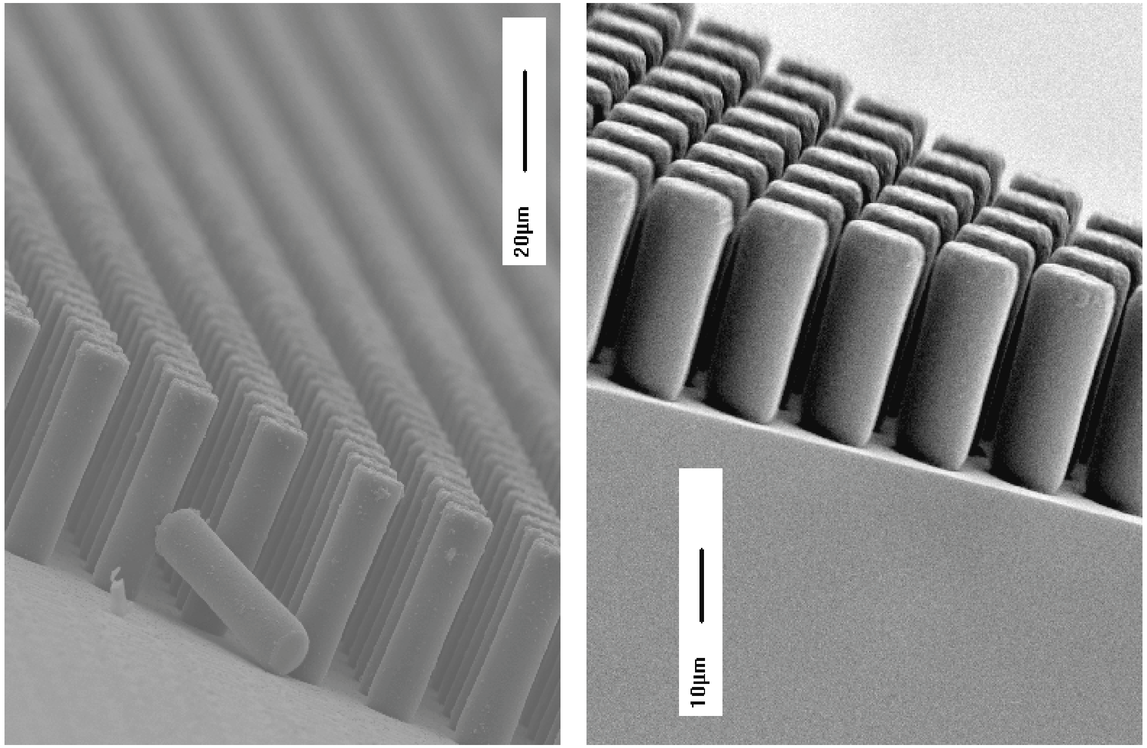


Reference McHale *et al*, Analyst 129 (2004) 284-287; McHale *et al*, Langmuir 20 (2004) 10146-10149

NTU Materials Work

1. SU-8 Photoresist Pillars

SEMs of Pillars

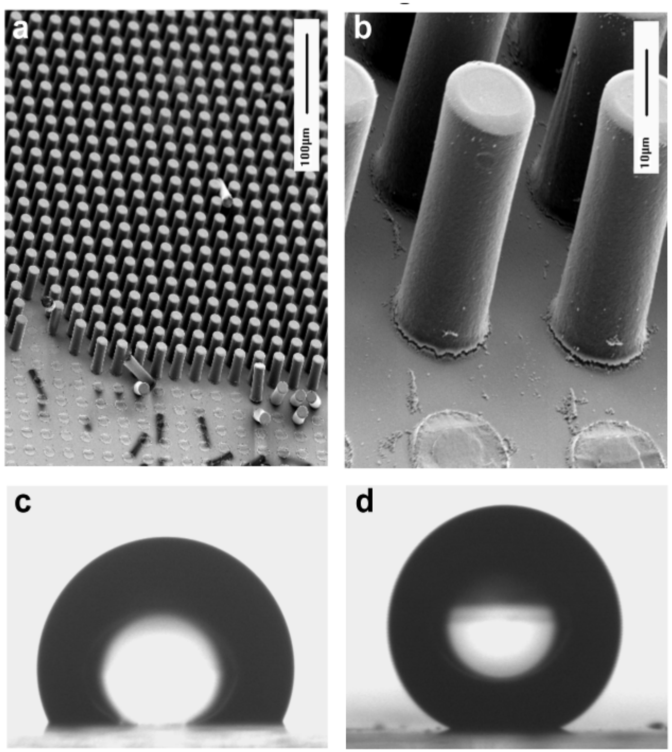


Tall structures to 45-75 µm

smooth and straight walls

Aspect ratios up to ~ 7

Effect on Water



a), b) Pillars D=15 µm, L = 2D

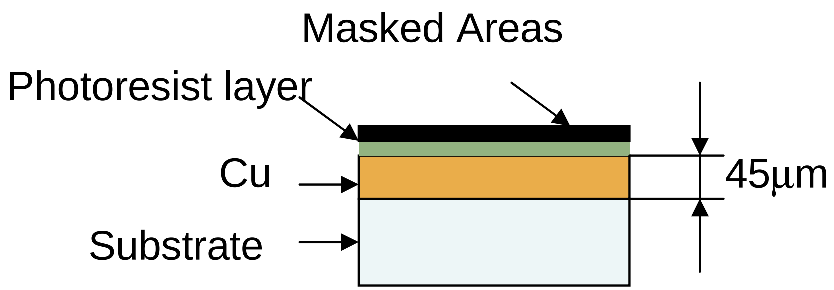
c) Flat and hydrophobic

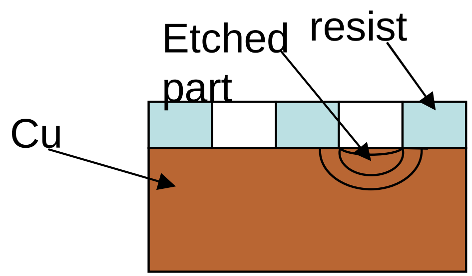
d) Tall and hydrophobic

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

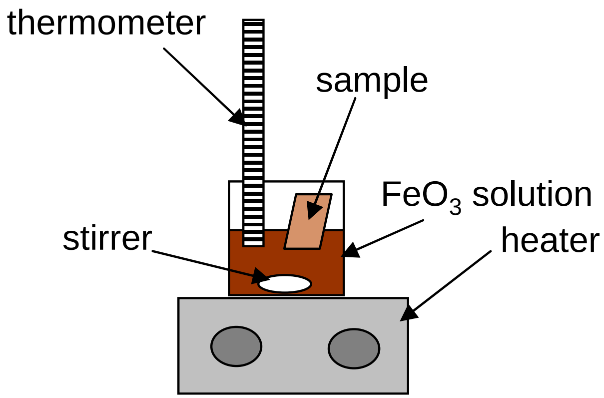
2. Etching of Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

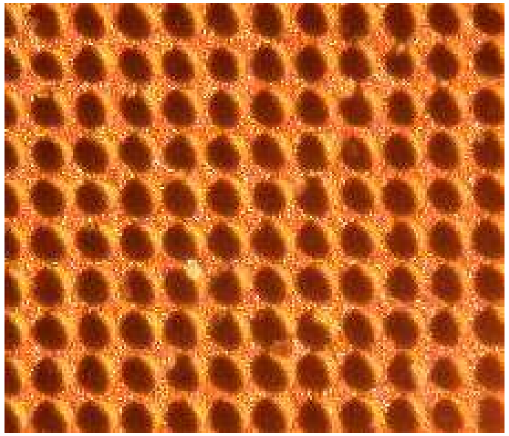




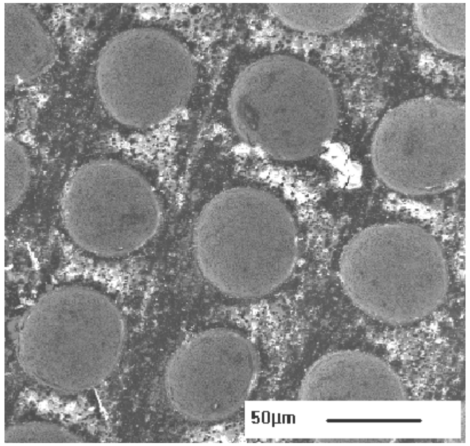
hole growth



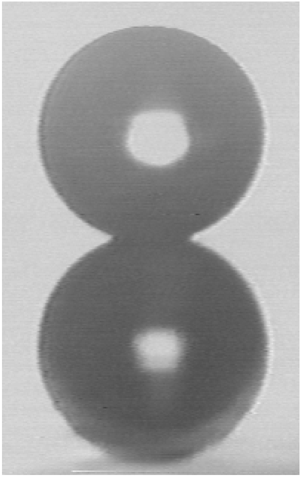
Setup of the copper etching



Copper sample etched through a 30 µm pattern



SEM picture of the pattern of the etched copper surface



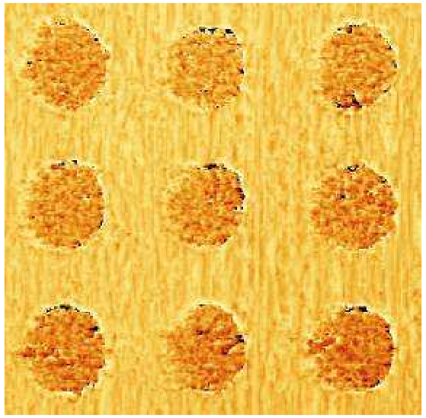
Water drop and reflection on an etched copper surface

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

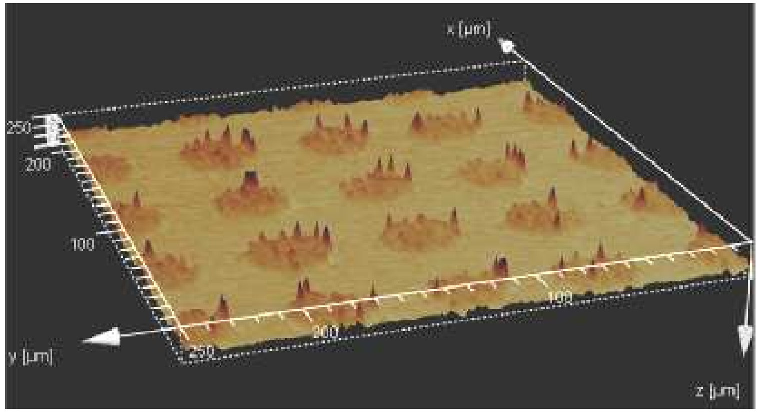
3. Electrodeposited Surfaces

- Diffusion limited aggregation – acid copper bath, fractal roughness

Base Cu electroplated surface

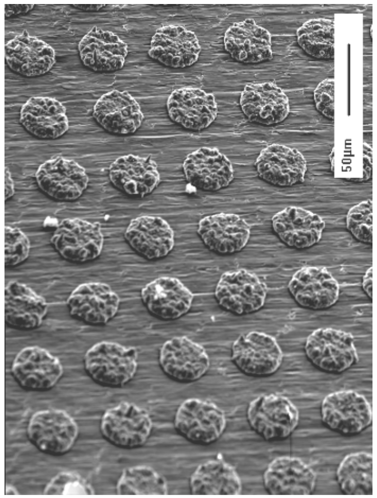


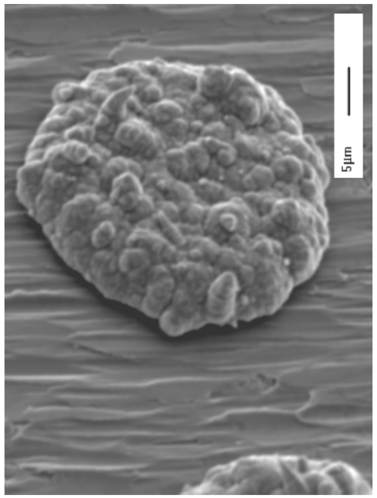
Confocal image of a 30μm textured electroplated Cu

