NOTTINGHAM
TRENT UNIVERSITY

Super-hydrophobic Surfaces

Glen McHale

School of Biomedical & Natural Sciences
Nottingham Trent University
Nottingham NG11 8NS, UK

Email: glen.mchale@ntu.ac.uk

Overview

1. Super-hydrophobicity

- Water repellence in nature
- Mechanisms

2. Surfaces & Materials

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

3. Experiments

- Double length scale systems
- Super-hydrophobic-to-porous transition
- Super-spreading on rough surfaces
- Granular/”soil” systems

4. Electrowetting

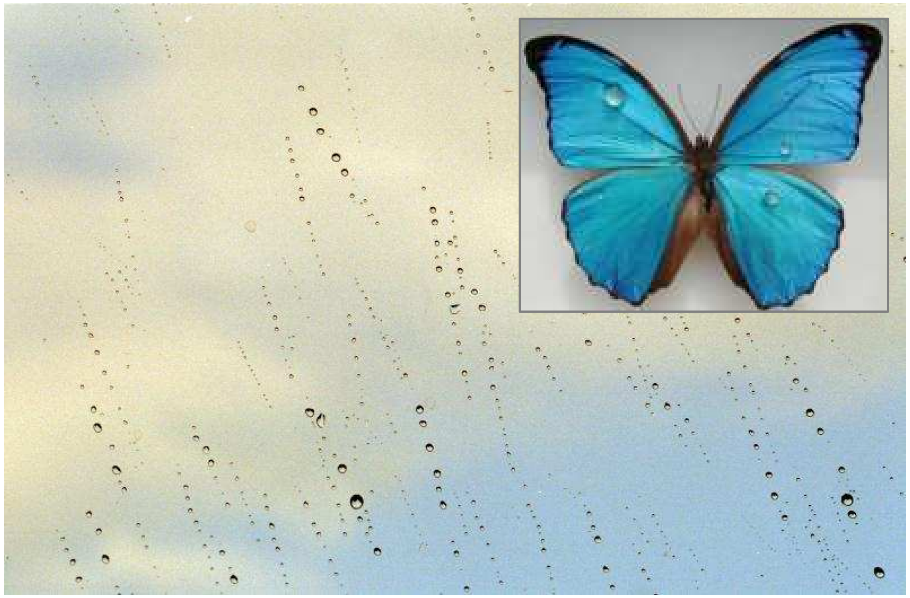
- Electrowetting-on-dielectric (EWOD)
- Combining with super-hydrophobic surfaces

Water Repellence in Nature

Sinking and Falling?

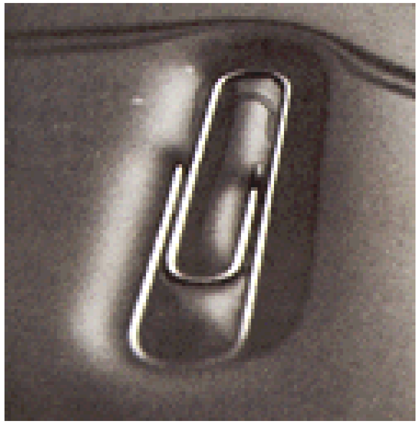
Water-on-Solids

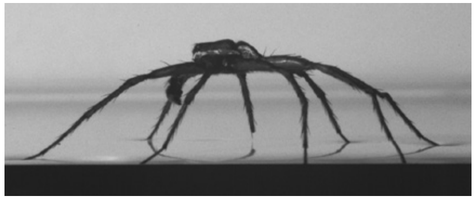
- Liquids sometimes form drops, and sometimes spread over a surface and wet it. Why does this happen?
- Why are raindrops never a metre wide?
- Why don’t they run down the window?
- Why do butterfly wings survive rain?



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?





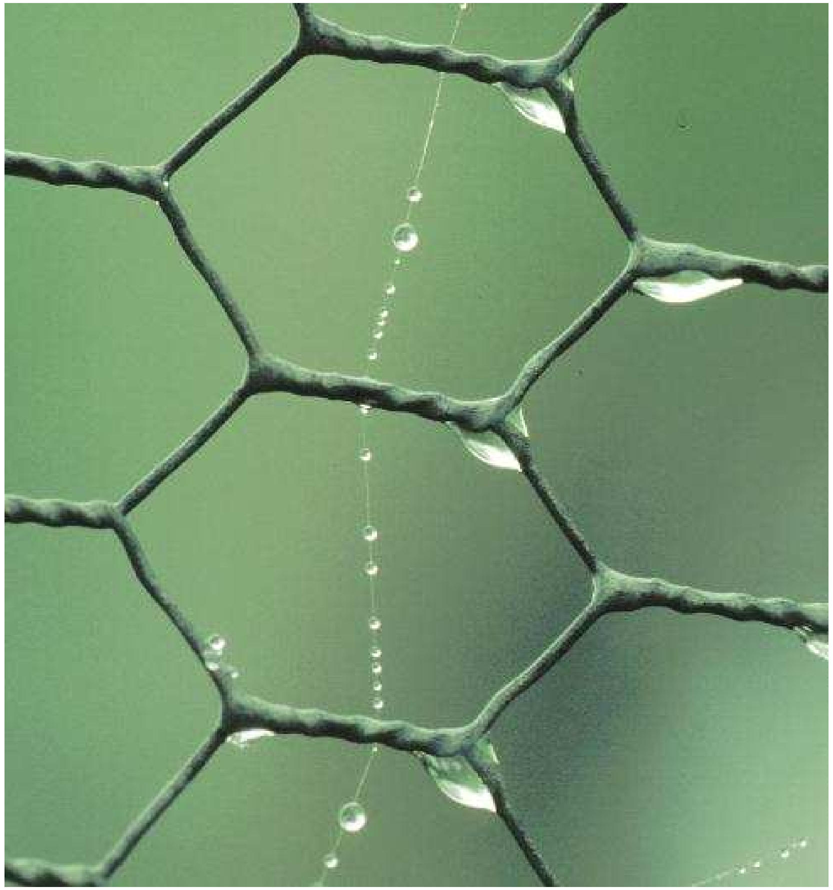
Plants and Leaves

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 ⇒ Surface tension wins

- Small means << 2.5 mm for water

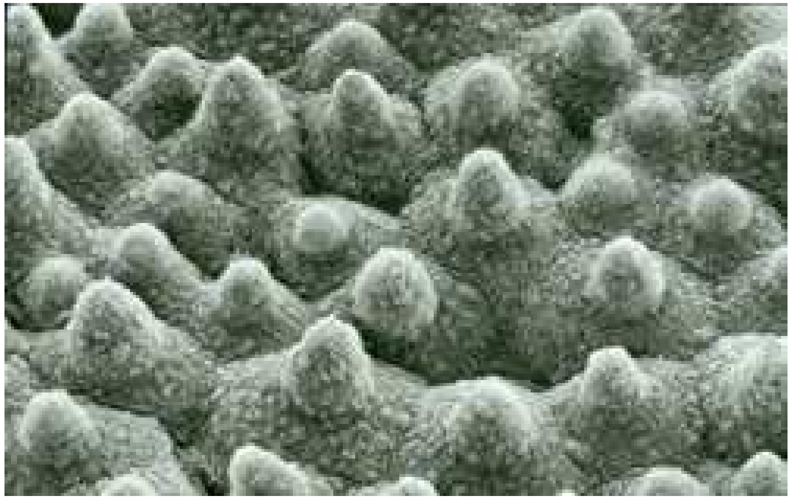
Acknowledgement www.brantacan.co.uk

The Sacred Lotus Leaf

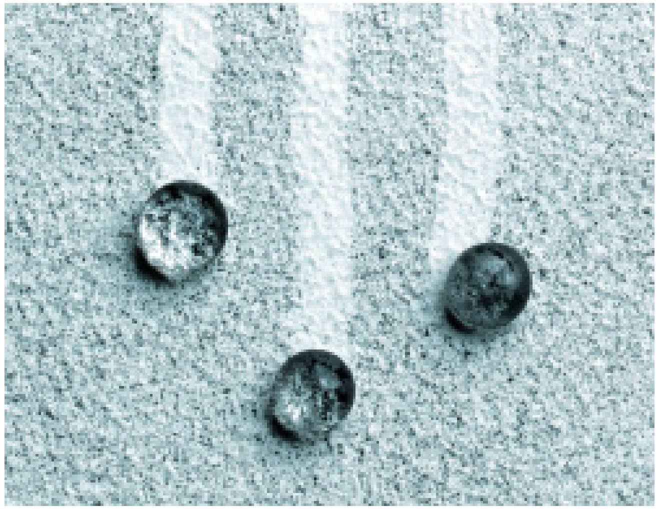
Plants

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

SEM of a Lotus Leaf



Self-Cleaning



Self-Poisoning

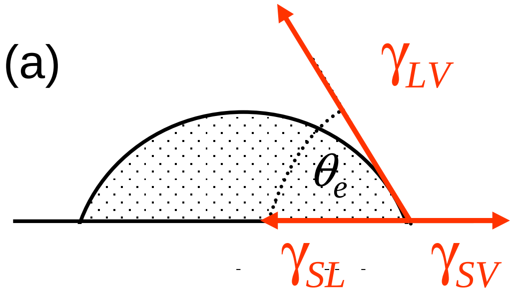
Acknowledgement Neinhuis and Barthlott

Mechanisms of Super-Hydrophobicity

Contact Angles & Topography

Smooth Surface

Young's equation summarises
the surface chemistry



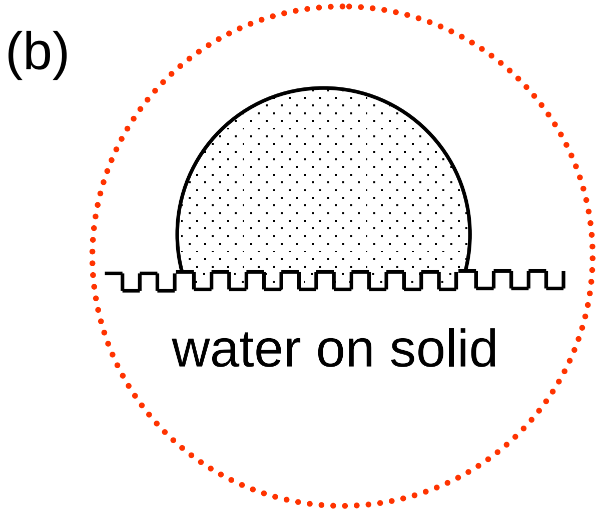
Force Balance

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

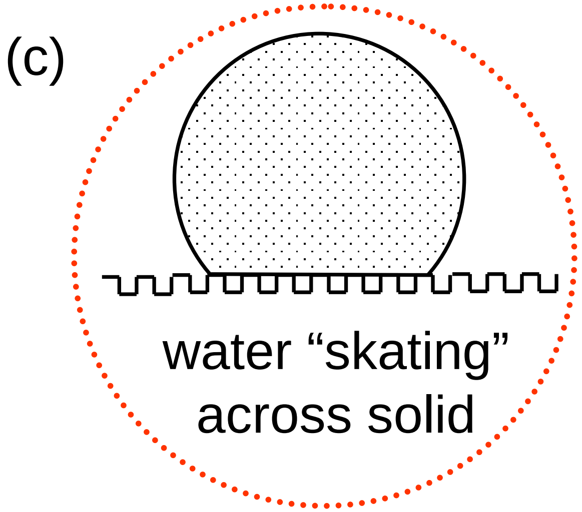
$$\boxed{\cos\theta_e = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}}}$$

Rough/Structured Surfaces - Identical surface chemistry

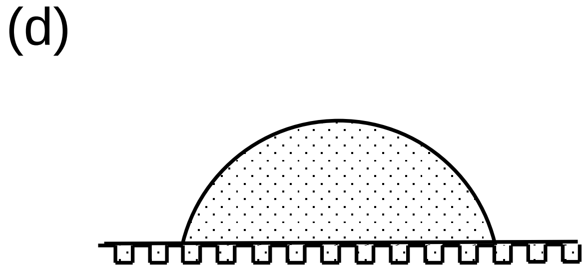
Wenzel *Cassie-Baxter*



water on solid



water "skating"
across solid



water on
solid-liquid surface

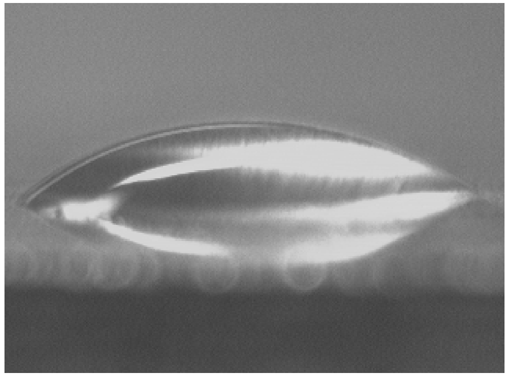
Wenzel ("Sticky")

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

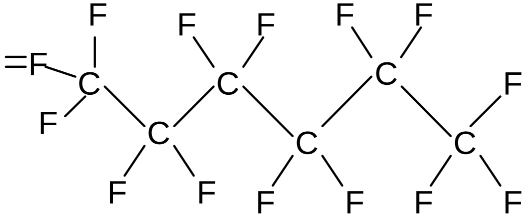
Cassie-Baxter ("Slippy")

