



Superhydrophobicity

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Overview

1. Basics of Superhydrophobicity

- Naturally occurring surfaces
- Skating and penetrating states: sticky/slippy, deposition/condensation
- Surface free energy derivations: Wenzel/Cassie-Baxter equations
- Advancing/receding contact angles, contact angle hysteresis, droplet collapse
- Complex topography: dual length scales, curvature and re-entrant shapes
- Defects and symmetric/random patterns

2. Materials Methods for Surface Fabrication

- Fibers, textiles and fabrics
- Lithography, aggregation/assembly of particles and templating
- Phase separation, porous and etched
- Crystal growth and diffusion limited growth

3. Beyond Simple Superhydrophobicity

- Unexpected superhydrophobicity
- Superspreading, superwetting, hemi-wicking and porosity

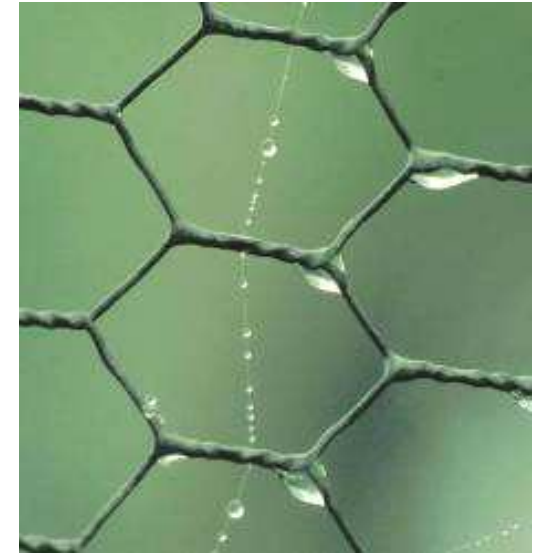
Basics of Superhydrophobicity

Naturally Occurring Surfaces

Surface Tension

Liquid Surface

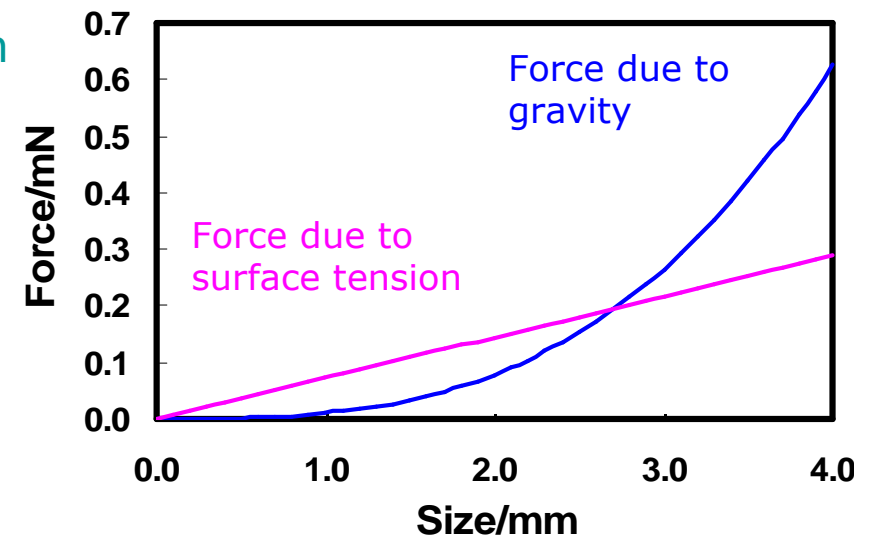
- Molecules at a surface have fewer neighbours
- Also have higher energy than ones inside the liquid
- Liquid surface behaves as if it is in a state of tension
- Tends to minimize its area in any situation
- For a free “blob”, the smallest area is obtained with a sphere



<http://www.brantacan.co.uk>

Surface Tension v Gravity

- Surface tension forces scale with length
e.g. $\text{Force} \sim R\gamma_{LV}$
- Gravity forces scale with length³
e.g. $\text{Force} \sim R^3\rho g$
- **Small sizes** \Rightarrow **surface tension wins**
- Small means \ll capillary length = κ^{-1}
 $\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2} \sim 2.73\text{mm}$ for water



Plants and Leaves



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

Effects of Surface Tension

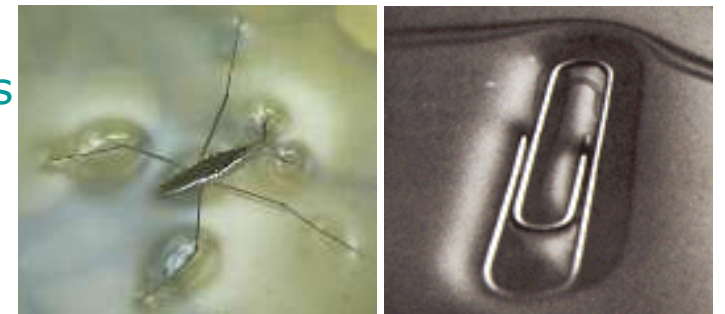
Water-on-Solids

- Liquids sometimes form droplets
- Liquids sometimes spread and wet a surface
- Raindrops are never a metre wide
- Raindrops don't run down the window
- Why do butterfly wings survive rain?