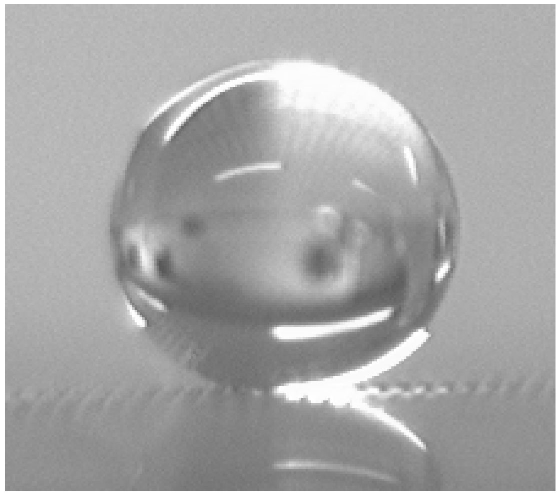


3D view of a electroplated copper sample

- “Chocolate Chip Cookies” - Electroplating through a mask



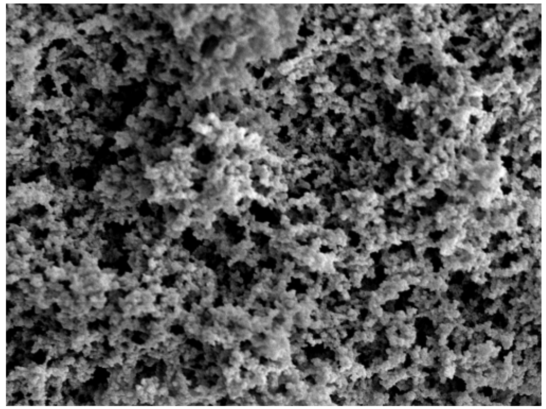




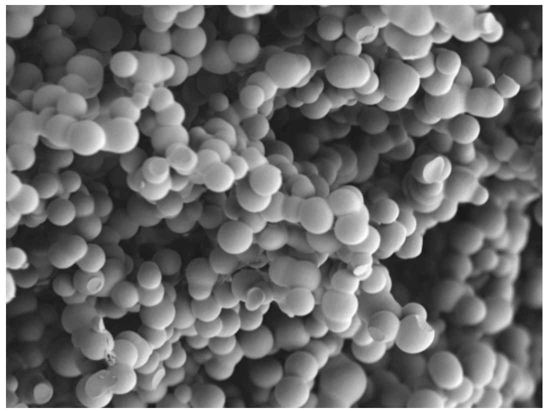
Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932; Shirtcliffe *et al*, Langmuir 21 (2005) 937-943.

4. 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 super-hydrophobic surfaces*
  - Pore size controllable nano- to macro-porous
  - Contact angle hysteresis as low as 4^{o}
  - Hydrophobic-to-hydrophilic transition by heating

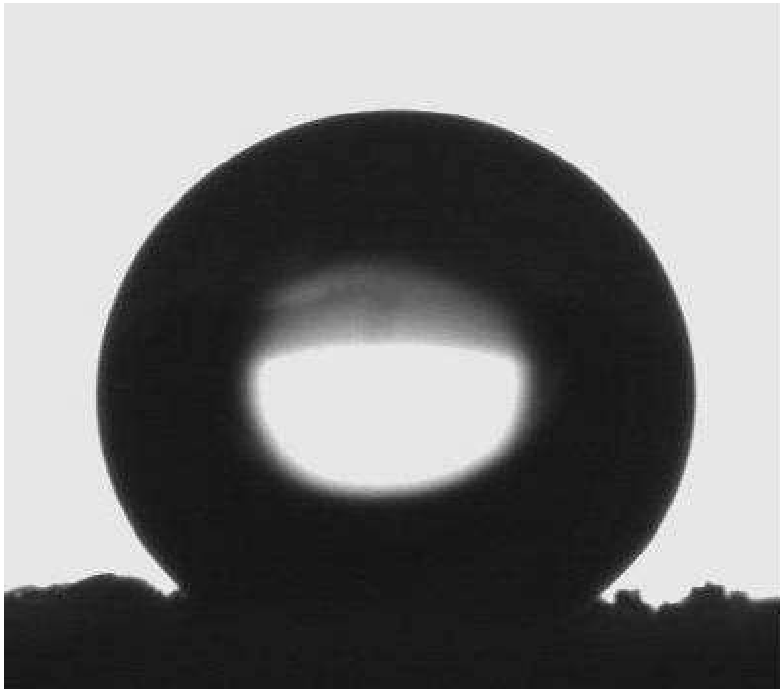


10 µm

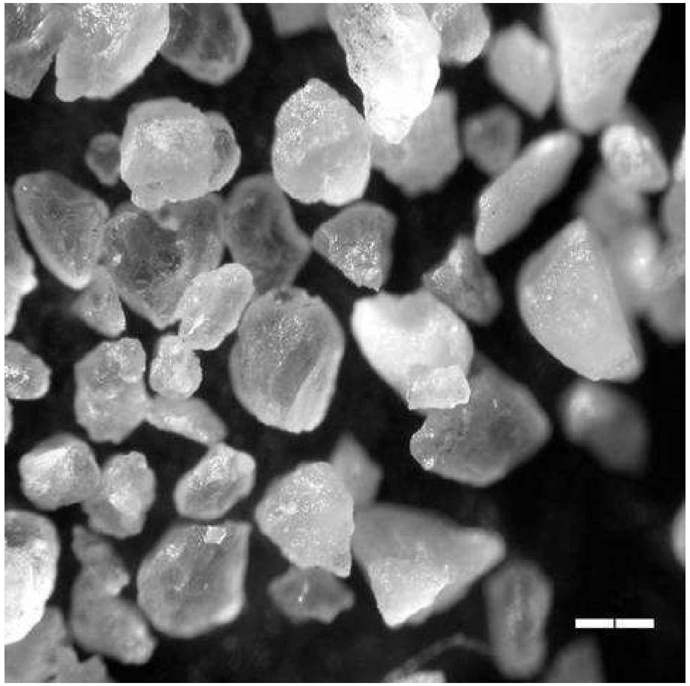
Reference Shirtcliffe *et al*, Langmuir 19 (2003) 5626-5631

5. Super Water-Repellent Soil

Sand with139°



Shape and Packing



200 μm

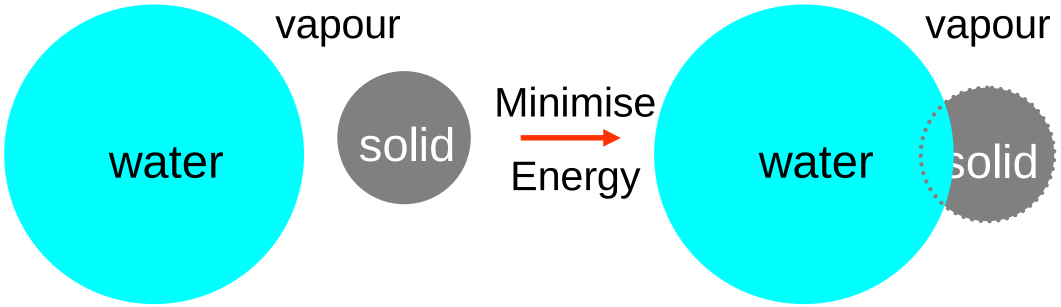
Comments

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).

6. Liquid Marbles

- Hydrophobic Grains Adhere to the Water-Air Interface

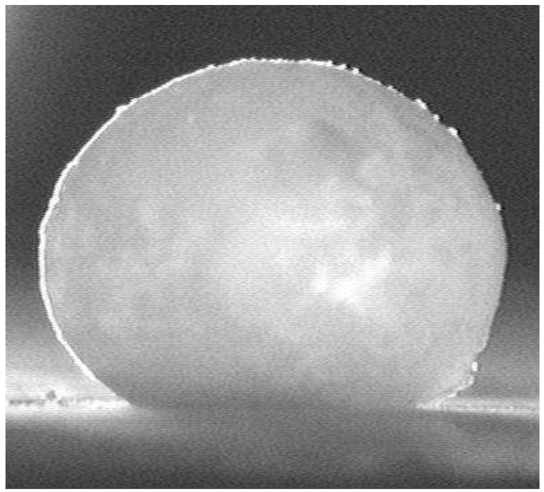


$$\Delta F = -\pi R_g^{\,2} \gamma_{LV} (1 + \cos\theta_e)^2$$

Lycopodium

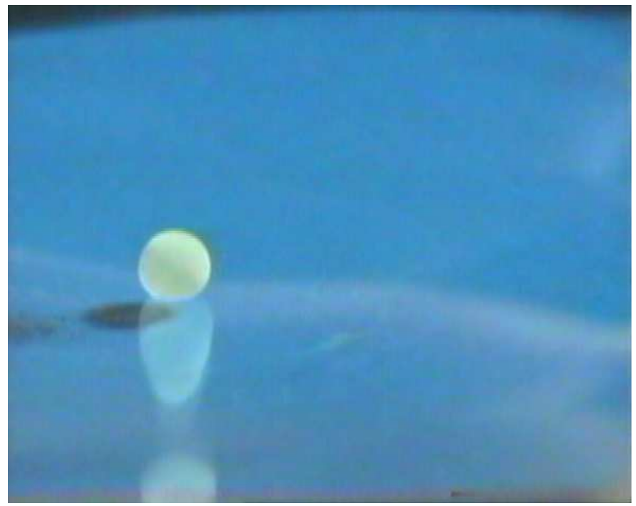
Lycopodium grains are 15-19 μm, but monolayers can be achieved

Silica Powder



Silica grains are sub-μm, but layer is thick

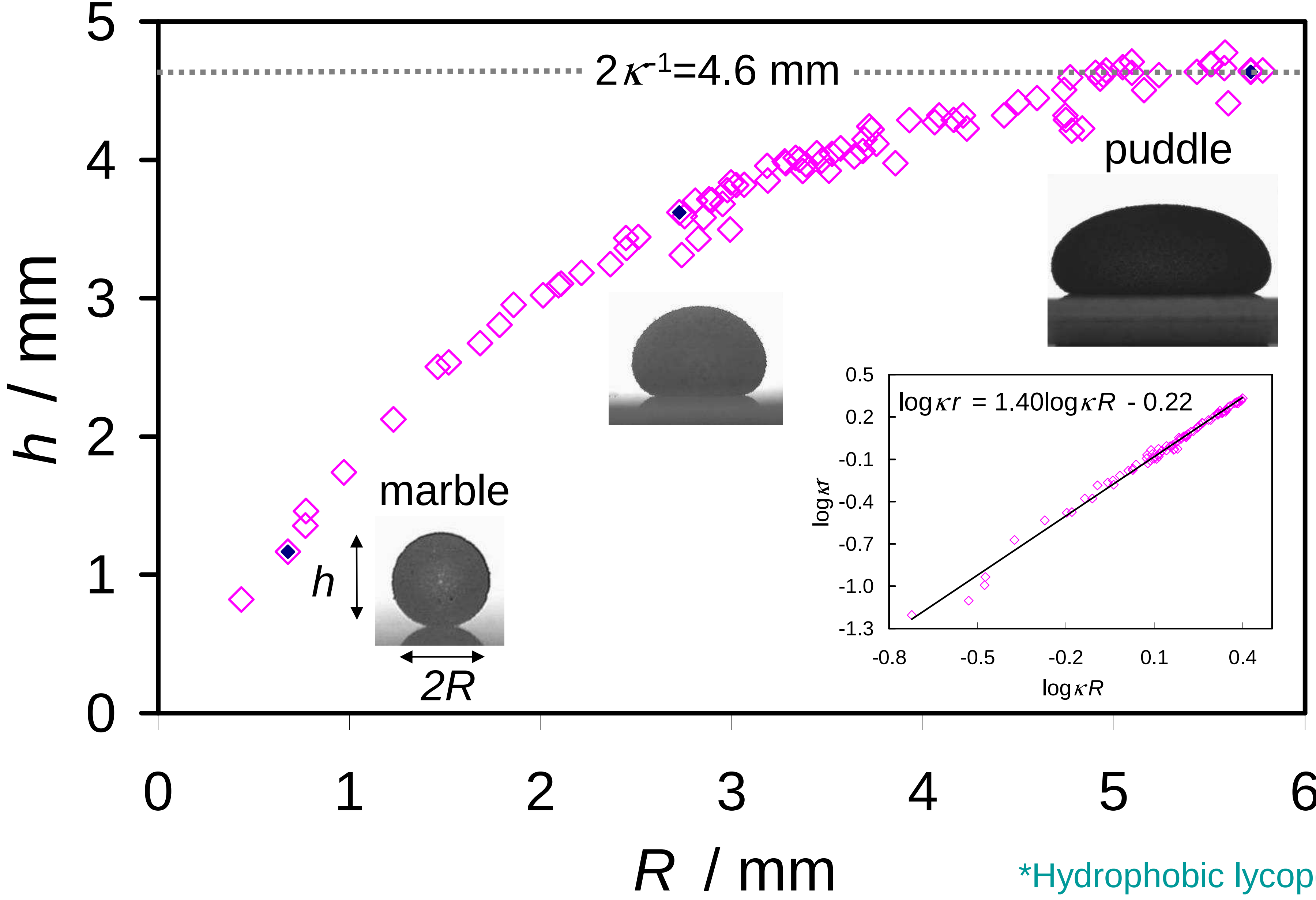
Mobility



Perfect non-wetting system with zero hysteresis

Acknowledgement David Quéré, College de France, Paris.