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

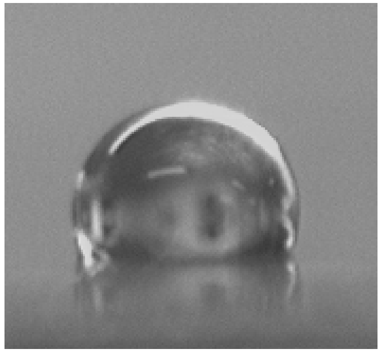
Super-hydrophobic Surfaces



Simple Cu surface

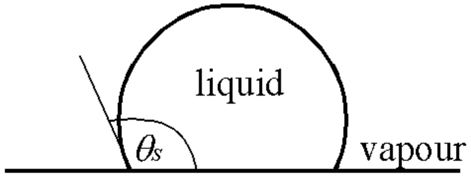


Grangers' molecular chain

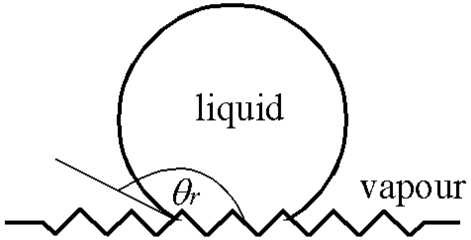


Hydrophobic surface

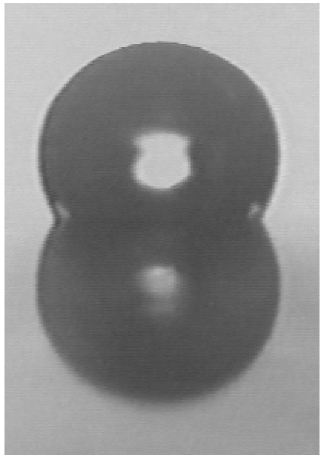
Water Drop (~ 2 mm)

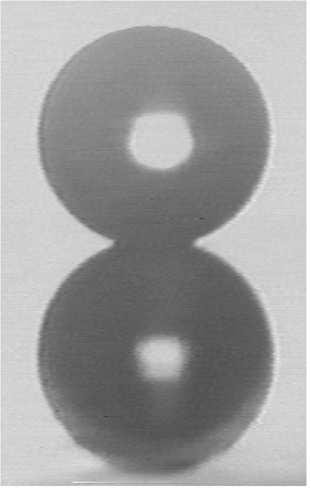


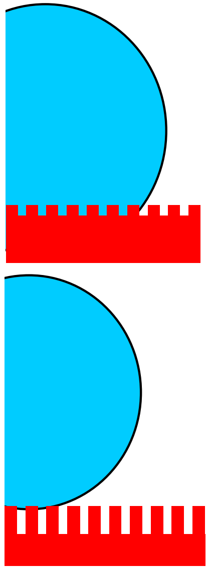
smooth solid surface



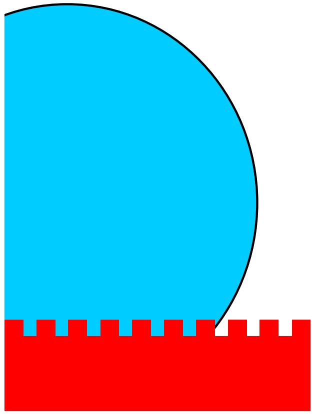
rough solid surface







Two Forms of Super-Hydrophobicity



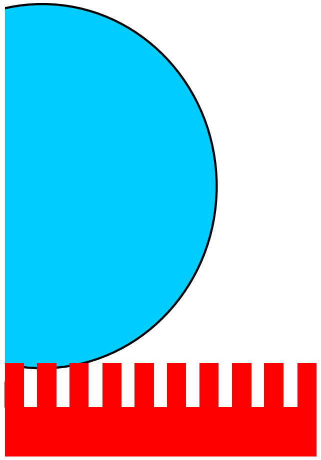
Wenzel's Equation

- Based on roughness, *r*

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

- Super-H with large hysteresis,

  i.e. "Sticky" surface



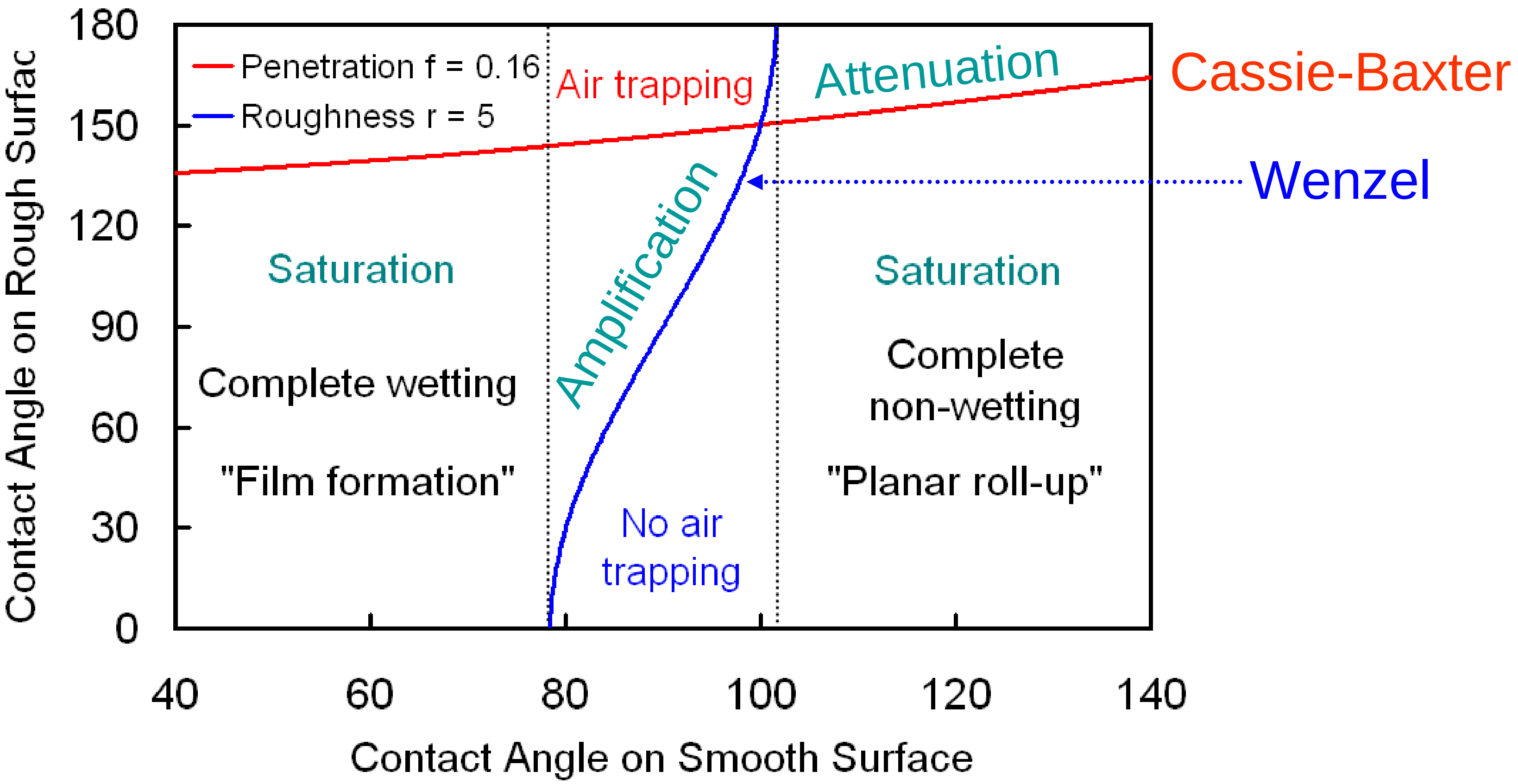
Cassie-Baxter Equation

- 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

Effect of Topography - Theory



Roughness/Topography

θ_e^s > threshold

⇒ enhances hydrophobicity

θ_e^s < threshold

⇒ enhances film formation

Super-hydrophobic

Air “trapping” (“Skating case”)