Solids-on-Water

- Pond skaters, fishing spiders and water striders walk, run and jump on water
- Metal objects "float" on water



Solids in and under Water

- Insects move from air to under water
- Diving insects carry films of air "plastrons"



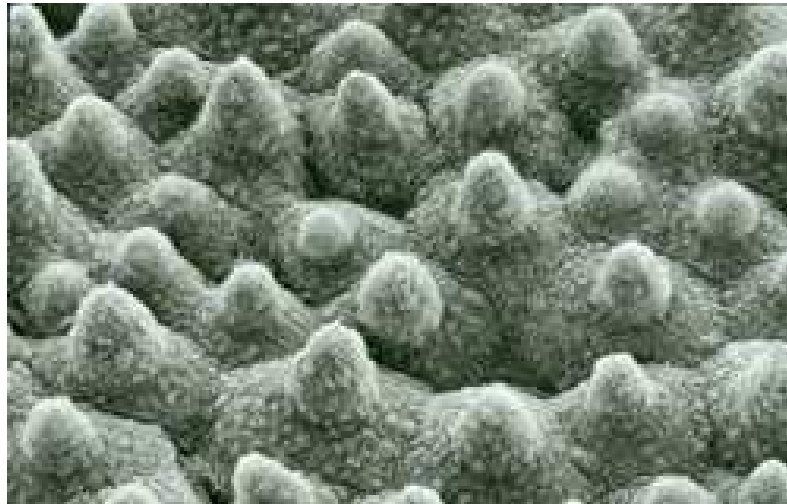
The Sacred Lotus Leaf

Plants

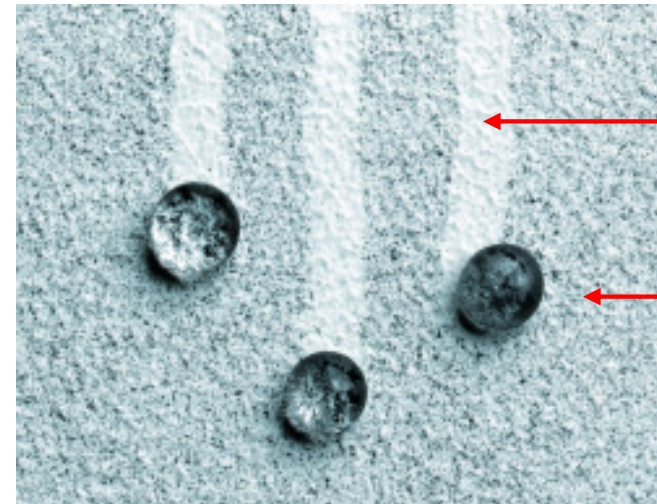
- Many leaves are super-water repellent (i.e. droplets completely ball up and roll off a surface)
- The Lotus plant is known for its purity
- Superhydrophobic leaves are self-cleaning (*under the action of rain*)



SEM of a Lotus Leaf



Self-Cleaning



Dust
cleaned
away
Dust coated
droplet
A “proto-marble”

Acknowledgement

Neinhuis and Barthlott

Self-poisoning surface

References Neinhuis, C.; Barthlott, W. *Ann. Bot.*, 79 (1997) 667-677; *Planta* 202 (1997) 1-8.
Onda, T. *et al.*, *Langmuir* 12 (1996) 2125-2127.

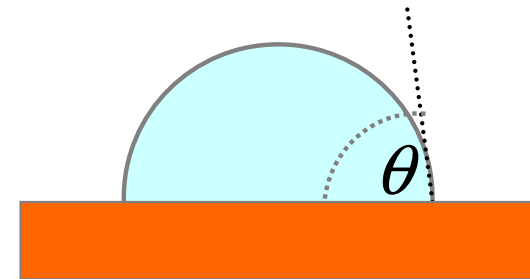
Water Repellency (Hydrophobicity)

Surface Chemistry

- Terminal group determines whether surface is water hating
- Hydrophobic terminal groups are Fluorine (F) and Methyl (CH₃)