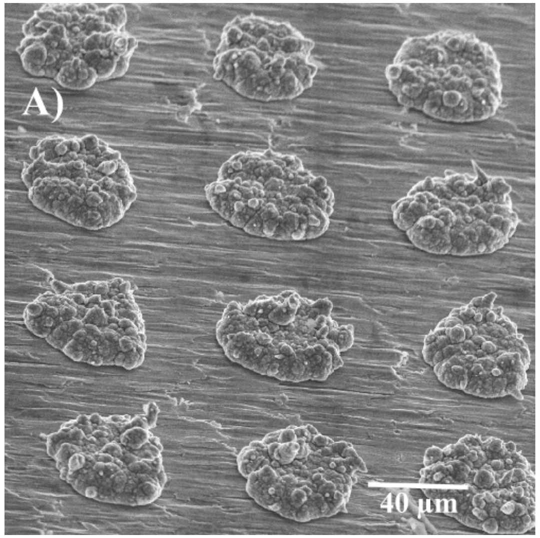
Perfect Non-Wetting Marbles*

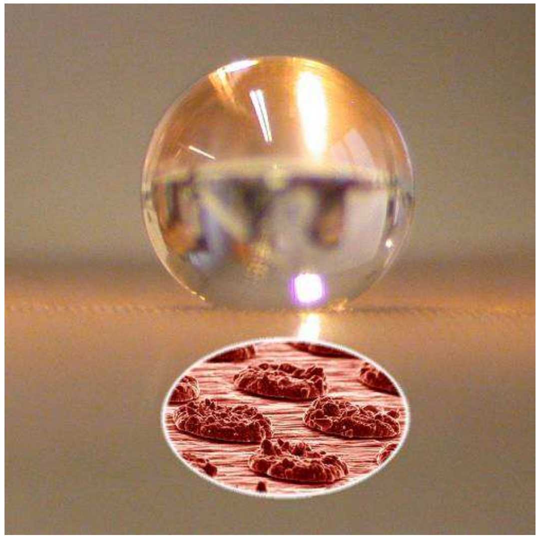


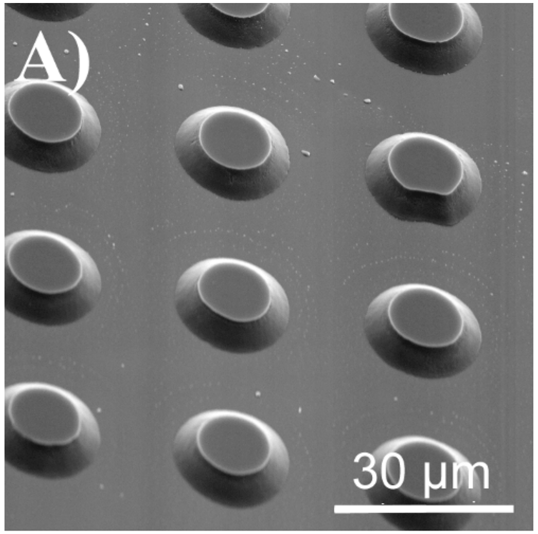
*Hydrophobic lycopodium

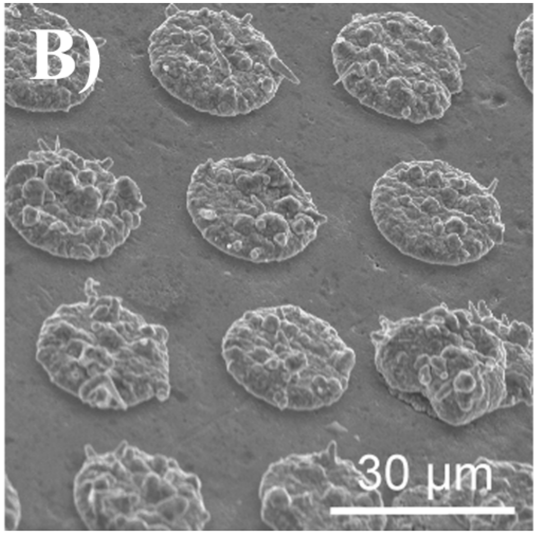
NTU Experiments

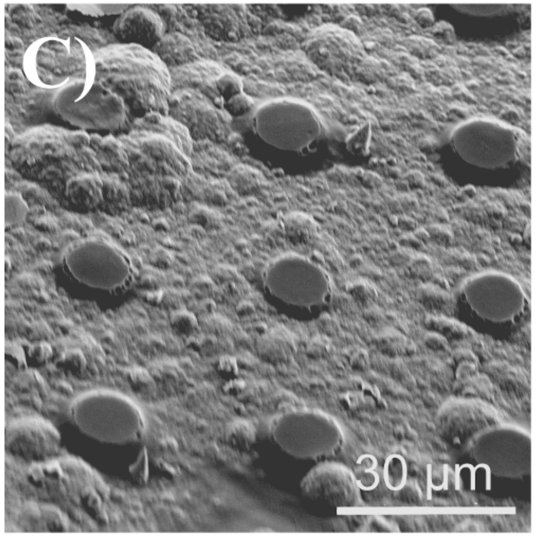
1. Double Length Scale Systems

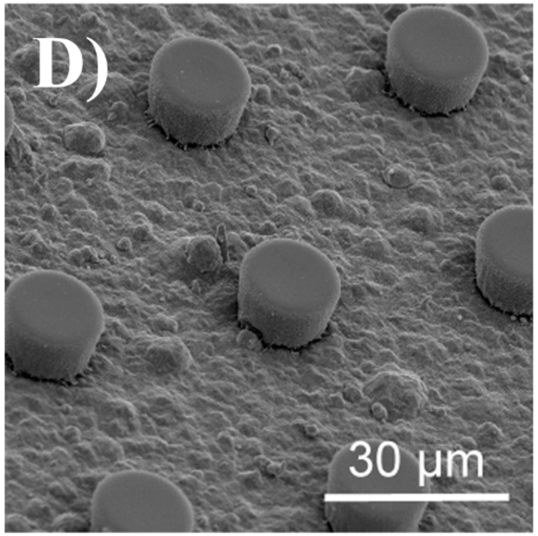








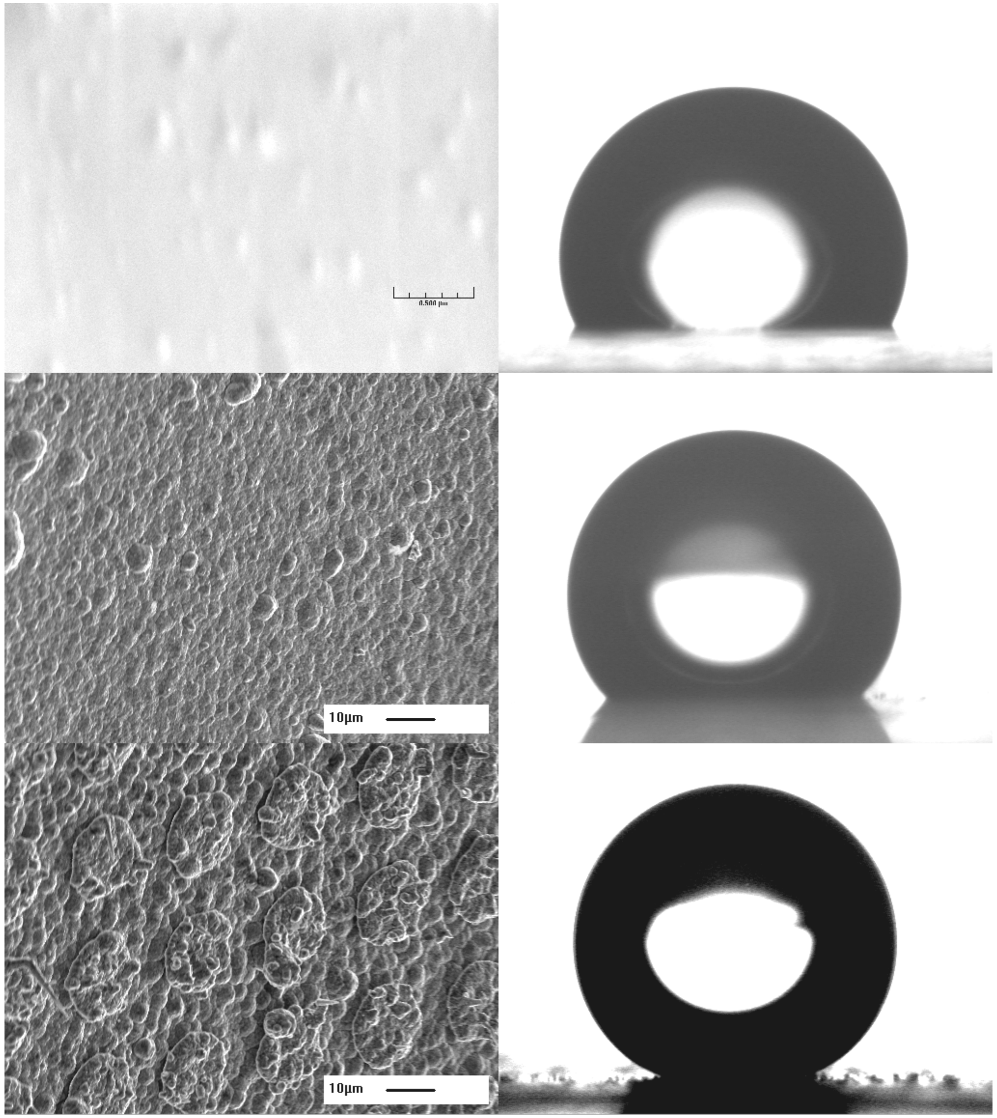




Combining Slight Roughness and Texture

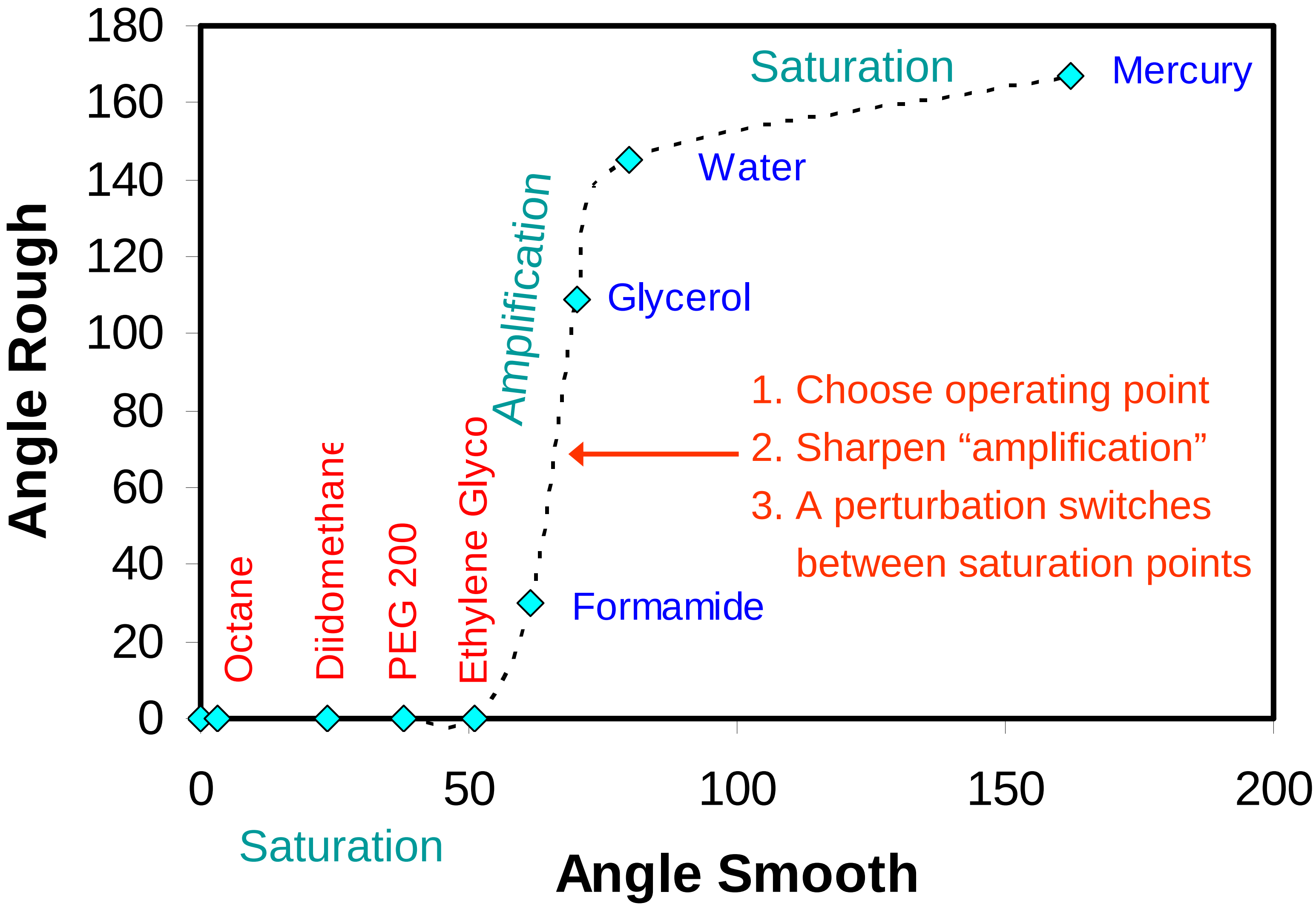
- Smooth and Hydrophobised 115°
- Slightly Rough and Hydrophobised 136°
- Slightly Rough, Textured and Hydrophobised 160°

Two length scales is extremely effective



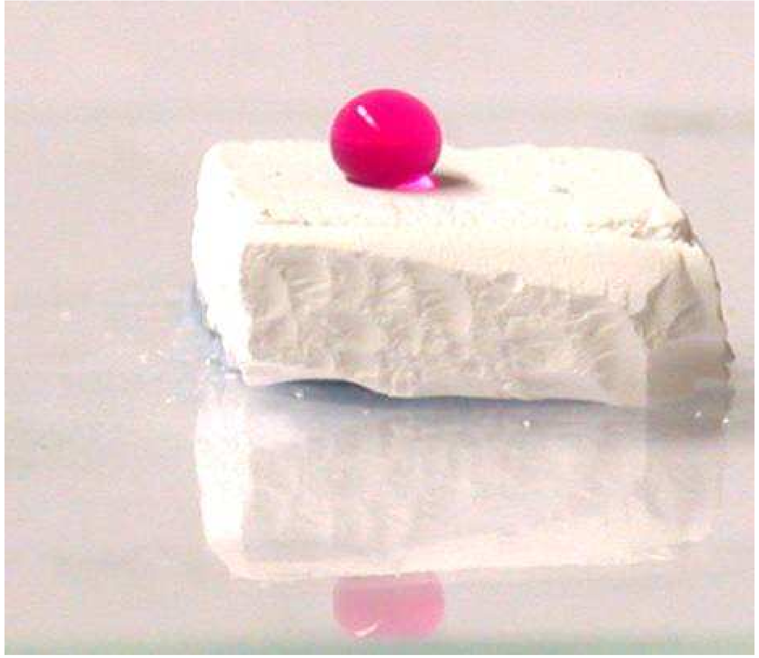
Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932 (Theory is in the supplementary information).

2. “Digital” Switching - Recall



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