⇒ most existing examples

Pressure

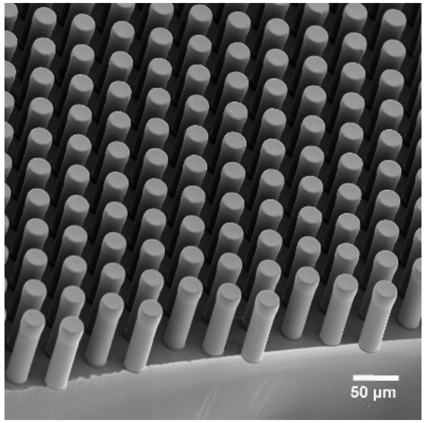
⇒ air “trapping” disappears

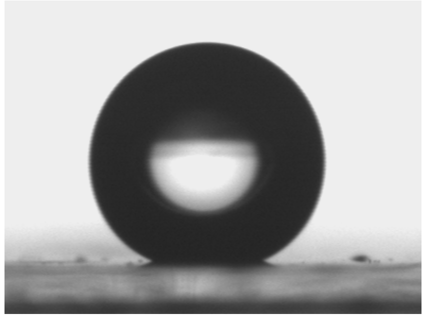
Penetration-to-Skating Transition

Micro-Structured Surface

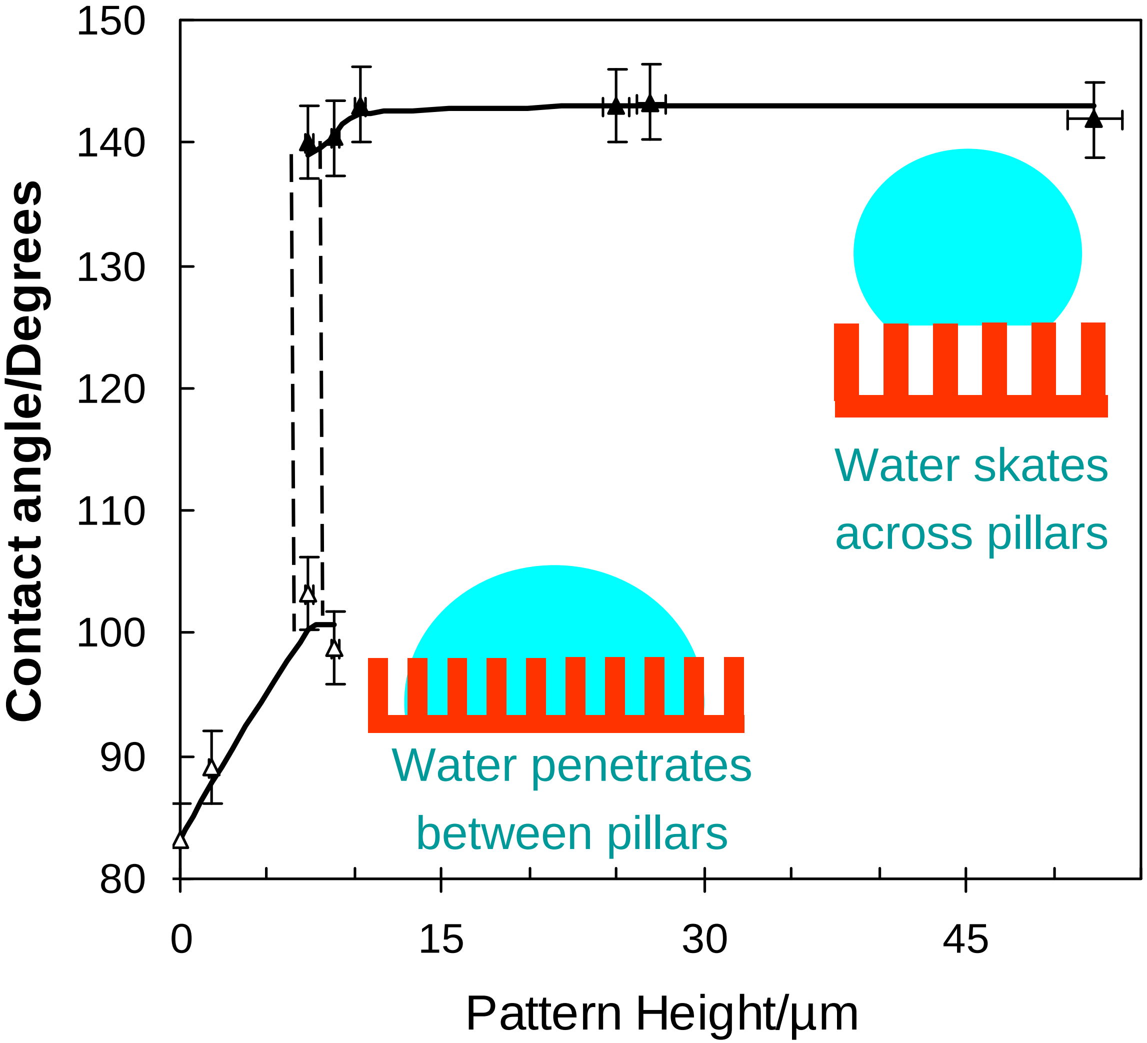
SU-8 pillars 15 µm

Hydrophobic treatment

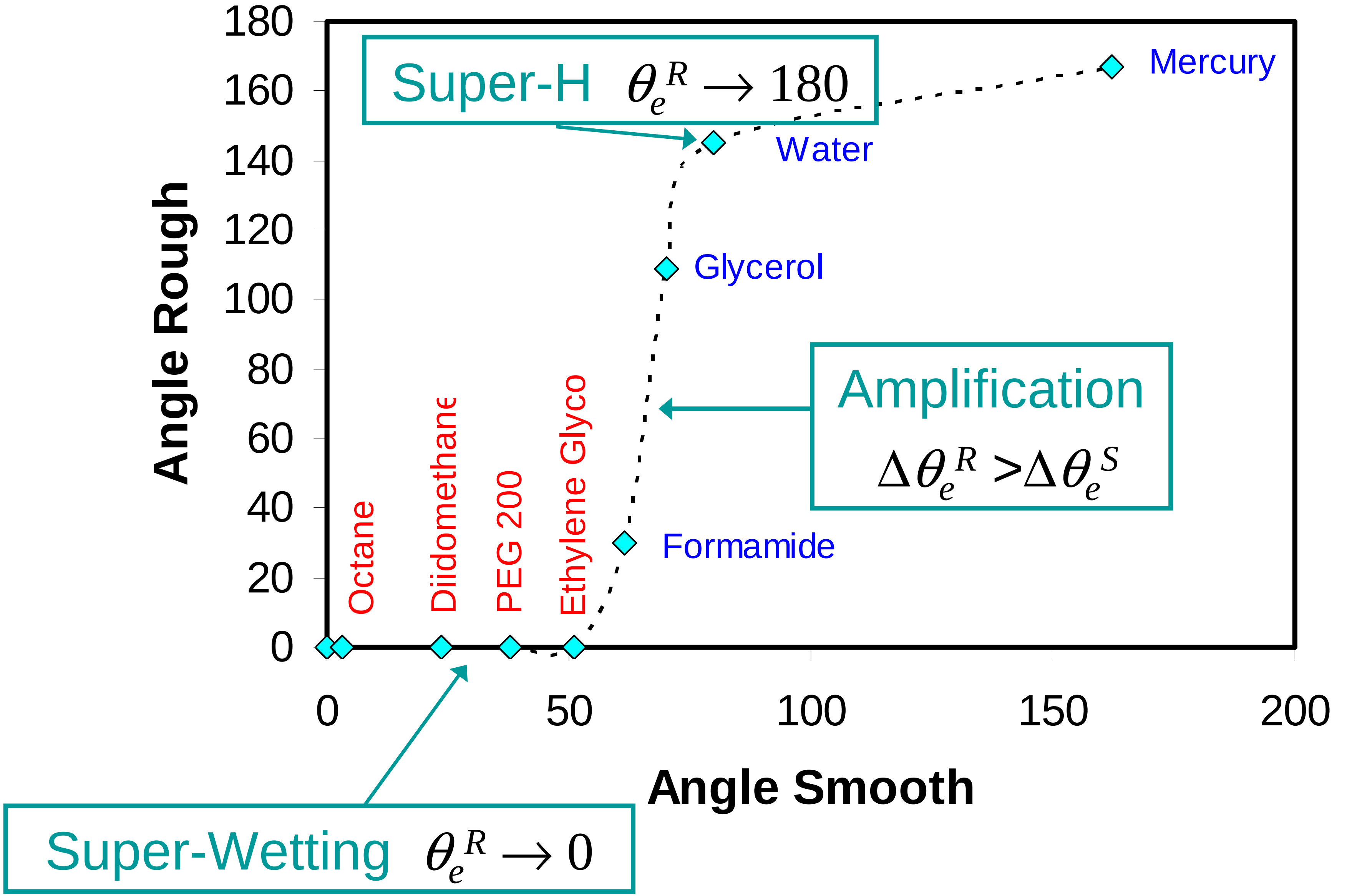




Change of Pillar Height



Different Liquids on a Super-H Surface



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

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

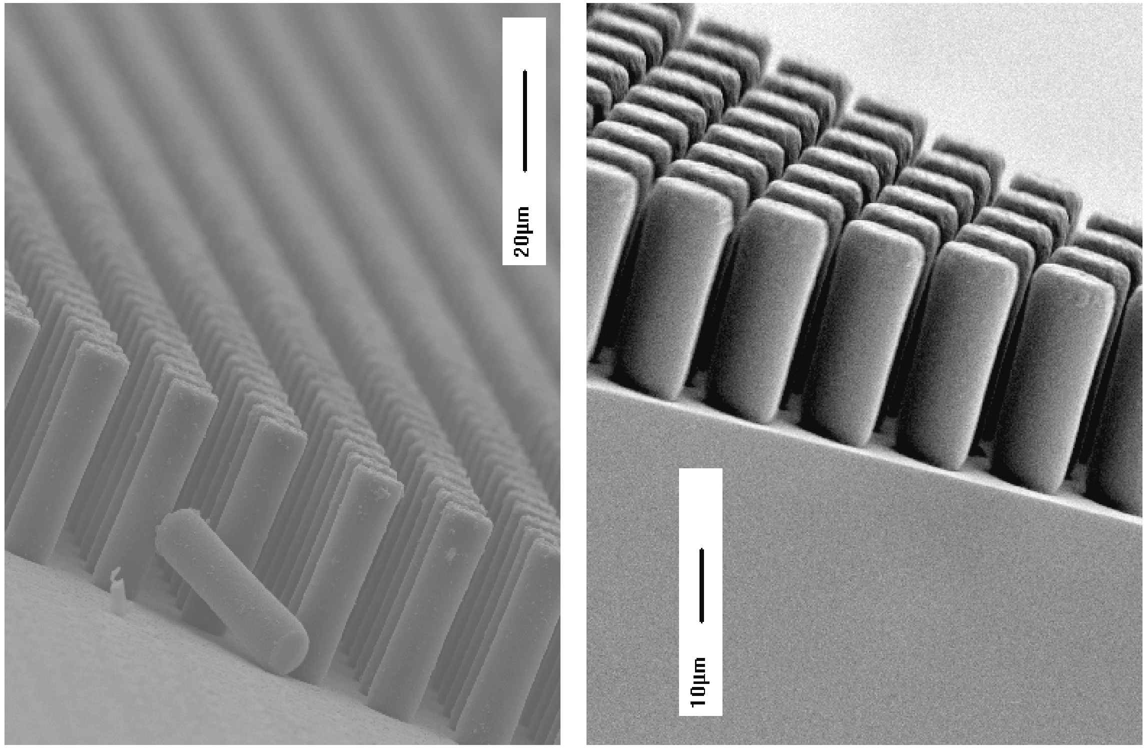
Super-Wetting $\theta_e^R \to 0$

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

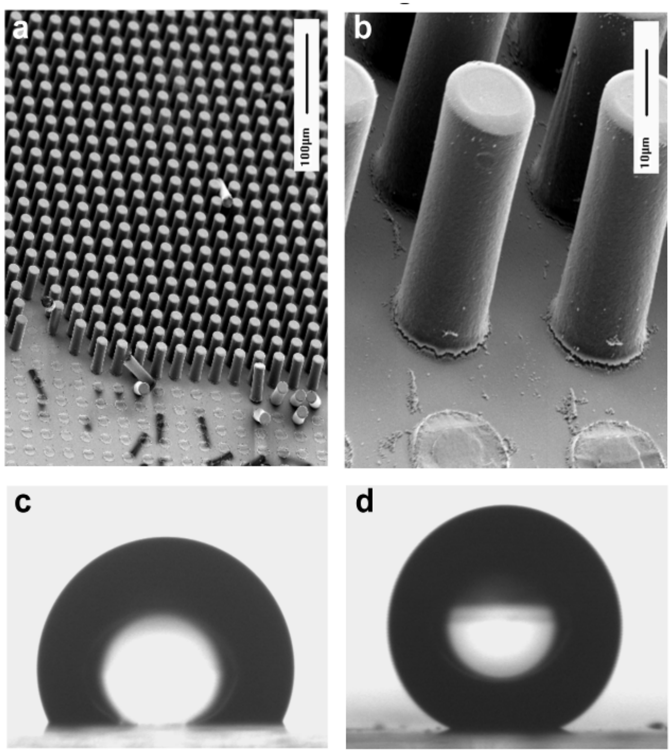
NTU Materials Work

1. SU-8 Photoresist Pillars

SEMs of Pillars



Effect on Water



Tall structures to 45-75 µm

smooth and straight walls

Aspect ratios up to ~ 7

a), b) Pillars *D*=15 µm, *L* = 2*D*

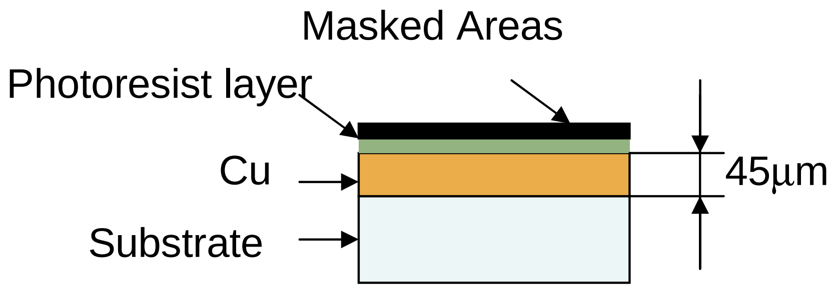
c) Flat and hydrophobic

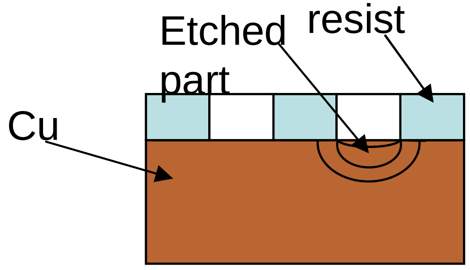
d) Tall and hydrophobic

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

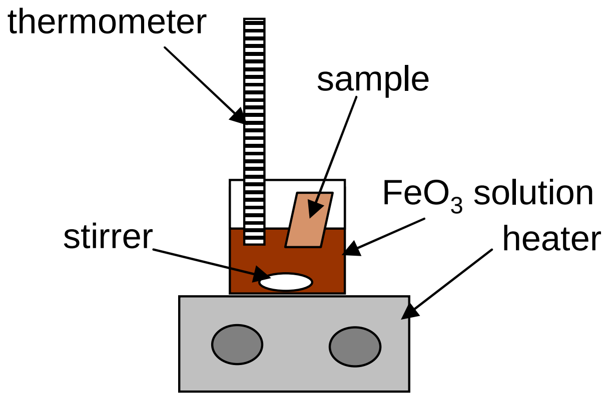
2. Etching of Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

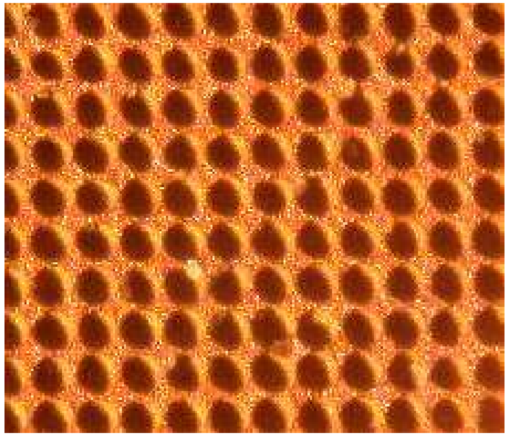




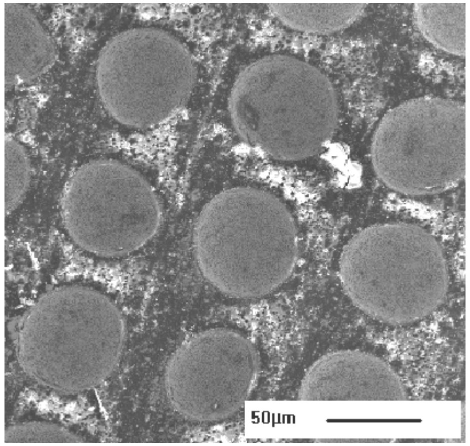
hole growth



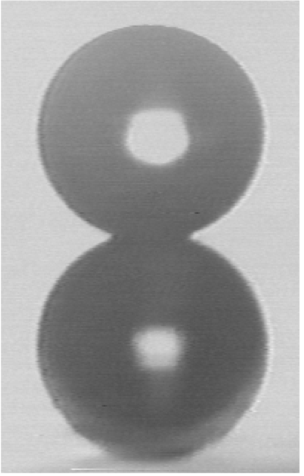
Setup of the copper etching



Copper sample etched through a 30 µm pattern



SEM picture of the pattern of the etched copper surface



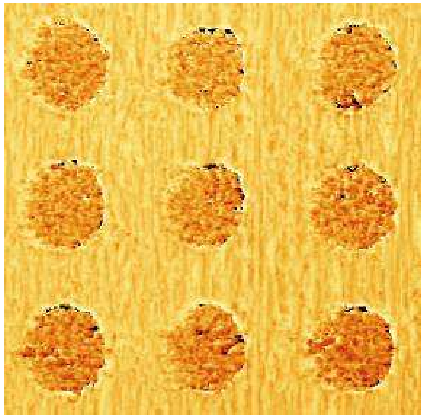
Water drop and reflection on an etched copper surface