Contact Angles

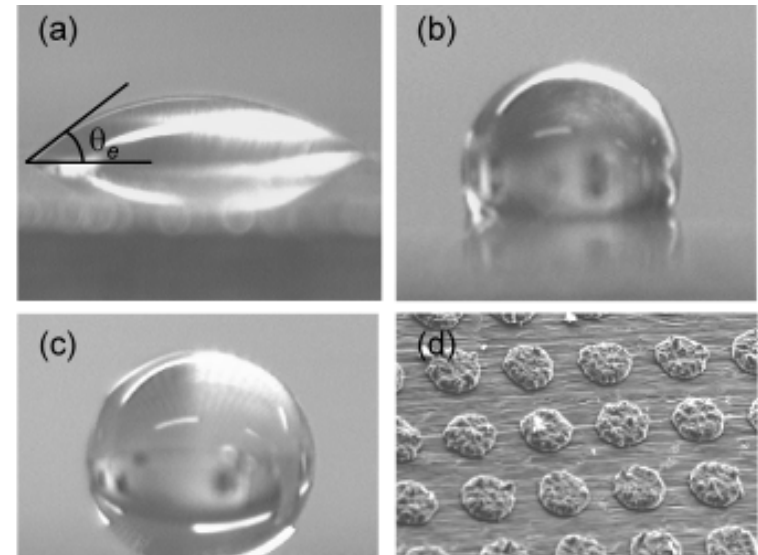
- Characterize hydrophobicity
- Water-on-Teflon gives $\sim 115^\circ$
- The best that *chemistry* can do



Physical Enhancement

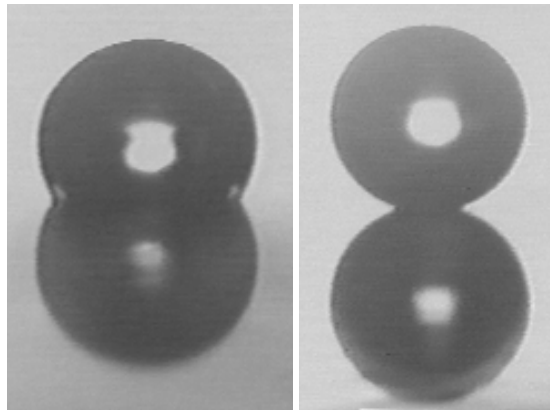
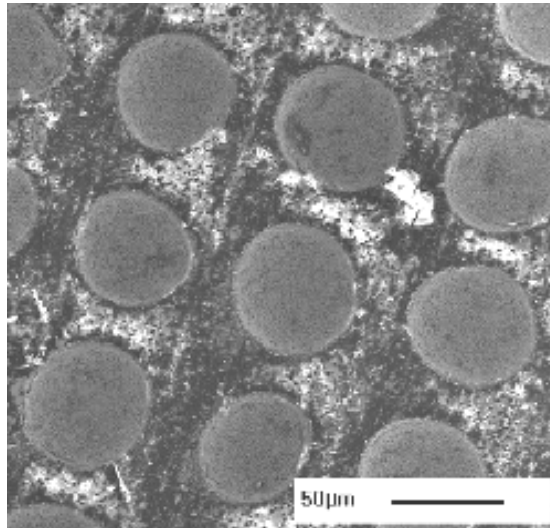
- (a) is water-on-copper
- (b) is water-on-fluorine coated Cu
- (c) is a super-hydrophobic surface
- (d) "chocolate-chip-cookie" surface

Superhydrophobicity is when $\theta > 150^\circ$
(and contact angle hysteresis is low)



Superhydrophobicity - Man-Made Examples

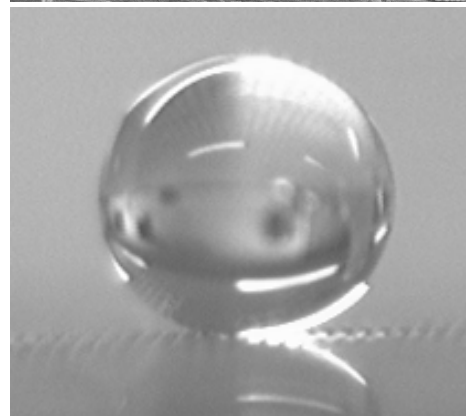
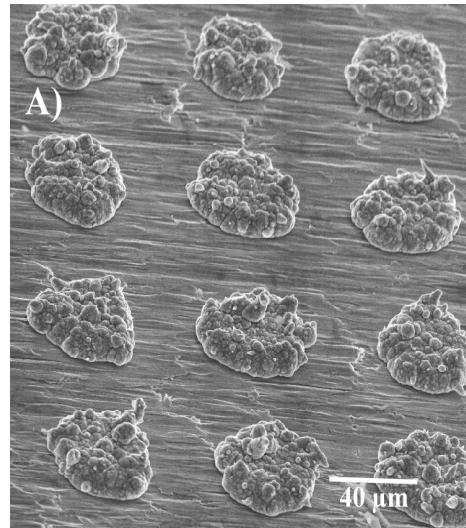
Etched Metal