2. Sol-Gel Foams – Switching from S/H



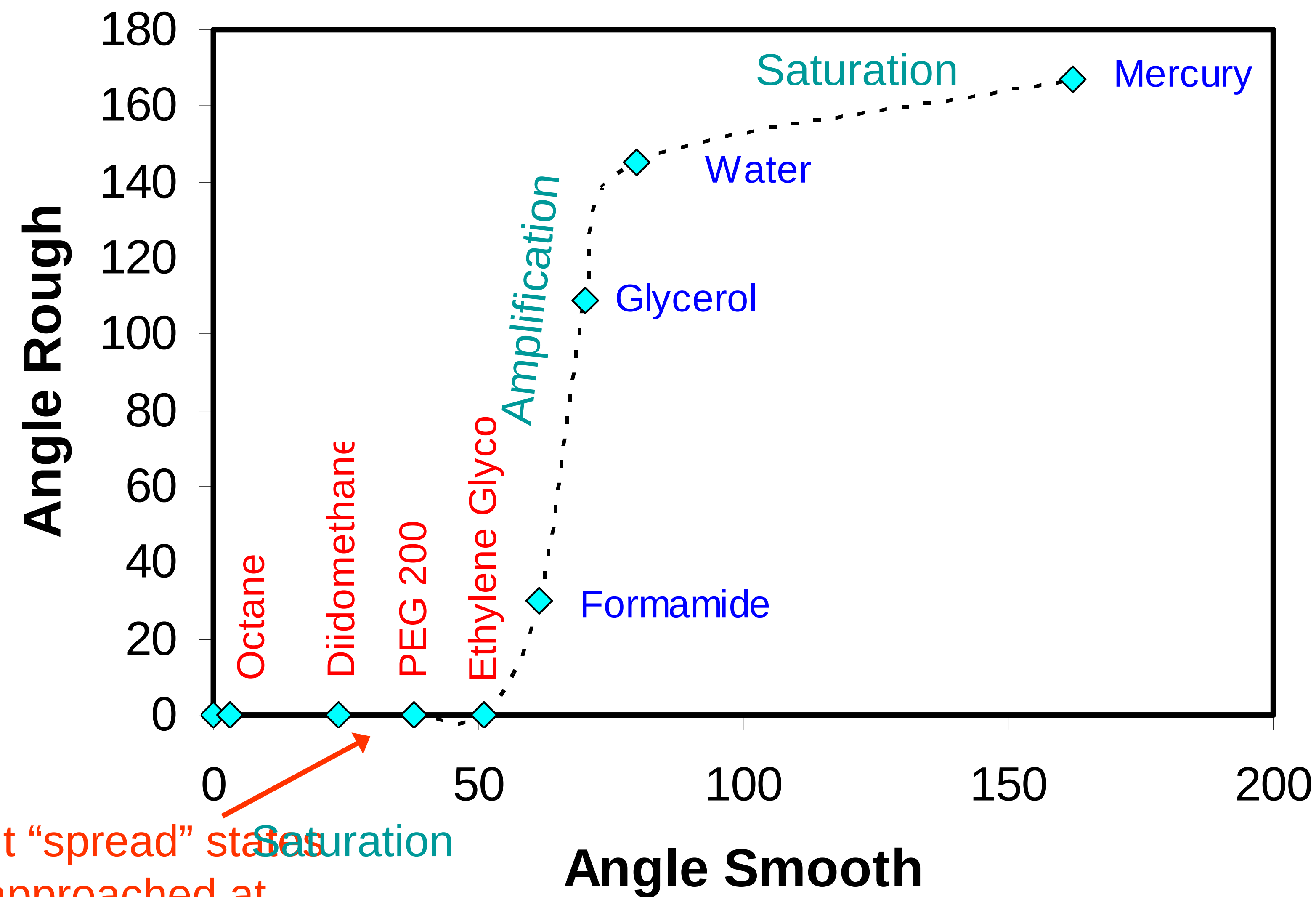
Foam heated
(and cooled)
prior to droplet
deposition

- 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)

3. "Super-spreading" - Recall



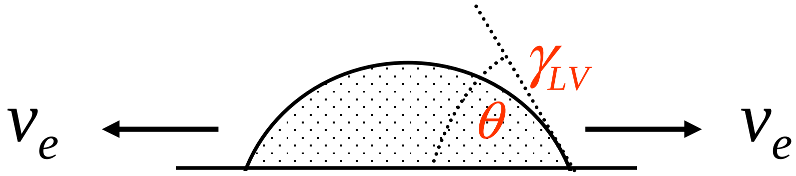
Different "spread" states are approached at different rates

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

3. 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 ~ $\gamma_{LV}(\cos\theta_e^s - \cos\theta)$

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

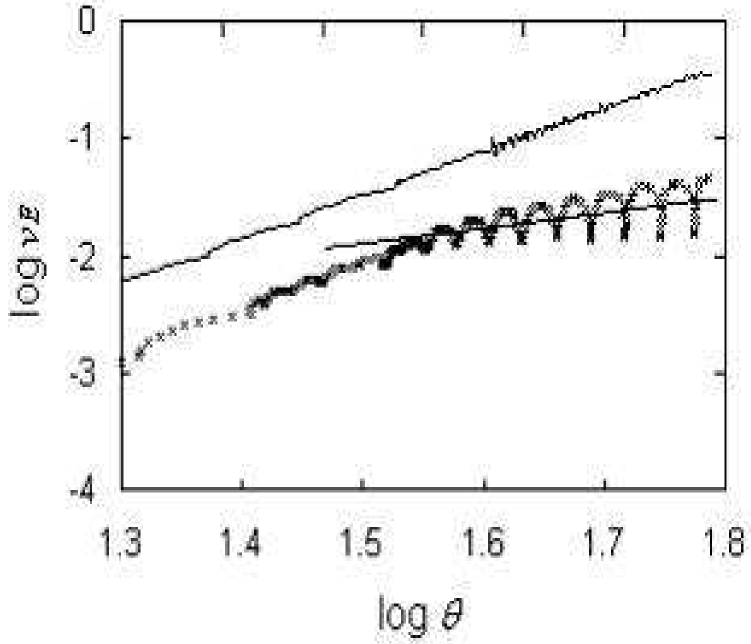
Weak roughness (or surface texture) modifies edge speed:

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

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

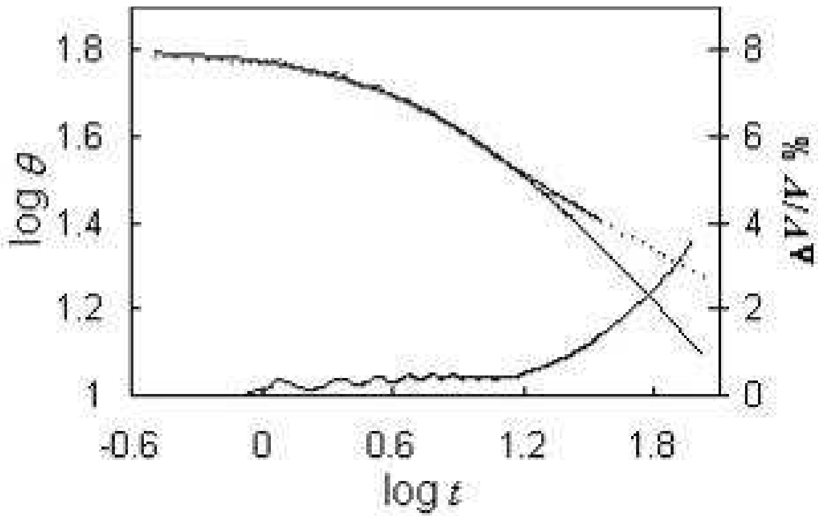
3. Superspreading of PDMS on Pillars

Tanner's Law exponents *p* and *n* (cubic to linear transition)