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

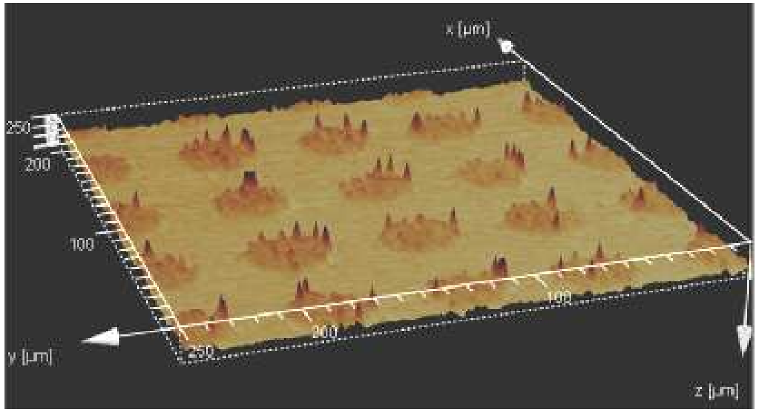
3. Electrodeposited Surfaces

- Diffusion limited aggregation – acid copper bath, fractal roughness

Base Cu electroplated surface

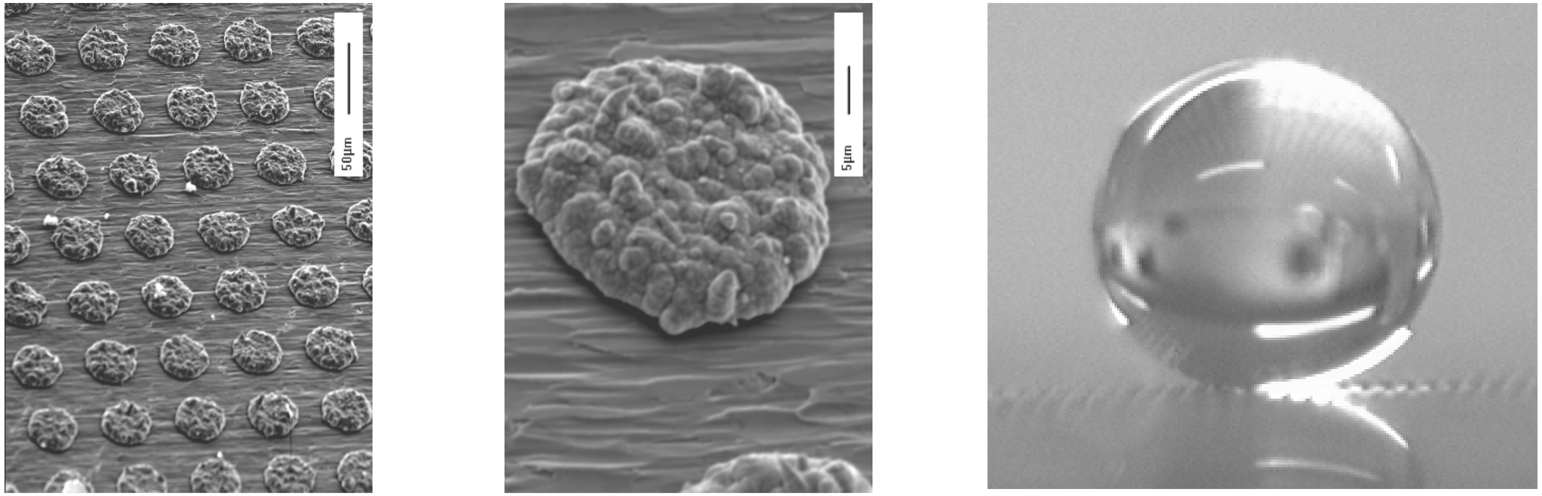


Confocal image of a 30µm textured electroplated Cu



3D view of a electroplated copper sample

- “Chocolate Chip Cookies” - Electroplating through a mask

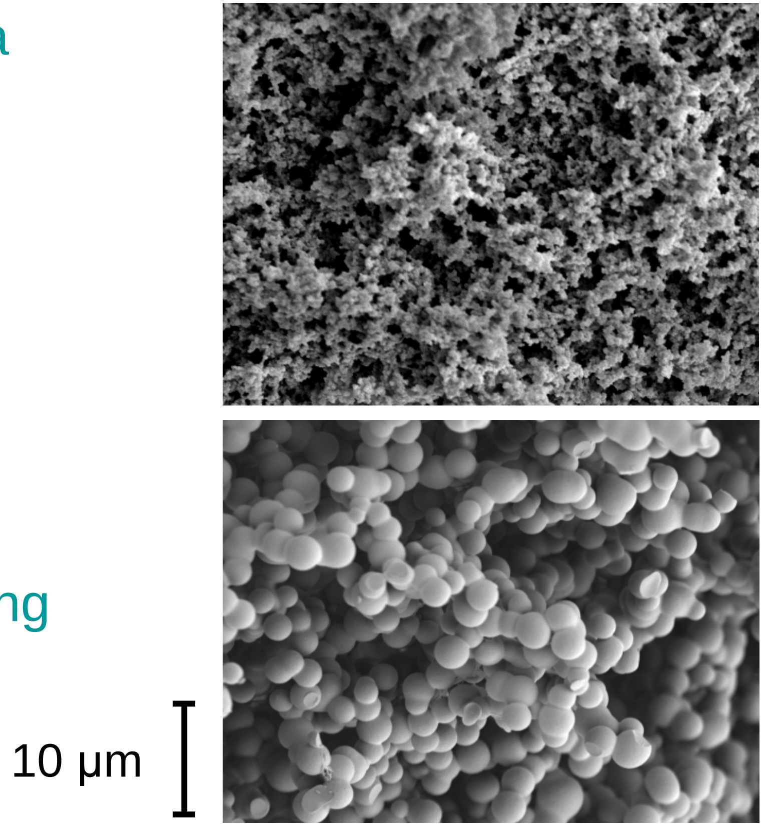


Reference   Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932.

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°
    - Hydrophobic-to-hydrophilic transition by heating

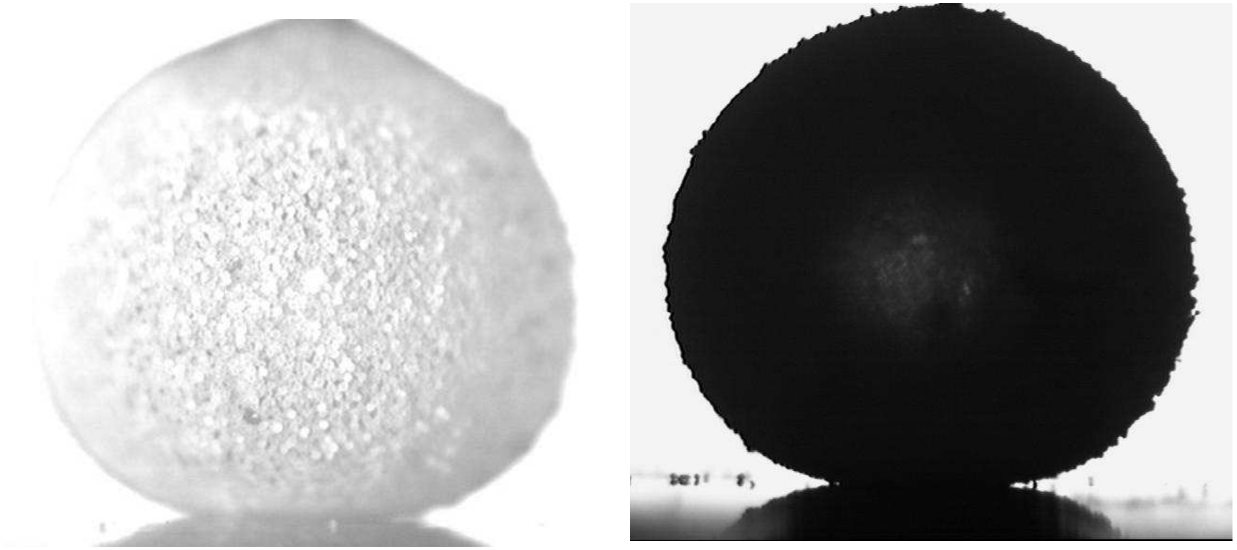


Reference Shirtcliffe *et al*, Langmuir 19 (2003) 5626-5631

5. Liquid Marbles

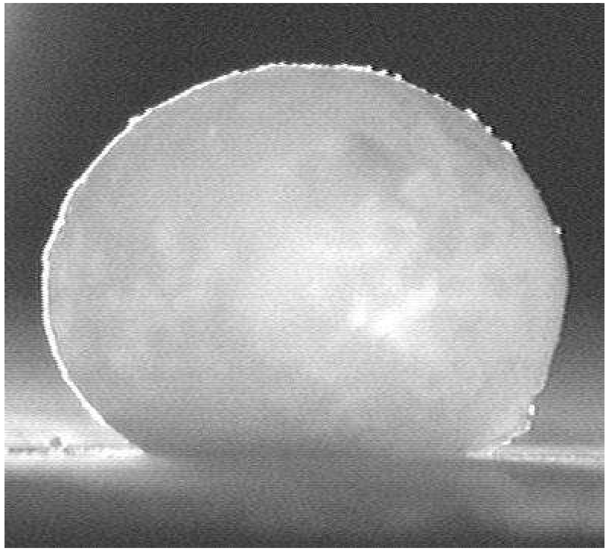
- Hydrophobic Grains Adhere to the Solid-Liquid Interface
  - Water droplets can self-coat to create perfect marbles
  - If done well - ideal 180^{o} system which rolls around on a solid surface

Hydrophobic Lycopodeum



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

Hydrophobic Silica

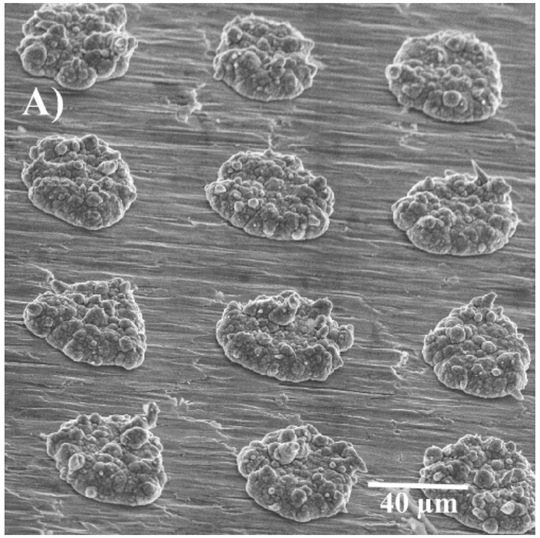


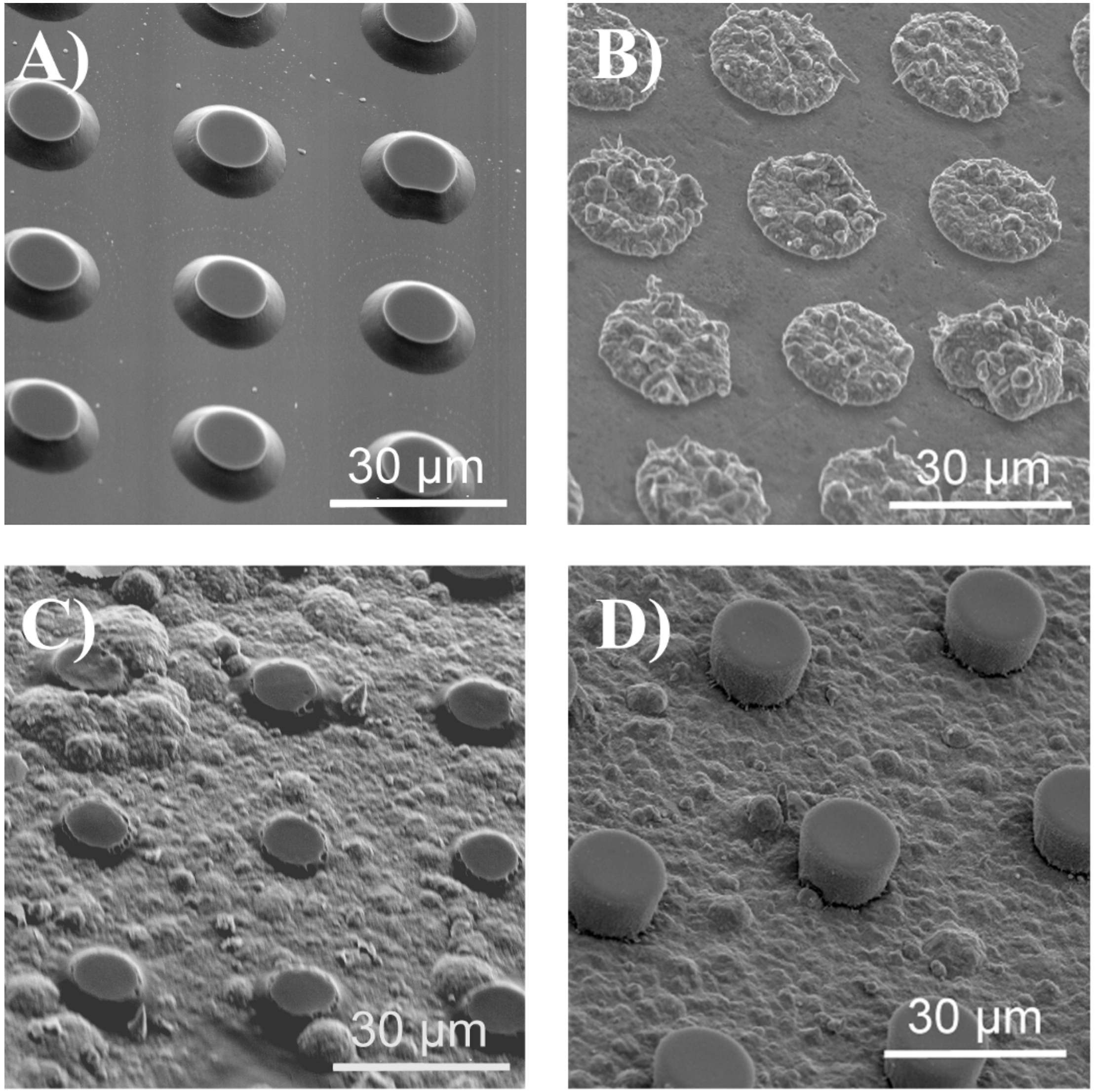
Silica grains are sub-µm,
but layer is thick

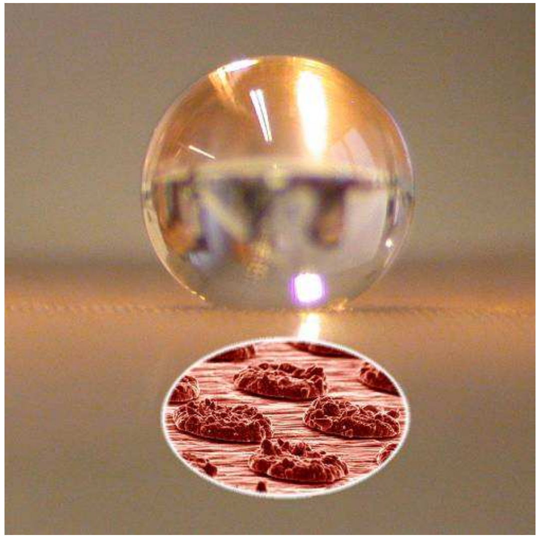
Acknowledgement David Quéré, College de France, Paris.

NTU Experiments

1. Double Length Scale Systems

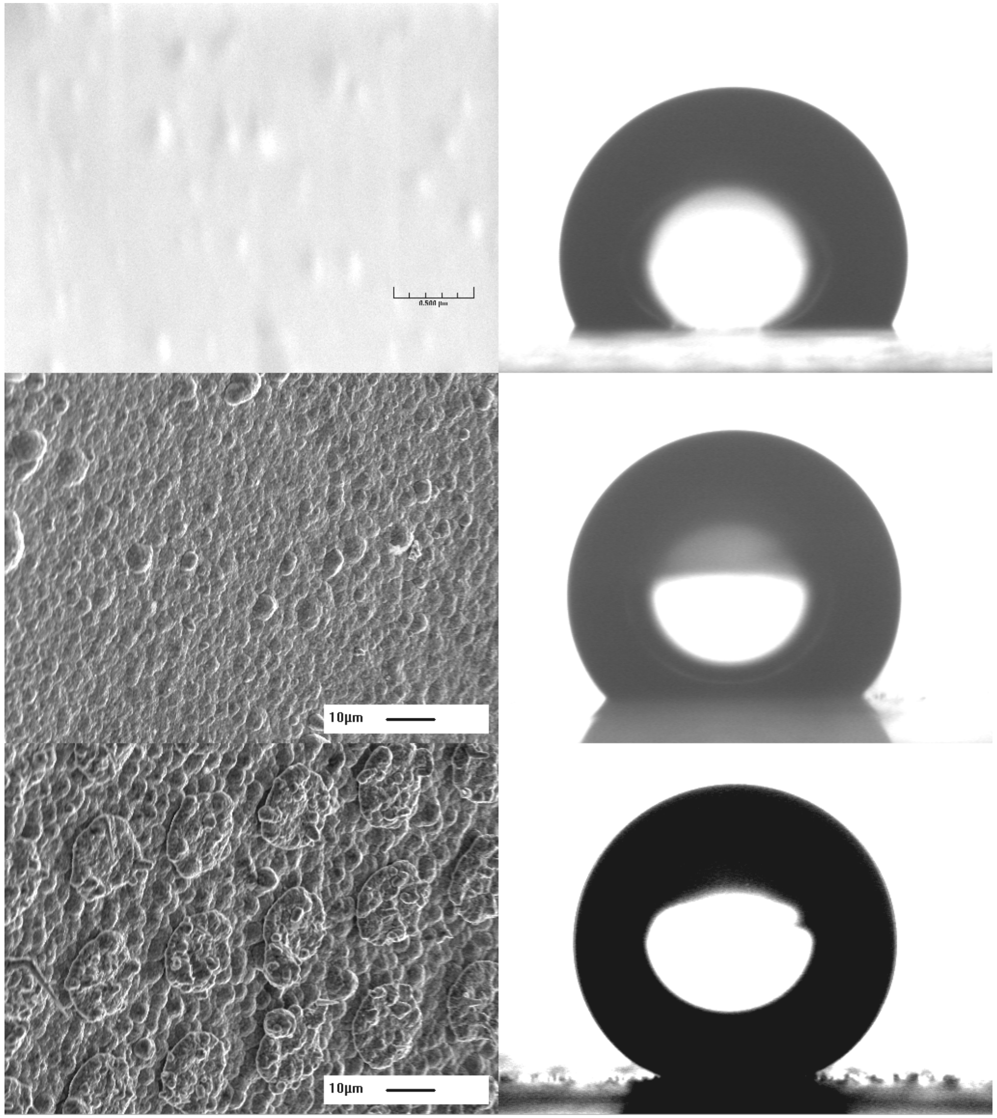






Combining Slight Roughness and Texture

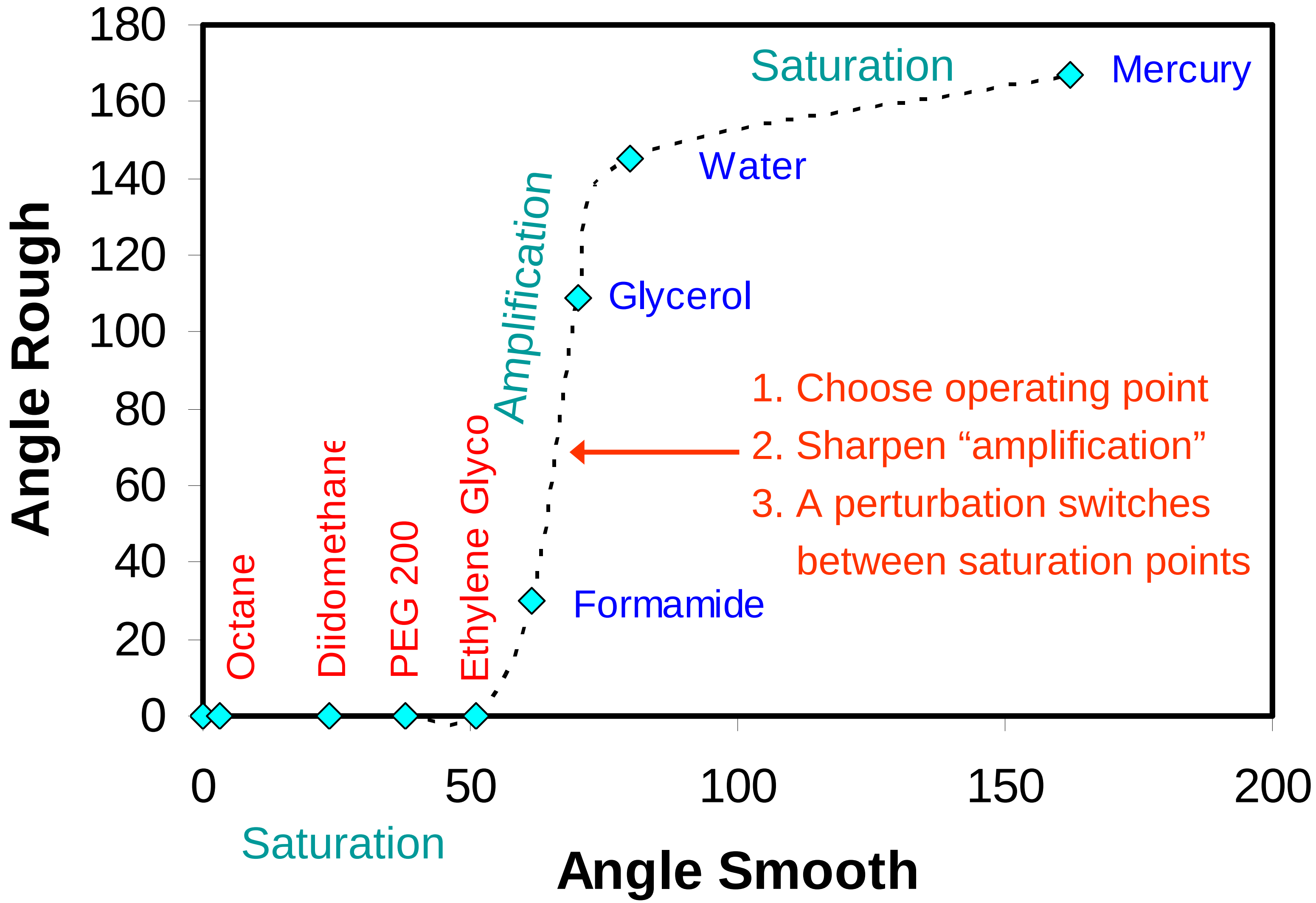
- Smooth and Hydrophobised 115^o
- Slightly Rough and Hydrophobised 136^o
- Slightly Rough, Textured and Hydrophobised 160^o



Two Length Scales is extremely effective

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

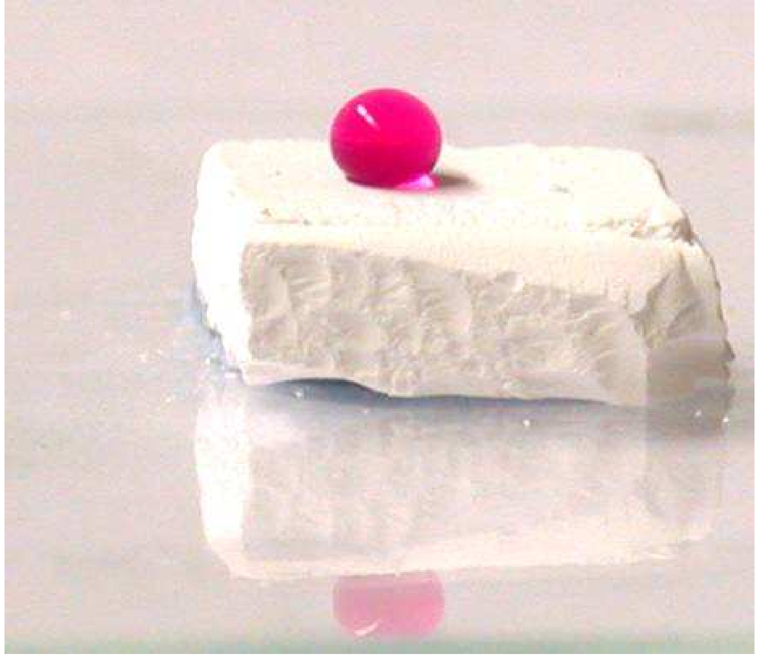
2. "Digital" Switching - Recall



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

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

2. Sol-Gel Foams – Switching from S/H



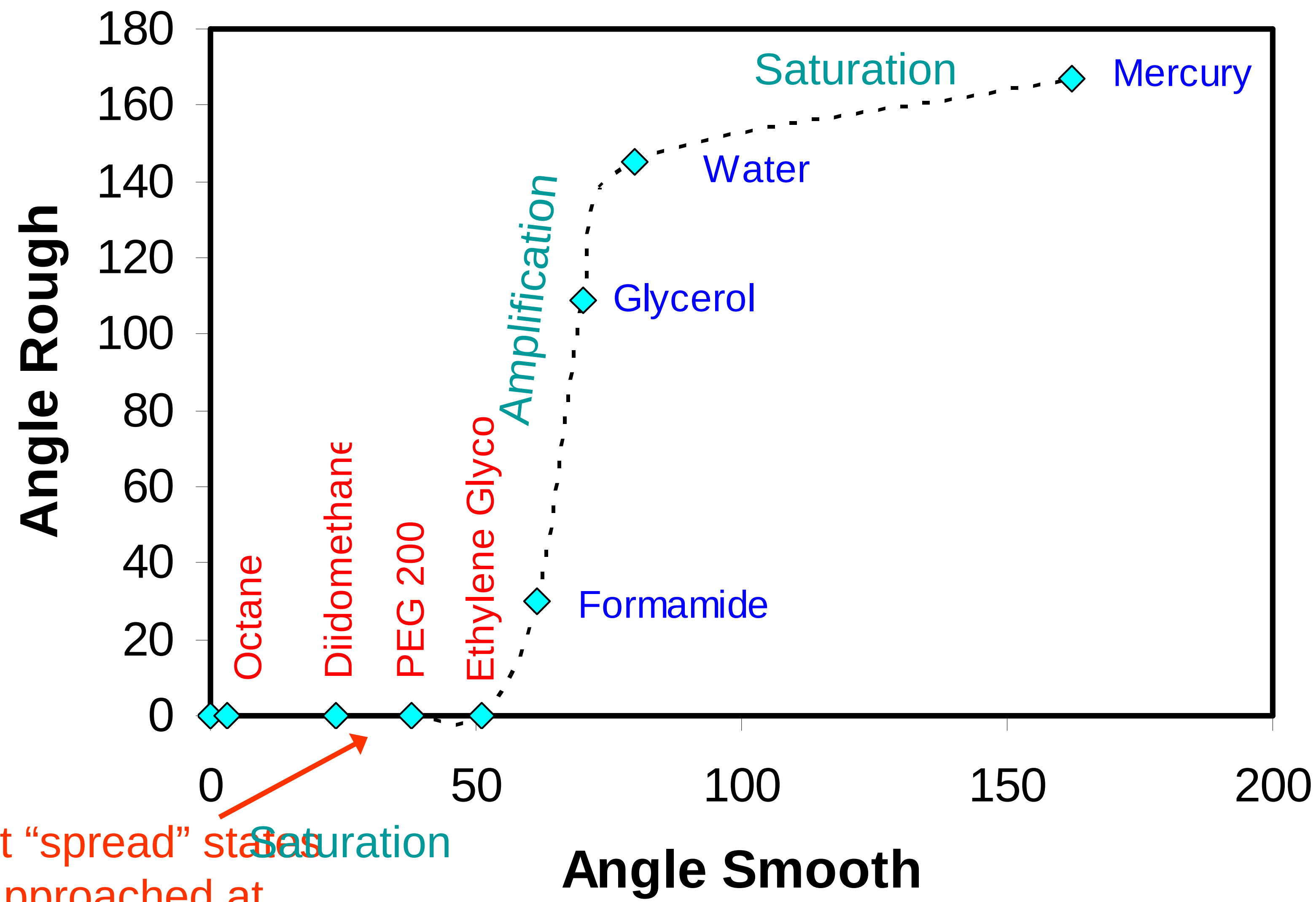
Foam heated
(and cooled)
prior to droplet
deposition

- 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



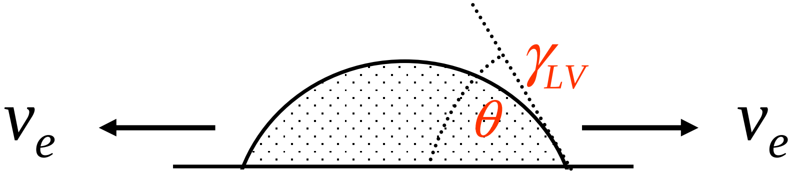
Different “spread” states
are approached at
different rates