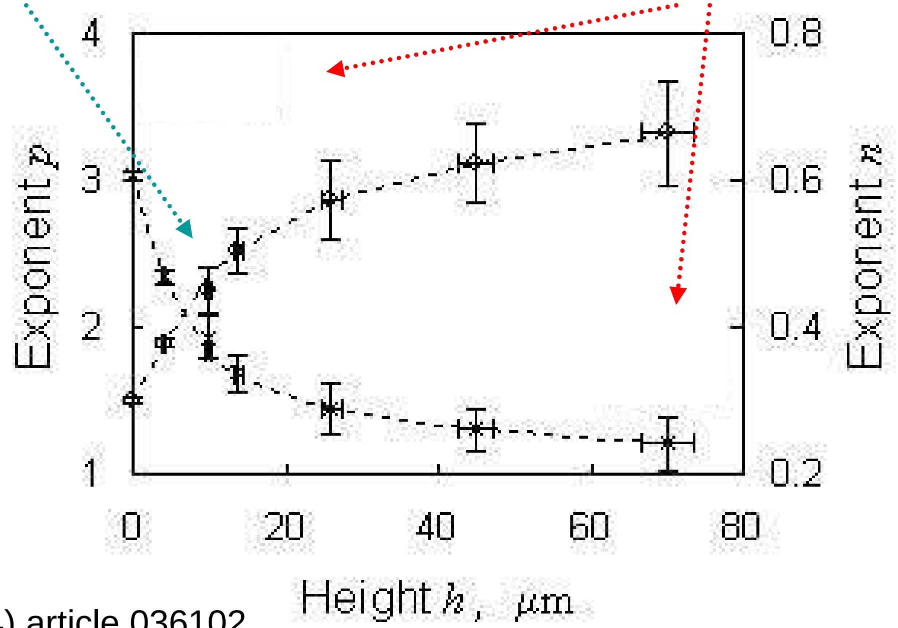
$$v_E \propto v^* \theta^p$$

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



Effect of substrate on PDMS

Effect of substrate on water



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

4. Path Definition & Self-Actuated Motion

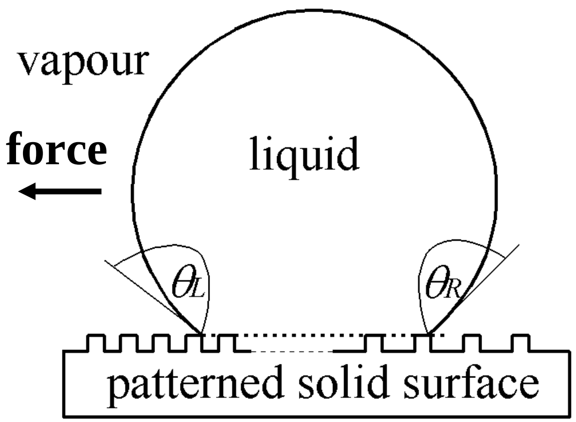
- Gradients in Contact Angle

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

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

Idea

Droplet experiences different contact angles



Driving force ~ $\gamma_{LV}(\cos\theta_R - \cos\theta_L)$

Experiment

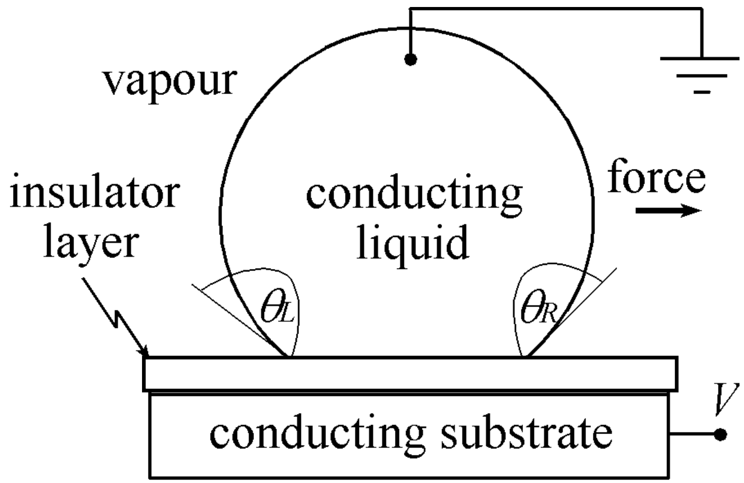
Radial gradient $\theta(r)$=110°→ 160°

Electrodeposited copper – fractal to overcome hysteresis

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

5. Electrowetting-on-Dielectric (EWOD)

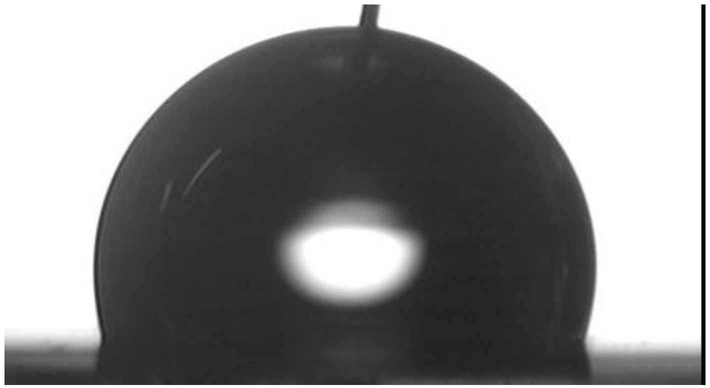
- Electrowetting Principle
  - Conducting liquid on electrical insulator on conducting substrate



  - Applying voltage electrically charges solid-liquid interface (i.e. a Capacitive effect)
  - Droplet spreads and contact angle reduces

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

  - Difference in angles at edge of droplet reflects an actuating force



5. Superhydrophobicity & EWOD

- Idea
  - Use S-H to gain high initial contact angle $\theta\uparrow$
  - Use electrowetting to tune over full angular range $\theta\downarrow$

- Thin Insulator, d
  - Capacitive energy $\propto V^2/d$
  - Thin insulator for lower voltages

- Electrowetting
  - Applying voltage causes electrocapillary pressure into surface texture ("Penetrating")

Contradiction 1

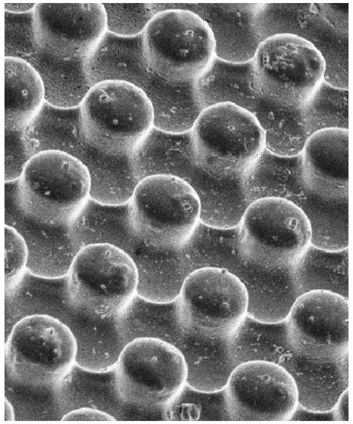
But Super-H via patterning insulator → high aspect ratio

Contradiction 2

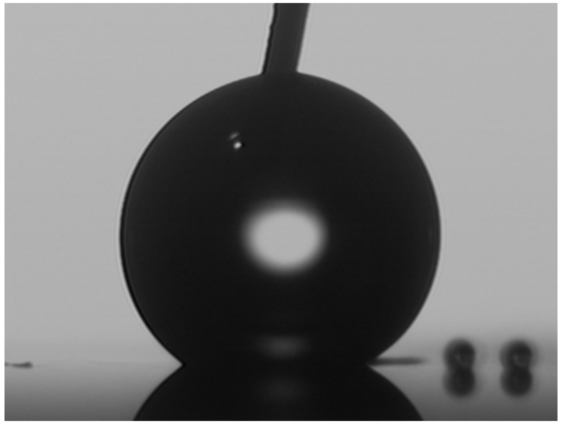
But low hysteresis requires "Skating"

5. Irreversible Electrowetting

- Lithographic System
  - Ti/Au on glass, SU-8 Pillars 7 µm diam, 15 µm cnt-cnt, ht 6.5 µm (roughness $r \approx 1.64$), teflon AF1600 capped
  - Droplets of deionised water with 0.01M KCl, DC voltage by steps up to 130 V



Initial Shape | Applied Voltage | Voltage Removed



152^o → 114^o

Irreversible, but EWOD does provide a roughness estimate

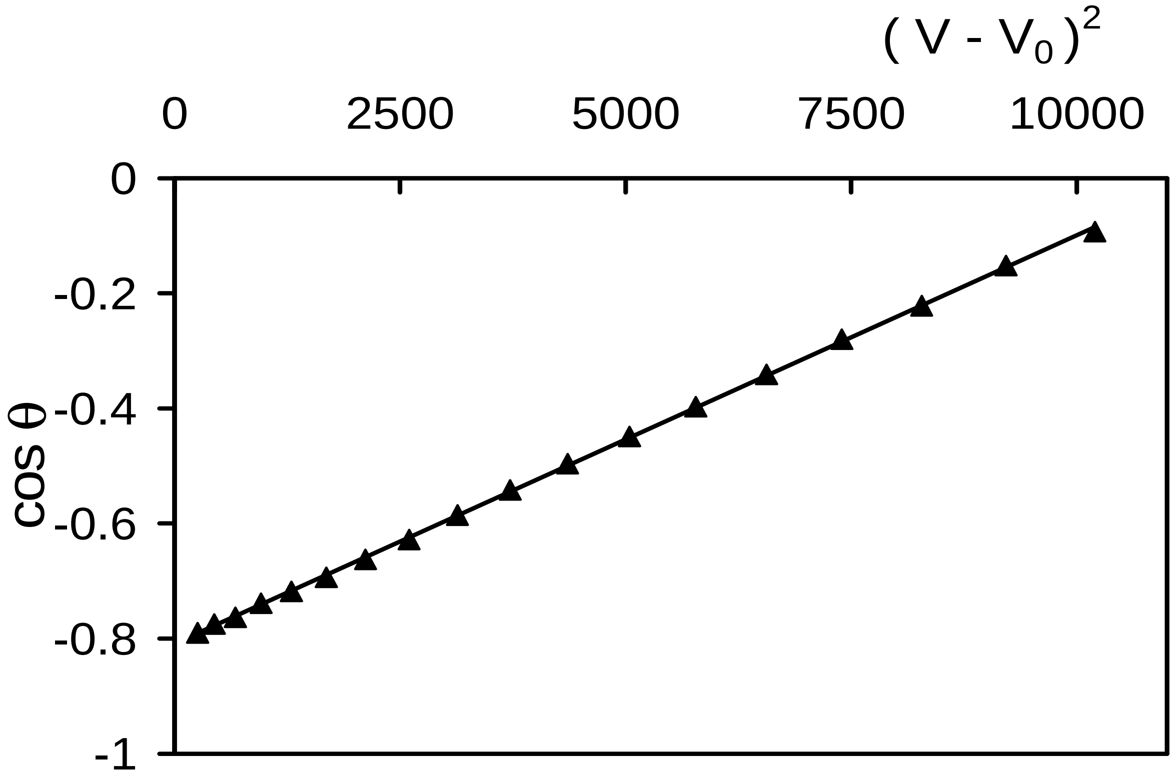
Reference Herbertson *et al*, Sens. Act. A. 130 (2006) 189-193.