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 $v_E \propto \theta$

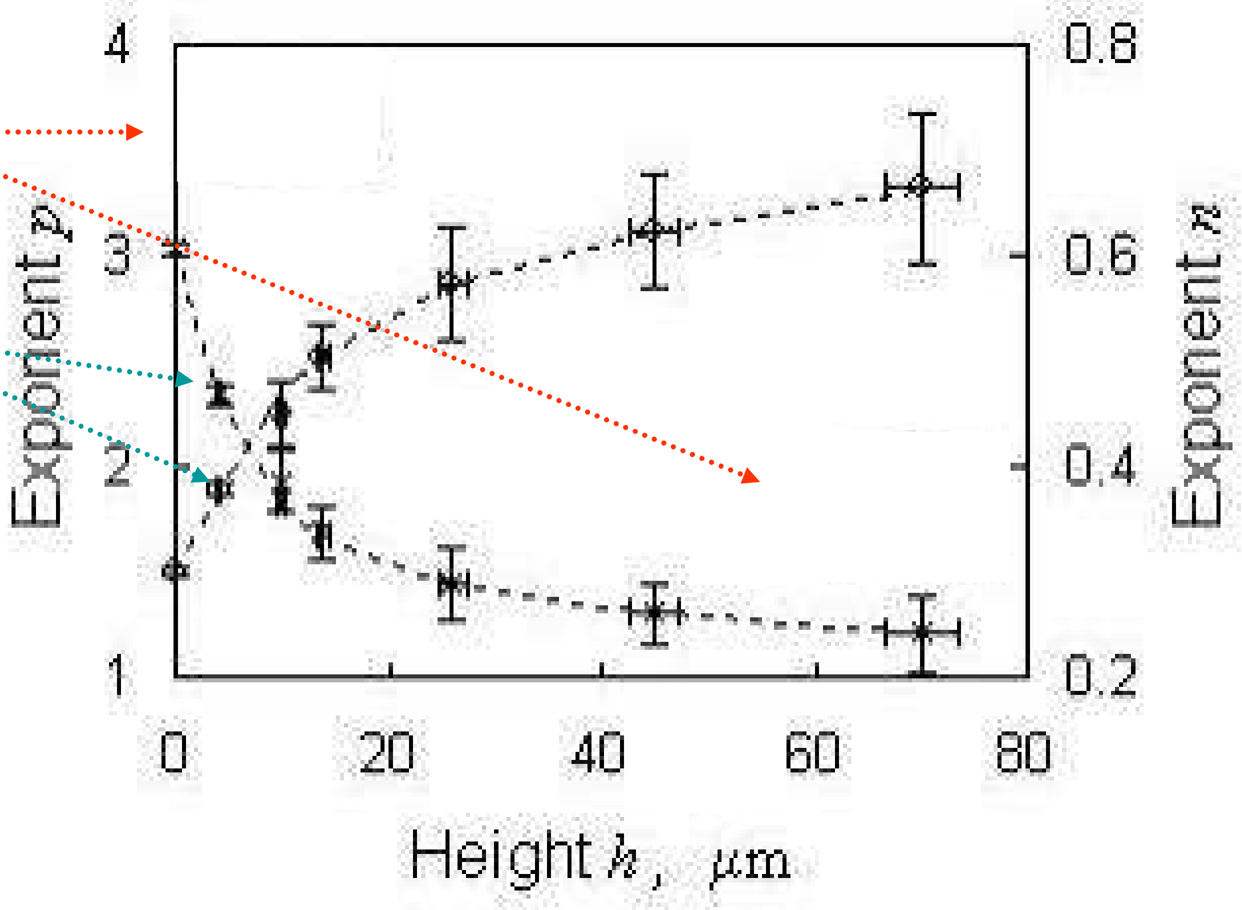
Reference McHale and Newton, Colloids & Surfaces, A206 (2002) 193-201.

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



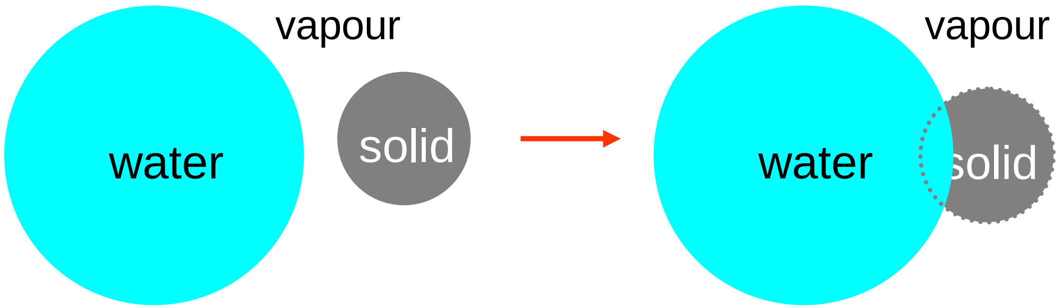
Effect of substrate
on water

Effect of substrate
on PDMS

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

4. Droplets on Granular Surfaces

Surface Free Energy

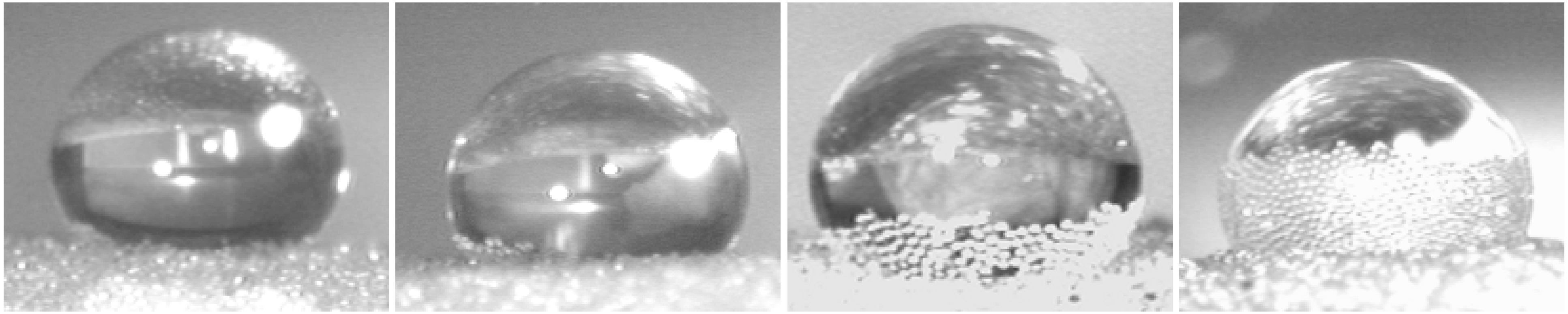


$$\Delta F = -\pi R_g^2 \gamma_{LV}(1 + \cos\theta_e)^2$$

Hydrophobic grains lift from surface and preferentially cling to solid-liquid interface

Hydrophobic Silica Particles

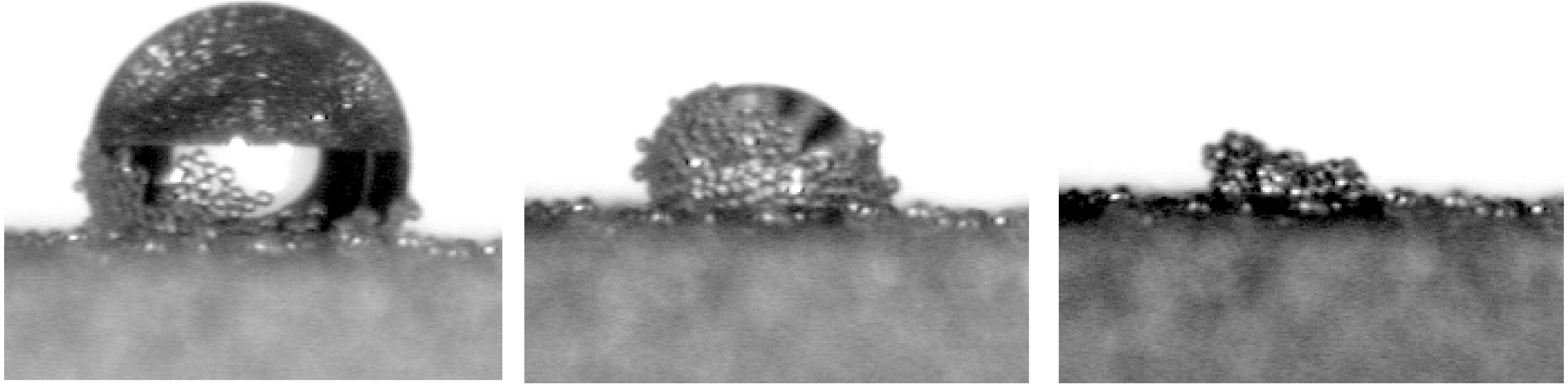
Initial coverage effect of different liquids



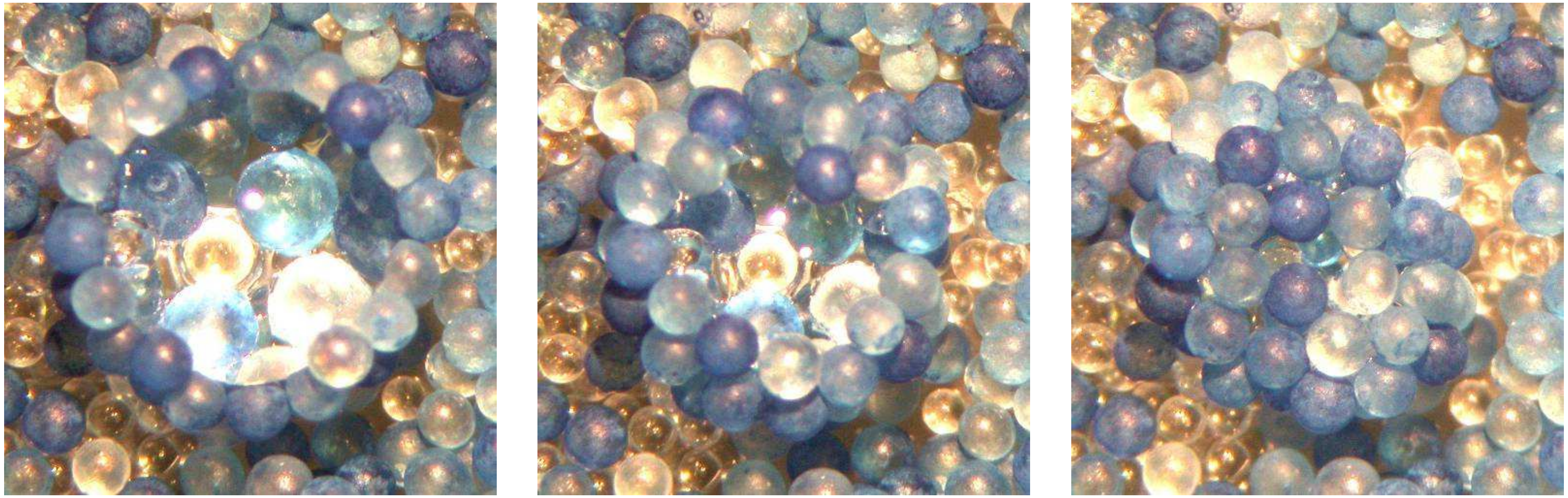
Reference McHale et al, Eur. J. Soil. Sci. 56 (2005) 445-452, and McHale *et al*, To be submitted.

Hydrophobic Granular Self Sorting

Water droplet digging during drying

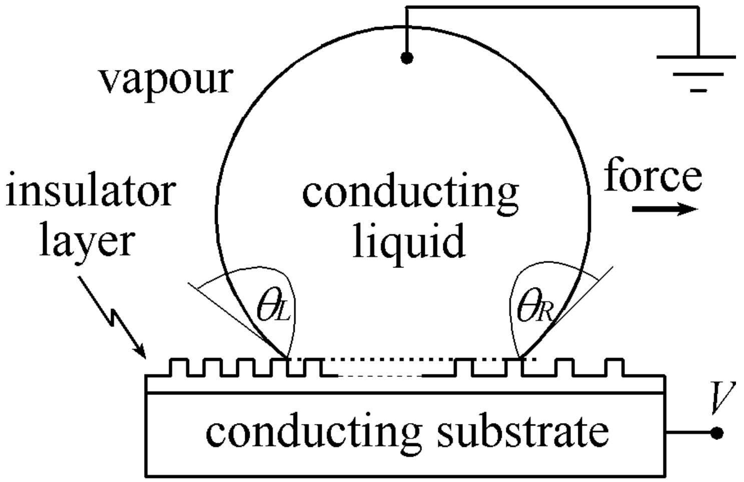


Mixed hydrophobic (blue)/hydrophilic (clear)



Electrowetting on S/H Surfaces

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

Super-hydrophobicity & EWOD

- Idea
  - Use S-H to gain high initial contact angle
  - Use electrowetting to tune over full angular range
- Thin Insulator, d
  - Capacitive energy $\propto V^2/d$
  - Thin insulator for lower voltages
- Electrowetting
  - Applying voltage causes electrocapillary pressure into surface texture (Wenzel)

Contradiction 1

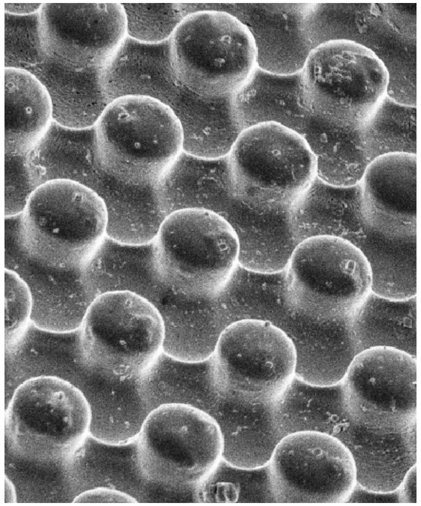
But Super-H via patterning insulator → high aspect ratio