5. Fitting of Wenzel EWOD

- Increasing Voltage Half Cycle
  - Advancing droplet charges substrate before contact with liquid
  - Modified fitting equation to include a constant V_o

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

$r\cos\theta_{flat}(0)$ *Wenzel*

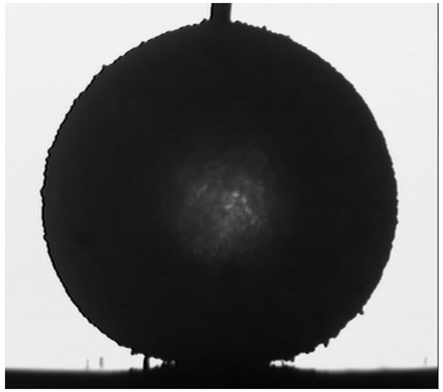


Interpretation

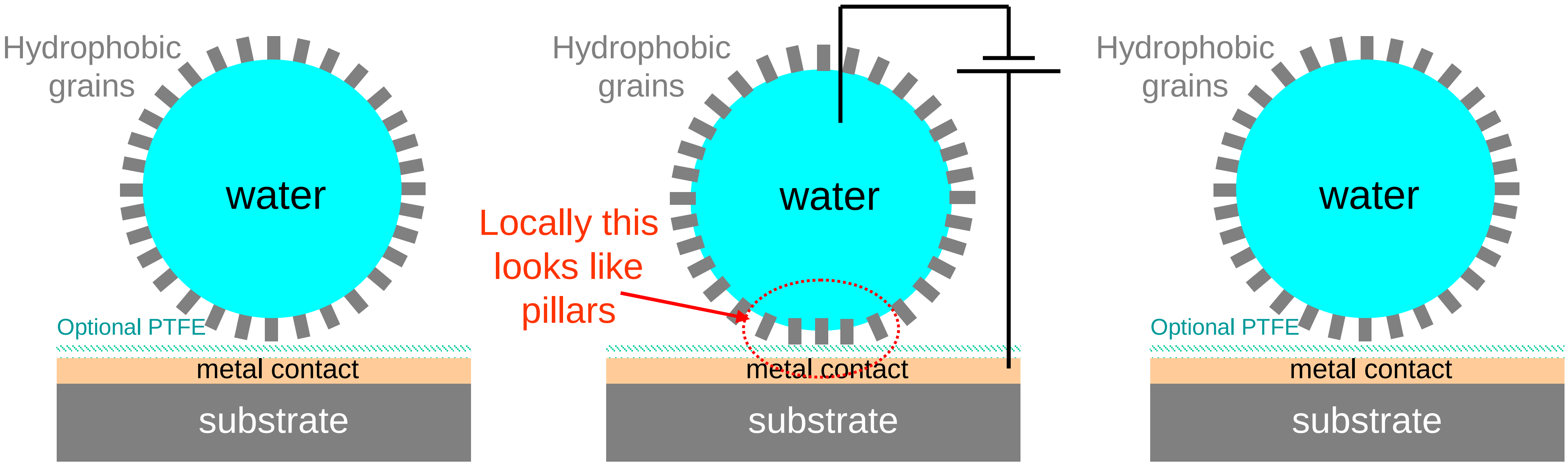
1. V_o=28V represents charging
2. Conversion from "skating" to "penetrating" regime
3. Fitted $\theta_e(0)$ gives Wenzel angle of 143° and predicts roughness of r=1.92

5. Electrowetting of Liquid Marbles

- Reversibility Idea
  - Make the solid "pillars" adhere more to the liquid than to the substrate
  - Provides insulating "pillars" conformal to the liquid shape
  - More hydrophobic grains "stick out" further (i.e. taller pillars)



Initial Shape | Apply Voltage | Remove Voltage



Reference Newton *et al*, J. Phys. D: Appl. Phys. 40 (2007); McHale *et al*, 20-24; Langmuir 23 (2007) 918-924.

5. Theory of Liquid Marbles

Minimise total energy of a spherical cap

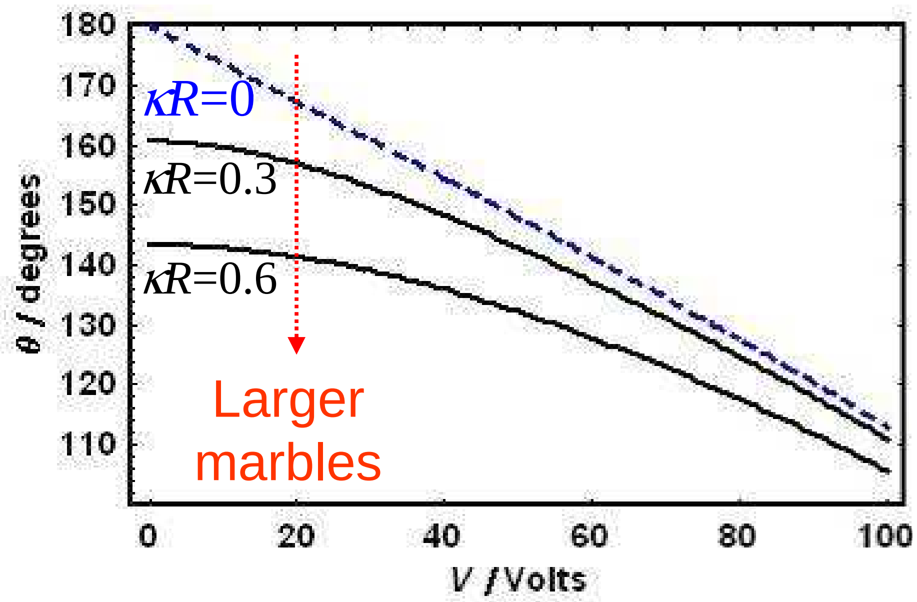
$$\cos\theta = \cos\theta_e + (\kappa h)^2/6 + CV^2/2\gamma_{LV}$$

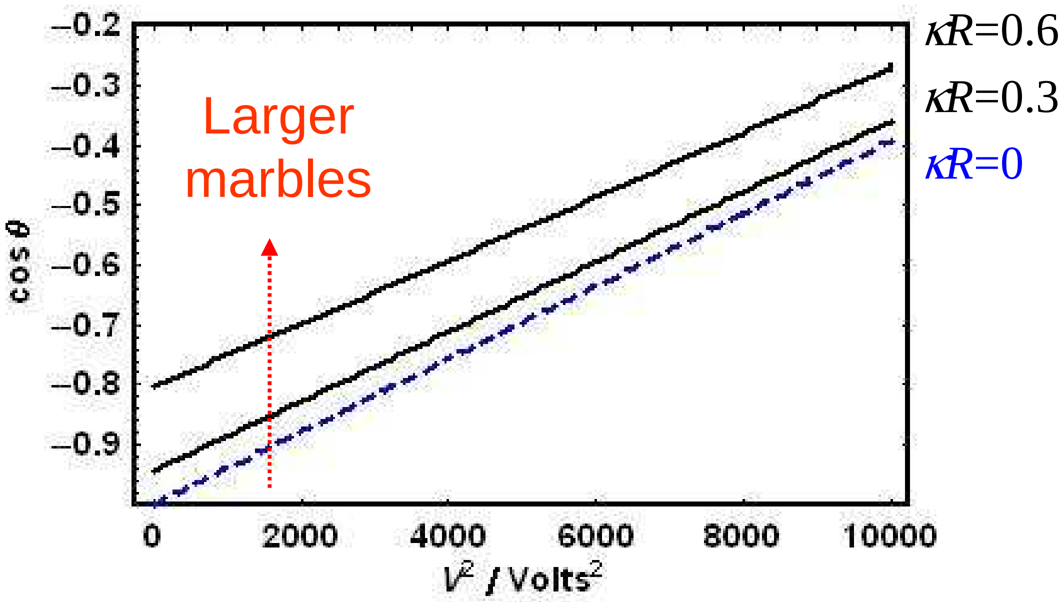
From surface energy
-1 for marble

Gravitational energy gives a drop
size factor with $h = h(\theta)$, so non-linear

Capacitive energy
from electrowetting

Numerical Results

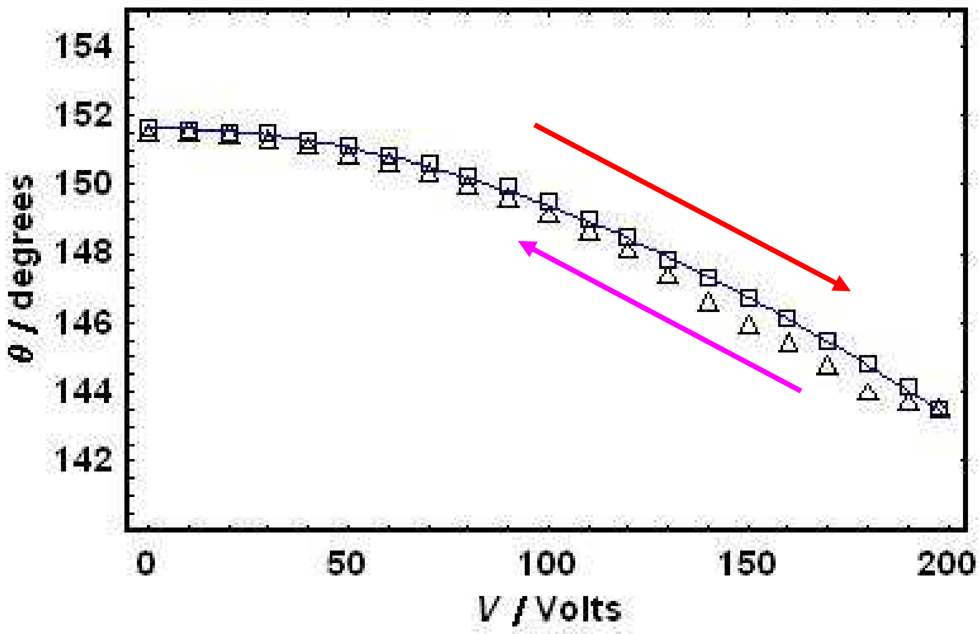




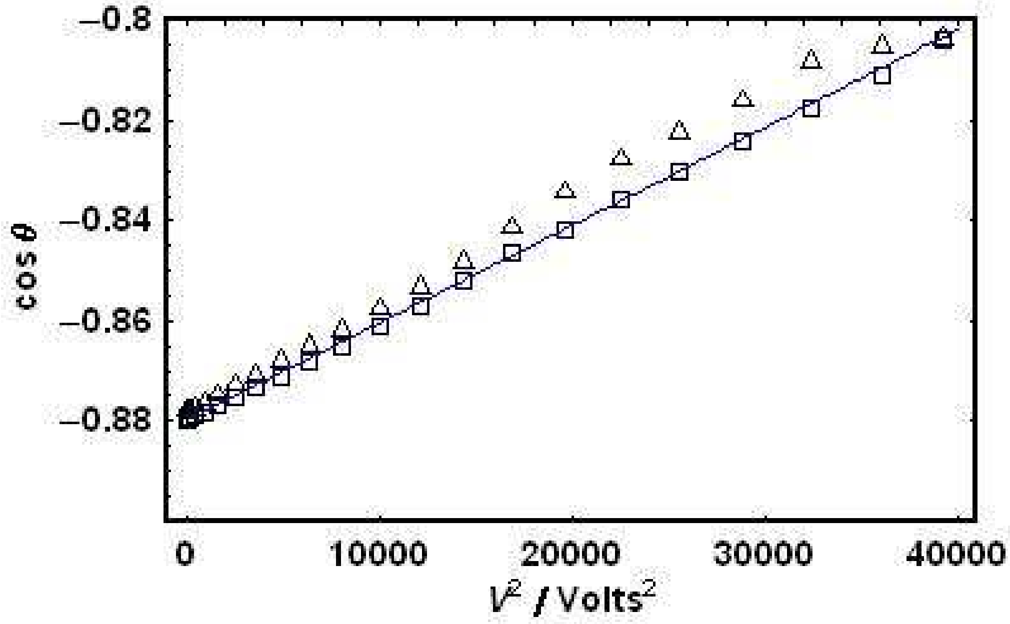
Reference McHale *et al*, Langmuir 23 (2007) 918-924.

5. Results using Hydrophobic Silica

Contact Angle



Fitting



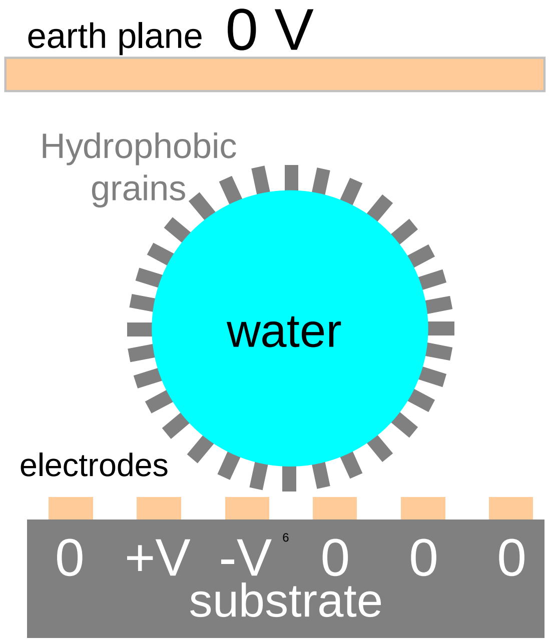
1. *No threshold* voltage
2. Virtually *no* contact angle *hysteresis*
3. Experiments show a limited range (155° to 130°)
4. Fit uses κR=0.45

Reference McHale *et al*, Langmuir 23 (2007) 918-924.