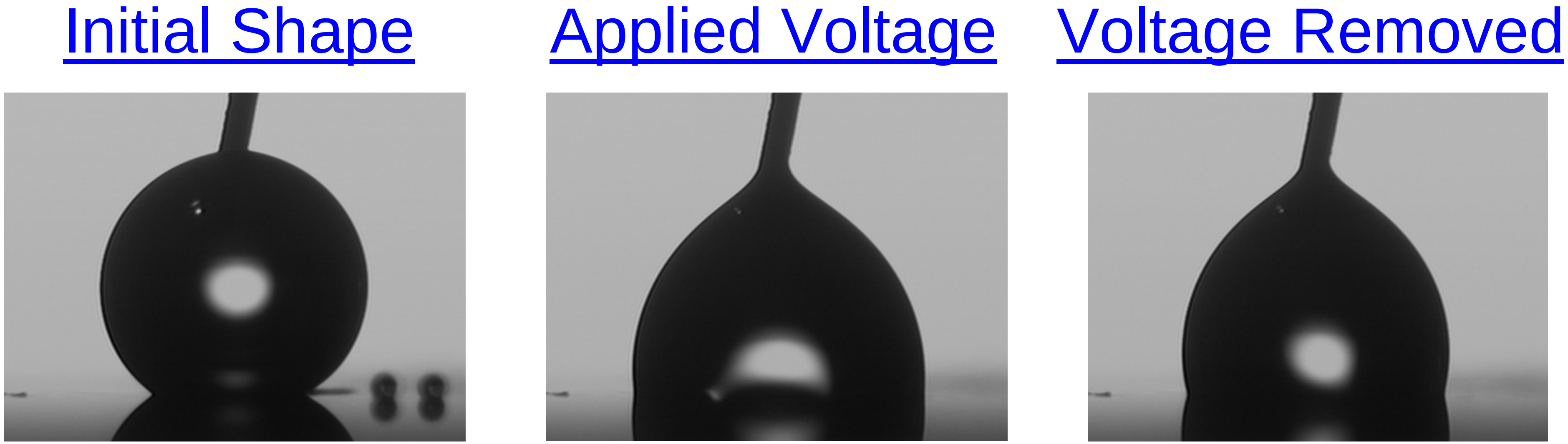
Contradiction 2

But low hysteresis requires Cassie-Baxter

Irreversible Electrowetting

- Lithographic System
  - Ti/Au on glass, SU-8 Pillars 7 µm diameter, 15 µm centre-centre, height 6.5 µm (roughness $r \approx 1.64$)
  - Spin coated Teflon AF1600 (not perfect, $r_{estimate} \approx 1.87$)
  - Droplets of deionised water with 0.01M KCl, DC voltage by steps up to 130 V

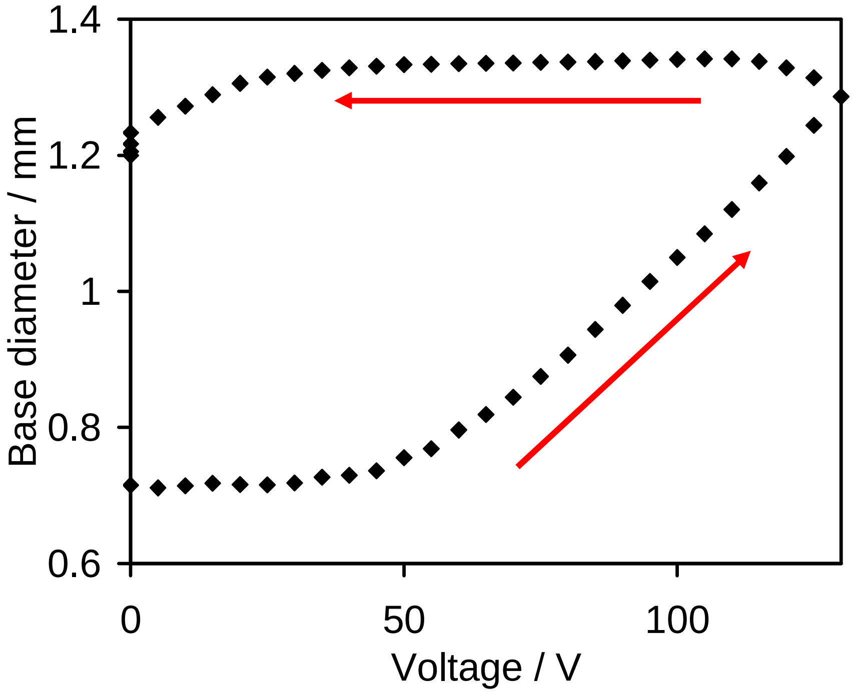




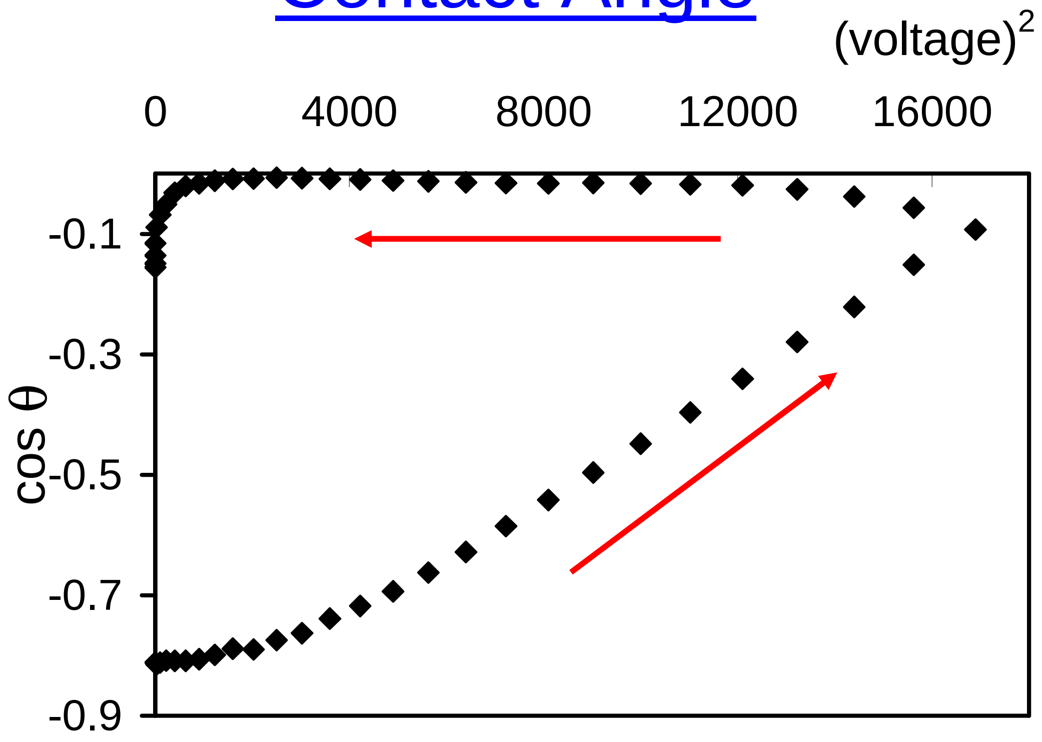
152° → 114°

Results on SU-8 Pillars

Base Diameter



Contact Angle

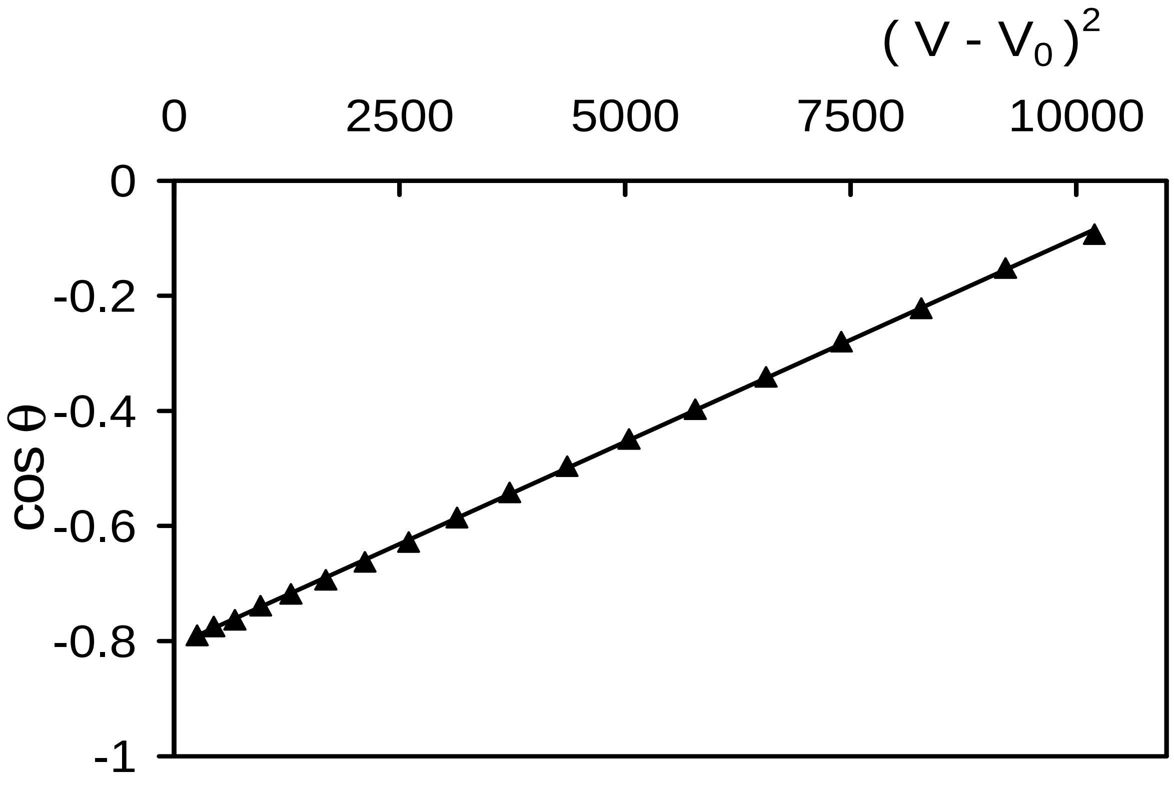


1. Threshold voltage (~ 45 V) before droplet spreads
2. Irreversible on removal of voltage

Fitting of Results

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

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

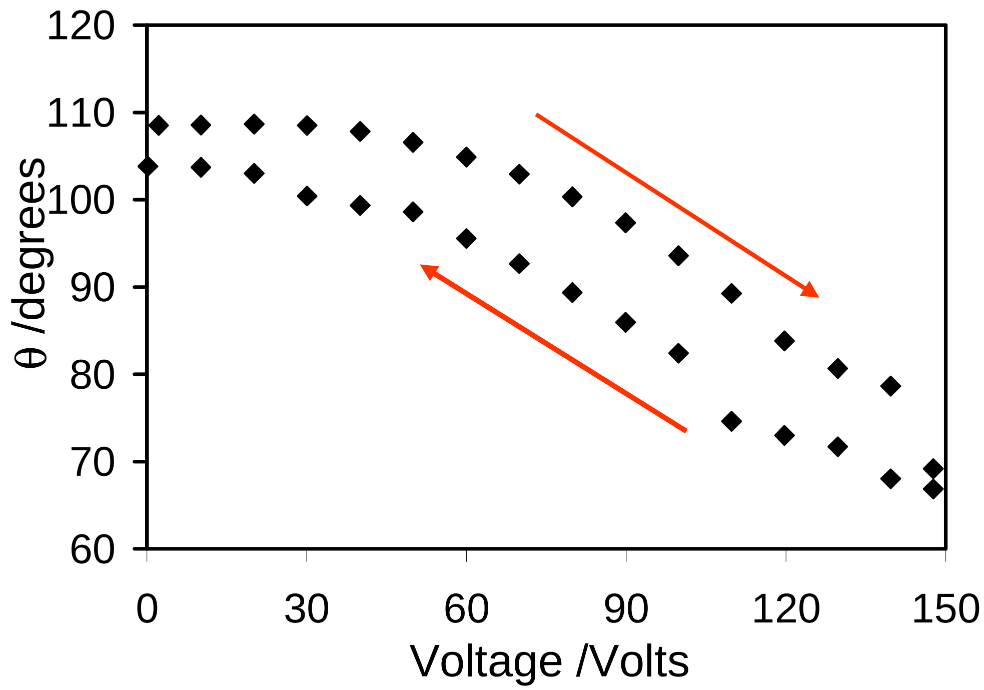


Interpretation

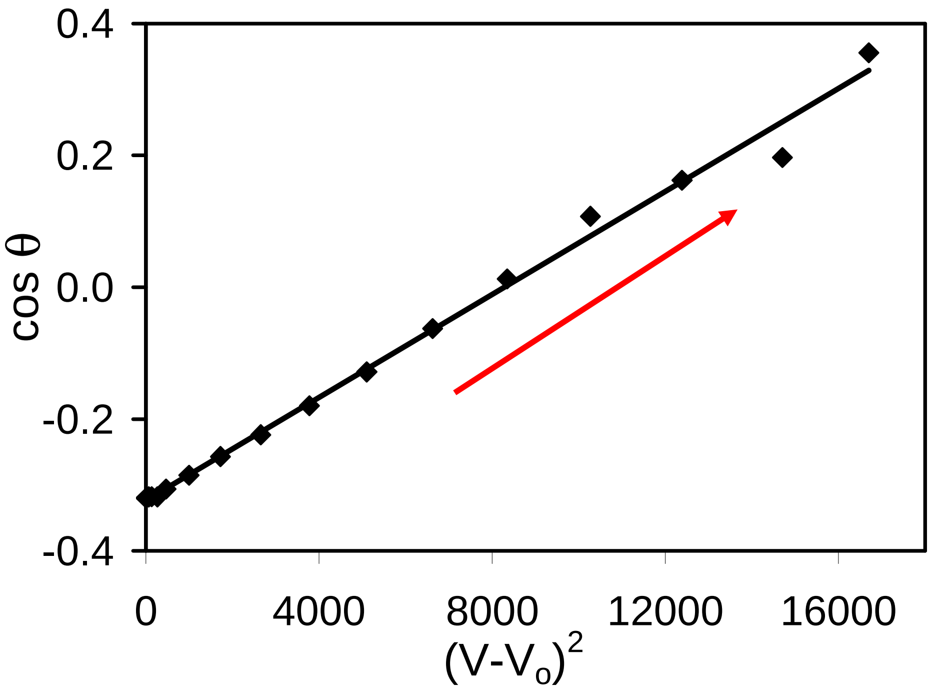
1. Conversion from C-B to Wenzel regime
2. V_o=28V represents charging
3. Fitted $\theta_e(0)$ gives Wenzel angle of 143° and predicts r=1.92 (SEM image 1.87)