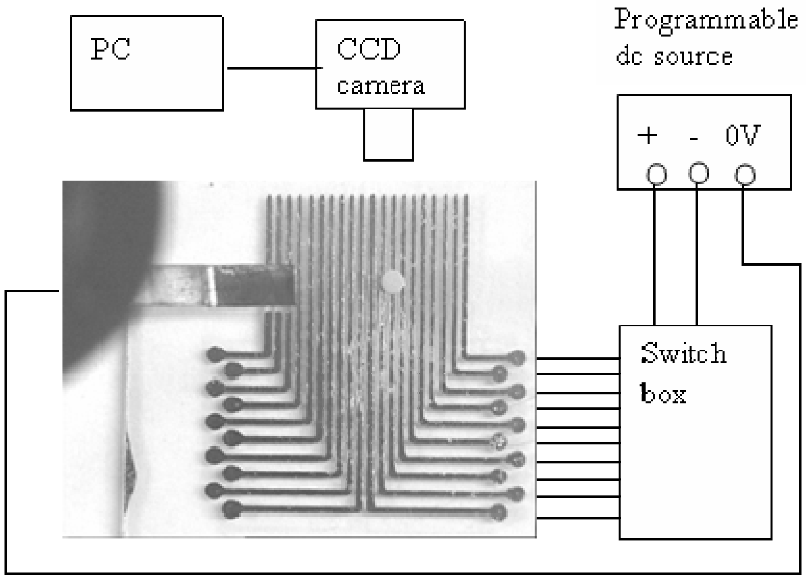
5. A Hint of Controllable Motion

1. Liquid marble using hydrophobic lycopodium
2. Upper earth plane, planar strip electrodes, pairs switched to ±150 V DC

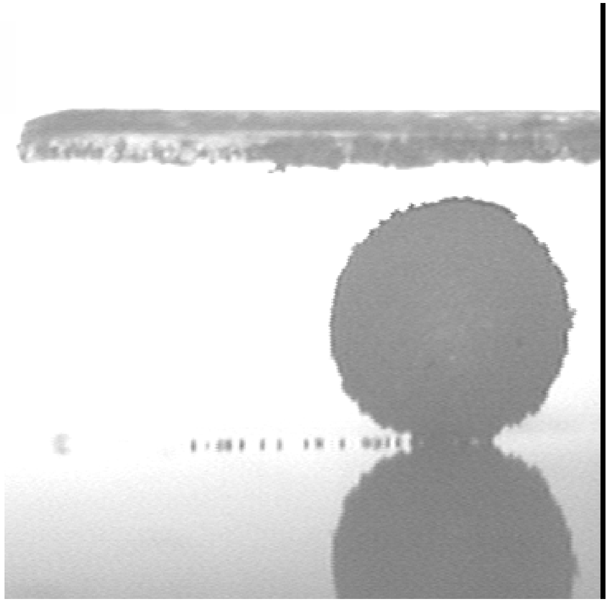
Concept



Method

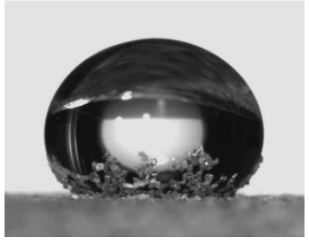


Results

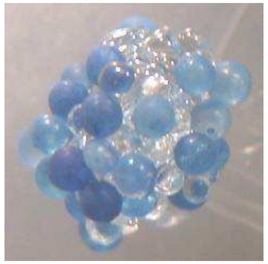


Reference Newton *et al*, J. Phys. D: Appl. Phys. 40 (2007) 20-24.

Other Work in Wetting

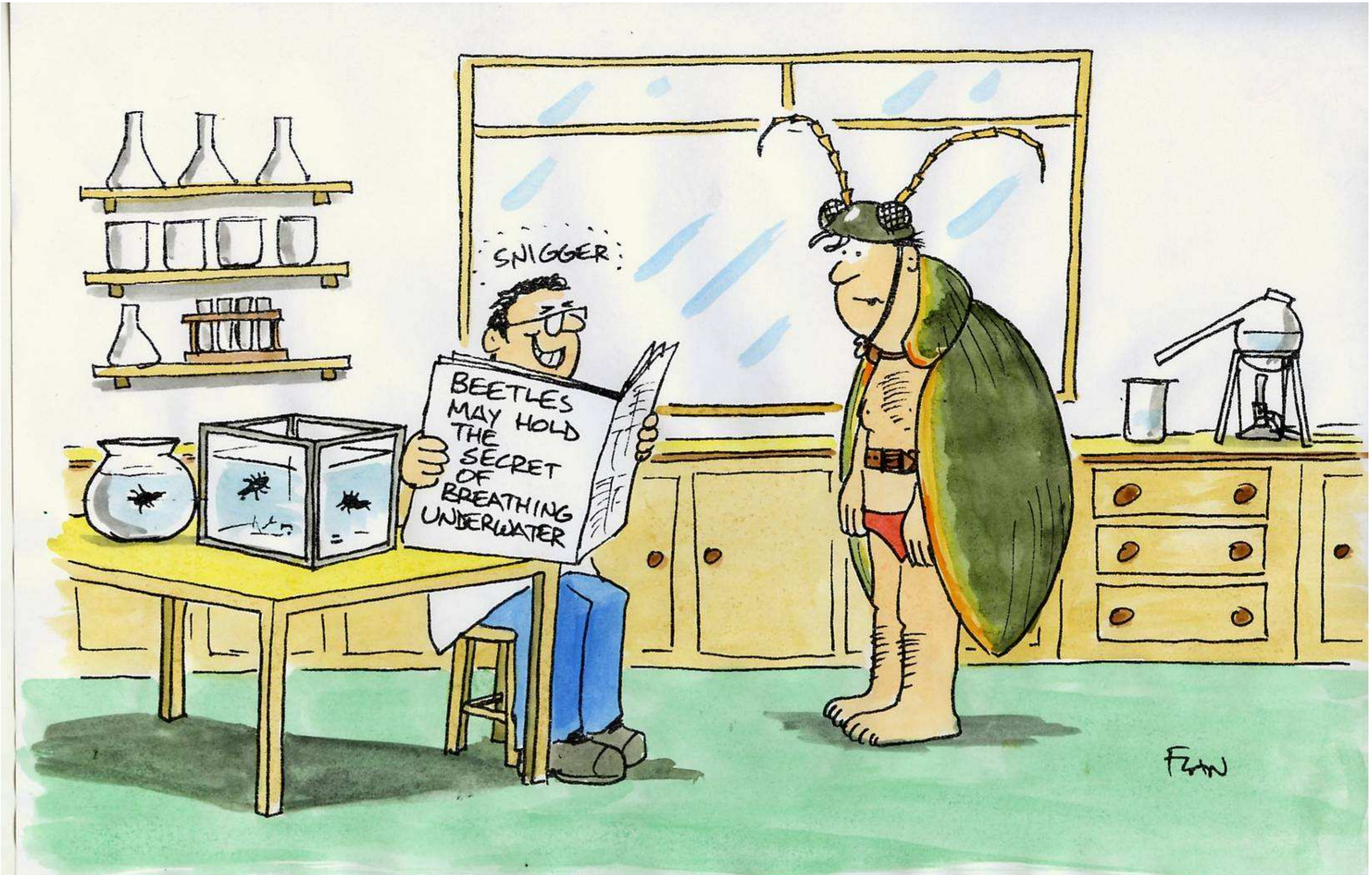


1. Soil as a Superhydrophobic Surface
   - Imbibition into bead packs (Appl. Phys. Lett. 89, 2006)
   - Droplet self-coating during evaporation and evaporatively driven self-sorting of grains (Appl. Phys. Lett. 2007)



2. Slip & Drag Reduction
   - High frequency oscillating surfaces (submitted to Langmuir 2007)
   - Flow down superhydrophobic pipes

3. Superhydrophobicity & Breathable Structures
   - Lichens with breathable membranes (J. Plant Phys. 163, 2006)
   - Underwater respiration/plastrons (Appl. Phys. Lett. 89, 2006)



OH COME ON, I BET PEOPLE THOUGHT SCUBA GEAR LOOKED SILLY WHEN IT WAS FIRST INVENTED

The End

Acknowledgements

Internal Collaborators

Academics Dr Mike Newton, Dr Carl Brown
Prof. Carole Perry (Chemistry), Prof. Brian Pyatt (Life Sciences)
PDRA's Dr Neil Shirtcliffe, Dr Dale Herbertson, Dr Carl Evans, Dr Paul Roach
PhD's Ms Sanaa Aqil, Mr Steve Elliott

External Collaborators

Prof. Mike Thompson (Toronto), Prof. Yildirim Erbil (Istanbul)
Dr Stefan Doerr (Swansea), Dr Andrew Clarke (Kodak), Dr Stuart Brewer (Dstl)

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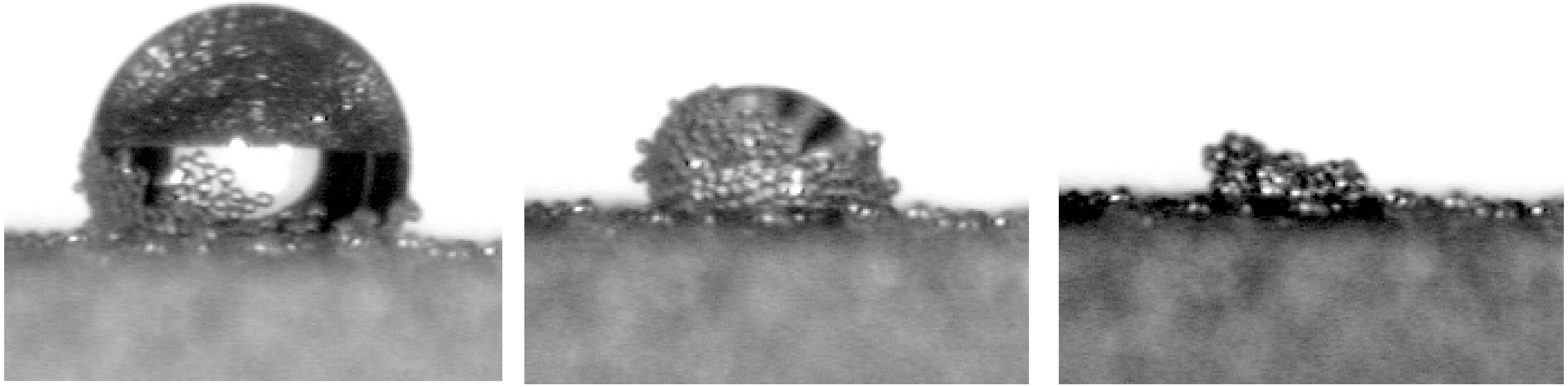
GR/S34168/01 – Electrowetting on superhydrophobic surfaces
EP/C509161/1 – Extreme soil water repellence
EP/D500826/1 & EP/E043097/1 – Slip & drag reduction
Dstl via EPSRC/MOD JGS
EU COST Action D19 - Chemistry at the nanoscale
EU COST Action P21 - Physics of droplets

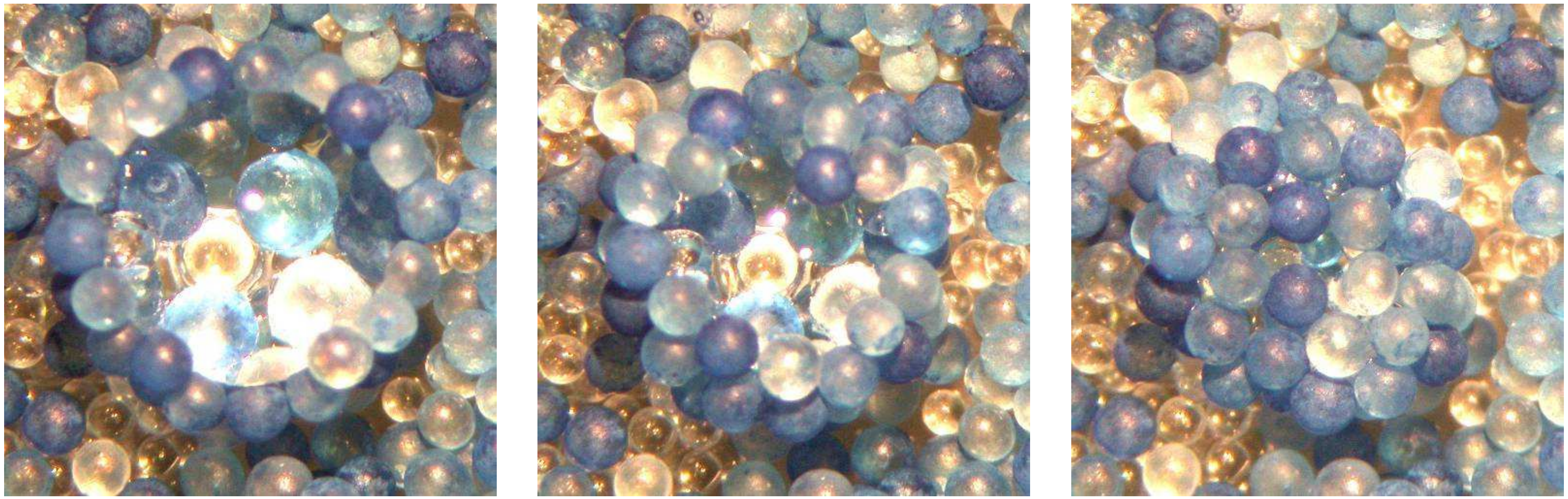
EPSRC
Engineering and Physical Sciences Research Council
Kodak
COST
COMIT Faraday Partnership
dstl
uk sport
NOTTINGHAM TRENT UNIVERSITY

Hydrophobic Granular Self Sorting

Water droplet digging during drying



Mixed hydrophobic (blue)/hydrophilic (clear)



Determination of Roughness Factor

SEM Measurements

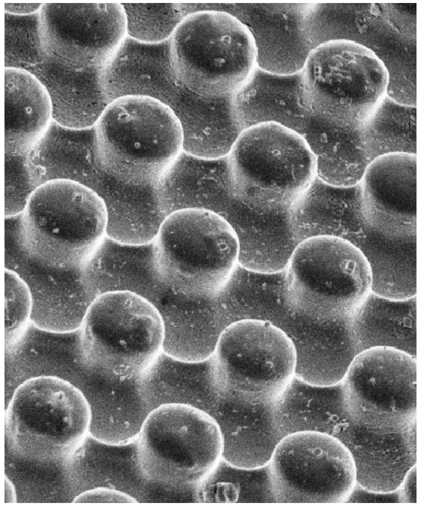
Pillar diameter = 7.5±0.5 μm

Centre-centre separation 15 μm

Height = 6.5±1.3 μm

Unintended "ribs"

Teflon on flat surface θ_e=114°



Comparison to EWOD Data

Cassie-Baxter solid factor of f = 0.12±0.02 *Pre-electrowetting*

$\cos\theta_{CB} = f\cos\theta_e - (1-f) \Rightarrow$ θ_{CB} = 152°±1° θ_{CB} = 152°

Ignoring "ribs" Wenzel factor is r = 1.7±0.1 *EWOD Intercept*

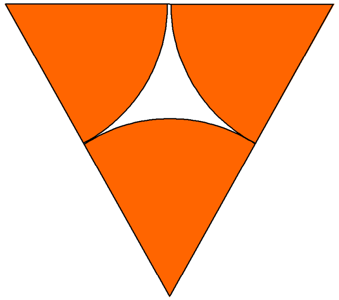
Assuming ribs are ~ 1/2 pillar heights r ~ 1.9 r = 1.92

Model for Capillary Imbibition

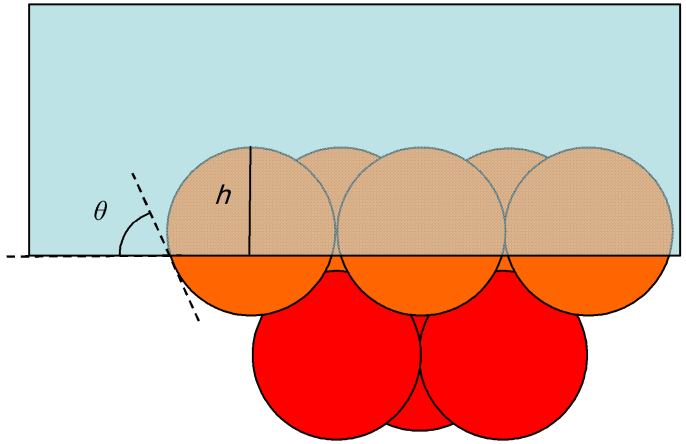
Assumptions

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

Top View



Side View



Results

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 imbibition occurs
4. Critical contact angle, θ_c, when h_c reached

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

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

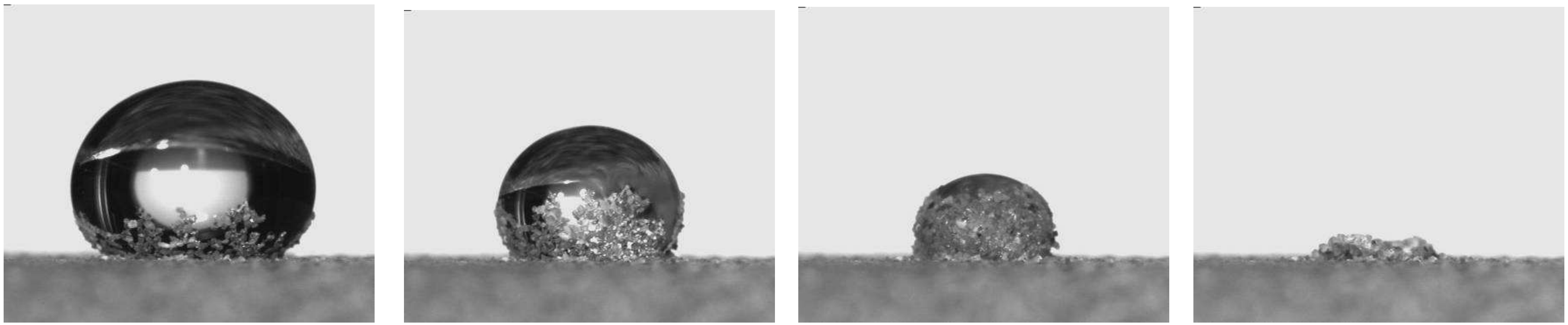
$\theta_c = 50.73^o$

*Consistent with experiments**

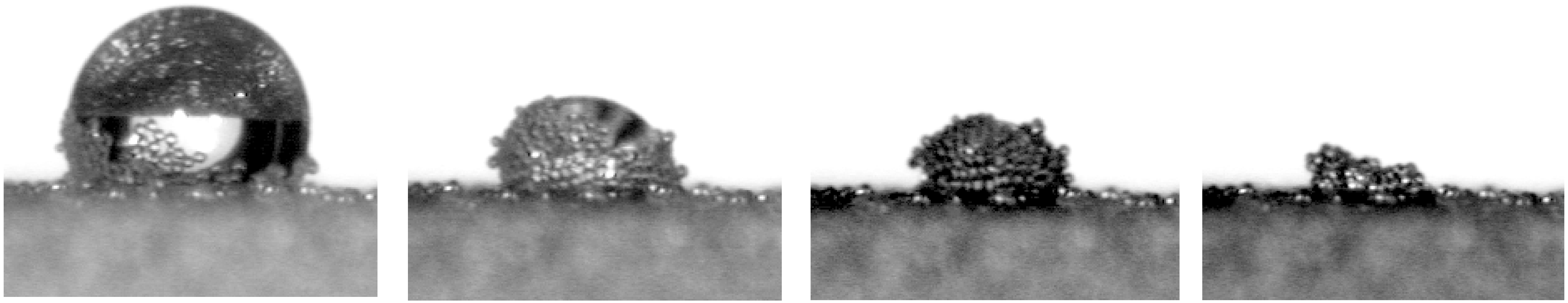
References: Shirtcliffe *et al*, submitted to Appl. Phys. Lett. (2006); *S. Bán, E. Wolfram, S. Rohrsetzher 22, 301-309 (1987).

Evaporatively Driven Coating

Water on Hydrophobic Sand



Water on Hydrophobic 75 μm Silica Beads



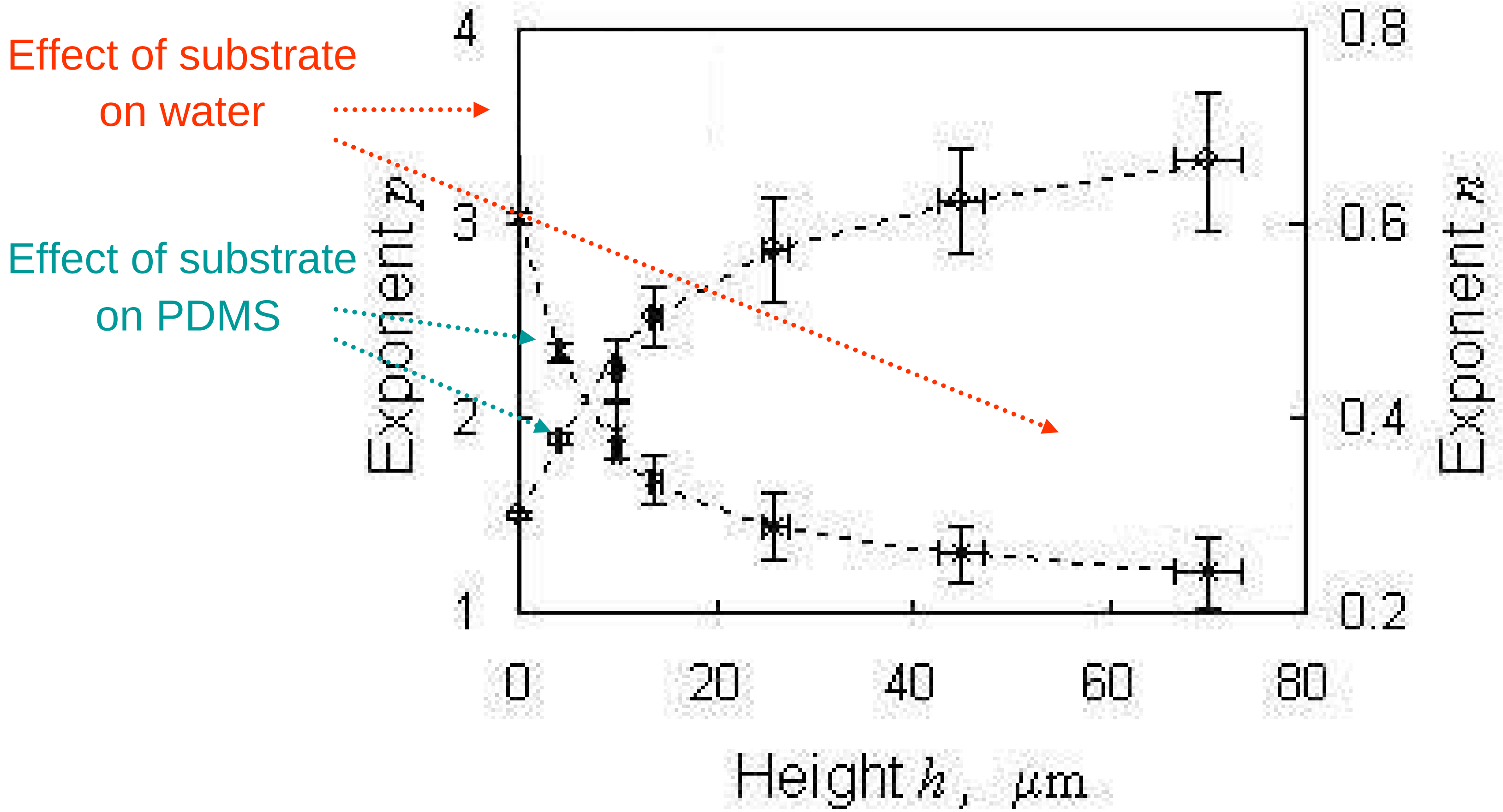
Reference Shirtcliffe *et al.*, submitted to APL (2006).

3. Super-spreading of PDMS on Pillars

- Data for Exponents *p* and *n*

  PDMS oil spreading down to zero degrees (i.e. film)

  Edge Speed $v_e \sim \theta^p$ shows cubic-to-linear transition as pillar height increases



<u>Reference</u> McHale *et al*, Phys. Rev. Lett. <u>93</u>, (2004) article 036102.