Results on Flat SU-8

Contact Angle



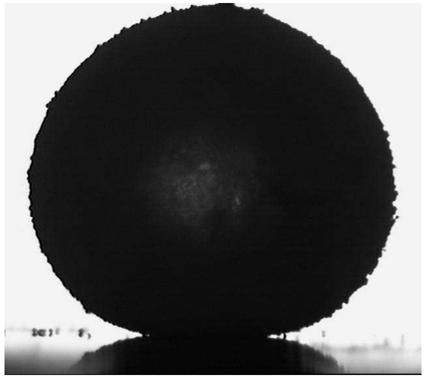
Fitting

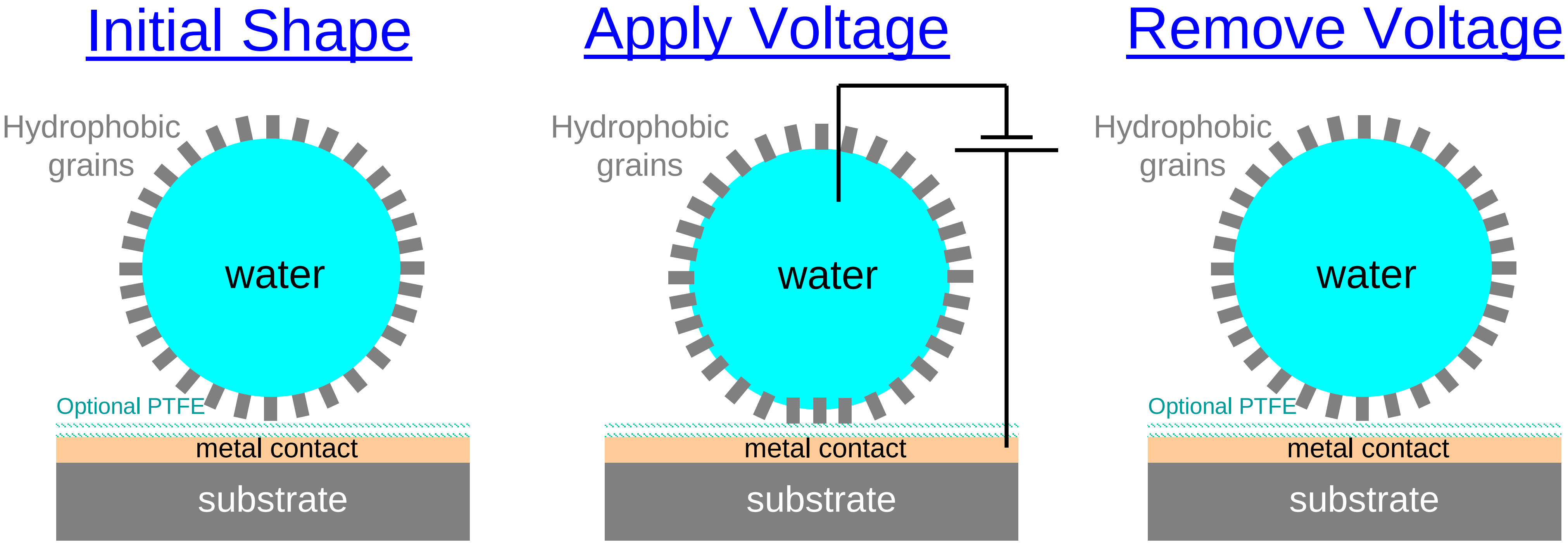


1. Threshold voltage of around 30 V
2. Contact angle hysteresis of around 5°
3. Offset voltage in fit (~ 18.4 V) represents charging

Electrowetting of Liquid Marbles

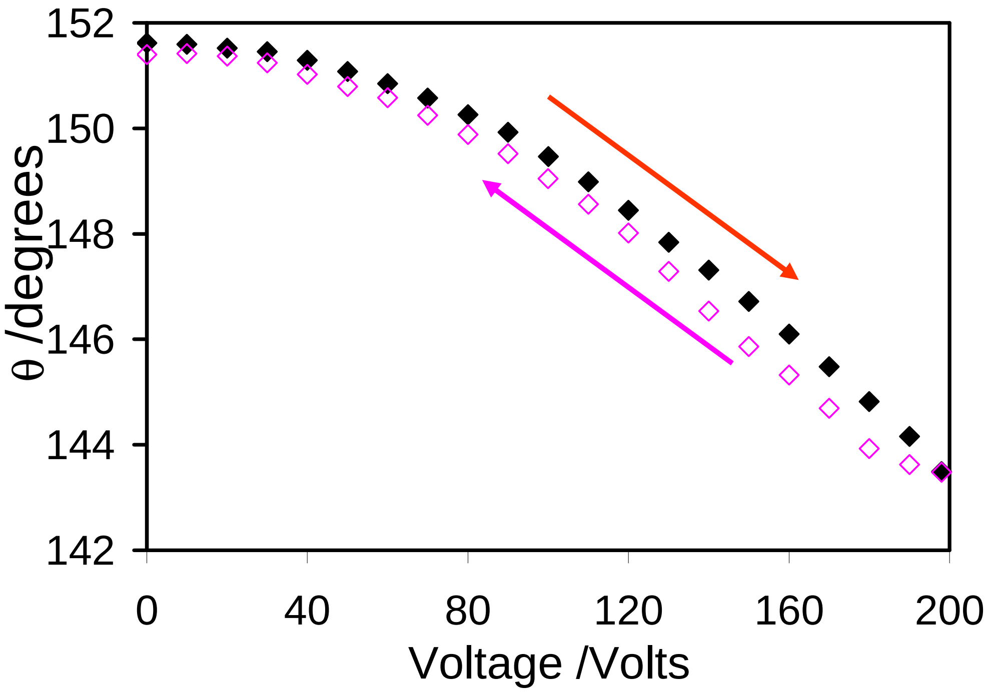
- Reversibility Idea
  - Make the rough solid adhere more to the liquid than the substrate
  - Provides a rough solid-insulator conformal to the liquid shape
  - Spin coated Teflon AF1600 on substrate to stop complete breakthrough if granular coating is breached



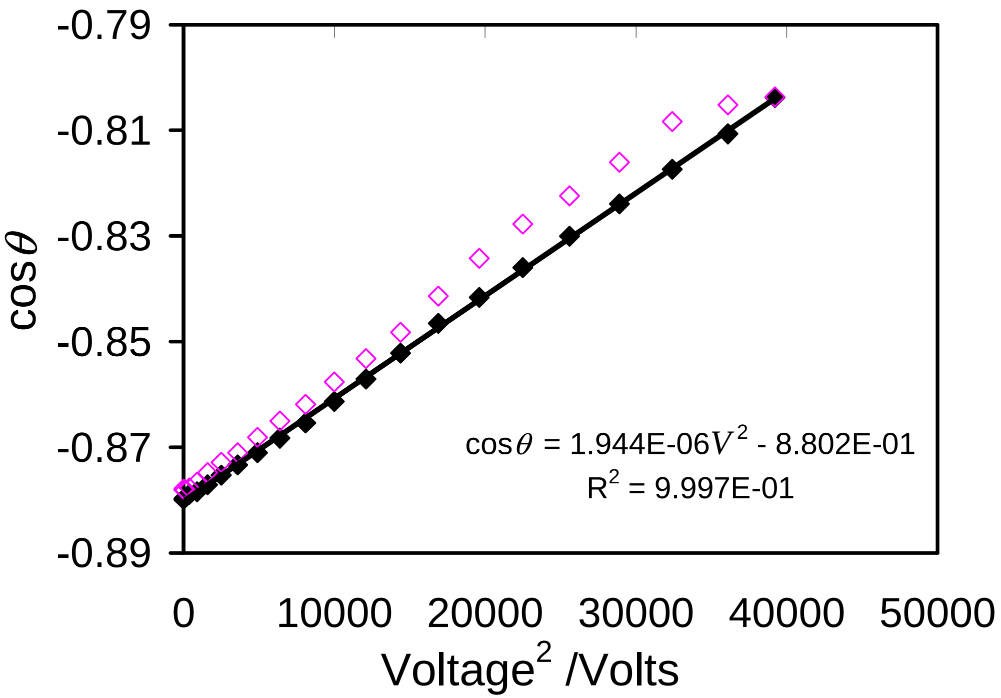


Results using Hydrophobic Silica

Contact Angle



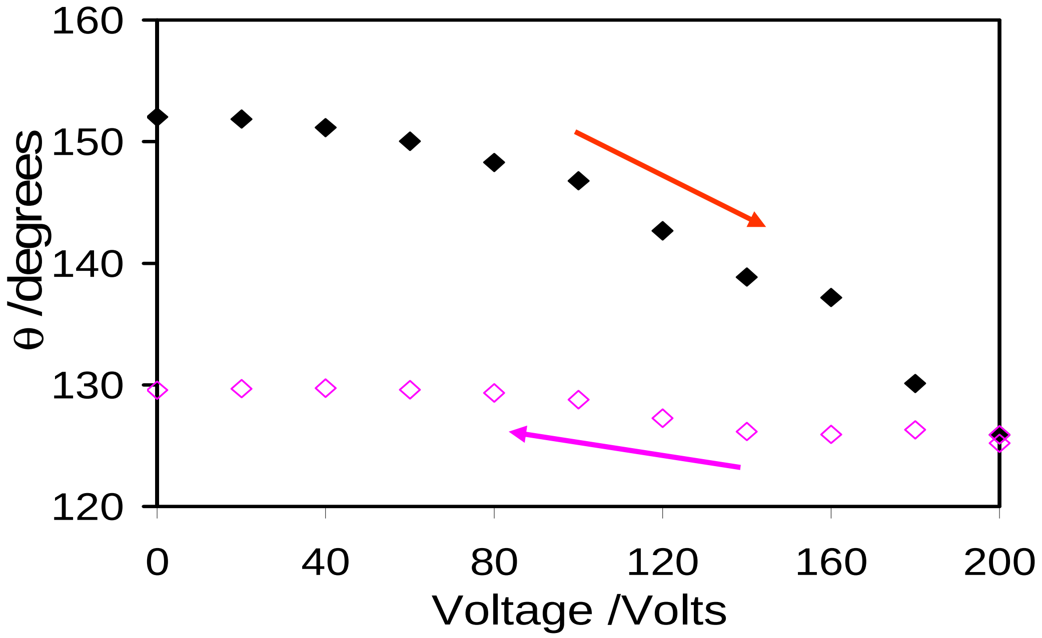
Fitting



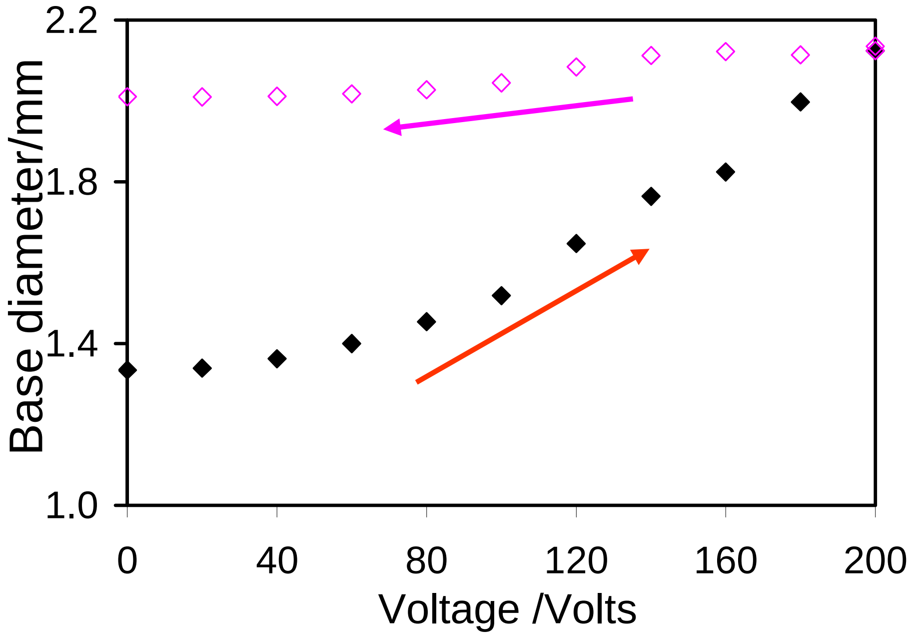
1. No obvious threshold voltage
2. Virtually no contact angle hysteresis
3. Current experiments show a limited range (155^{o} to 130^{o})
4. Wider range is possible using Lycopodeum
5. Without PTFE the liquid marbles eventually burst

Results using Hydrophobic Lycopodeum

Contact Angle



Base Diameter



1. No significant threshold voltage
2. Wider range of contact angles
3. Reversibility is compromised at highest voltages due to charging causing contact area to become pinned

Future Work

1. Different types of S-H Surfaces
    - Porous sol-gel surfaces – aim for reversibility
    - Rough etched surfaces - double length scale systems
    - Pattern variation with local position
2. Droplet Motion with Granular Systems
    - Preliminary work shows it is possible
    - No contact mode of generating contact angle changes
3. Modelling of Super-hydrophobic/EWOD Systems

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
PhD’s	Ms Sanaa Aqil, Mr Carl Evans

External Collaborators

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

Funding Bodies

GR/R02184/01 – Super-hydrophobic & super-hydrophilic surfaces
GR/S34168/01 – Electrowetting
EP/C509161/1 – Extreme soil water repellence
EP/D500826/1 – Slip and drag reduction
Dstl via EPSRC/MOD JGS
EU COST Action D19 - Chemistry at the nanoscale