Flat & hydrophobic

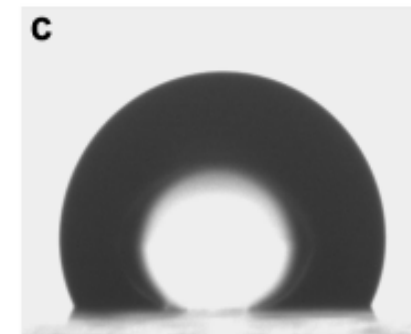
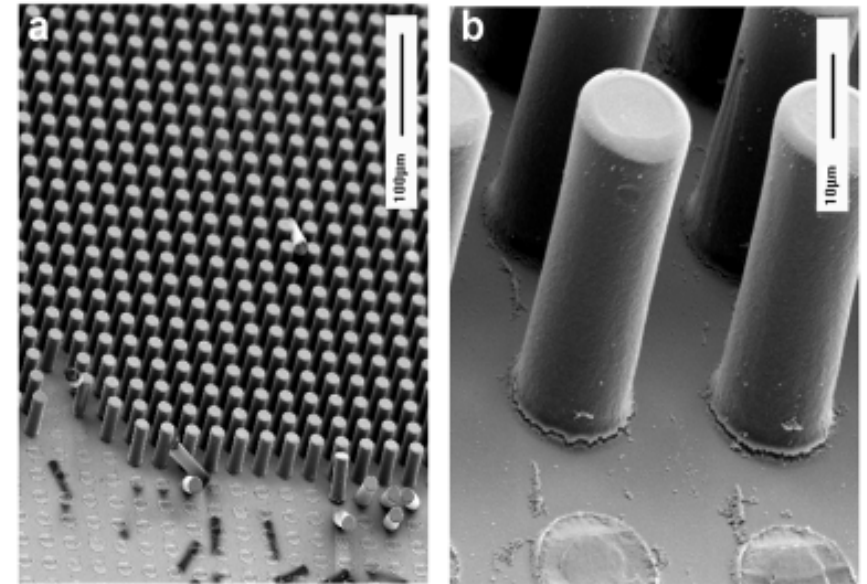
Patterned & hydrophobic

Deposited Metal

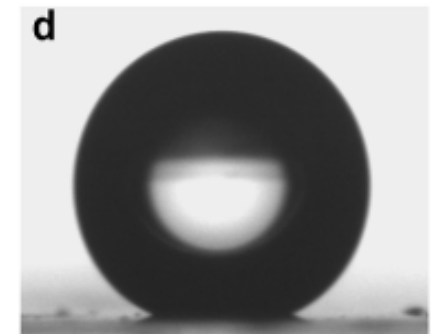


Patterned & hydrophobic

Polymer Microposts



Flat & hydrophobic



Patterned & hydrophobic

References: Shirtcliffe, N.J. *et al.*, *Langmuir* **21** (2005) 937-943; *Adv. Mater.* **16** (2004) 1929-1932; *J. Micromech. Microeng.* **14** (2004) 1384-1389.

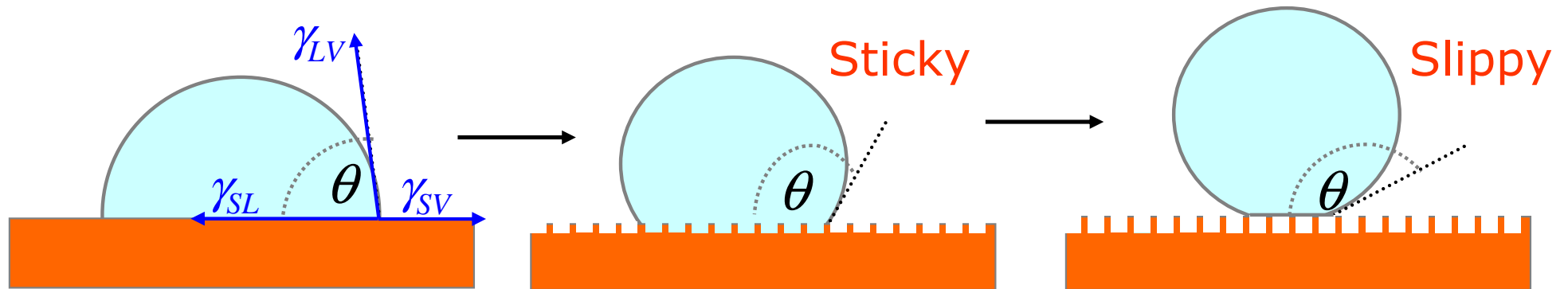
Basics of Superhydrophobicity

Surface Free Energy Derivations

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

Topography

Force view:

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

$r =$ true area/planar projection

Young's Law θ_e

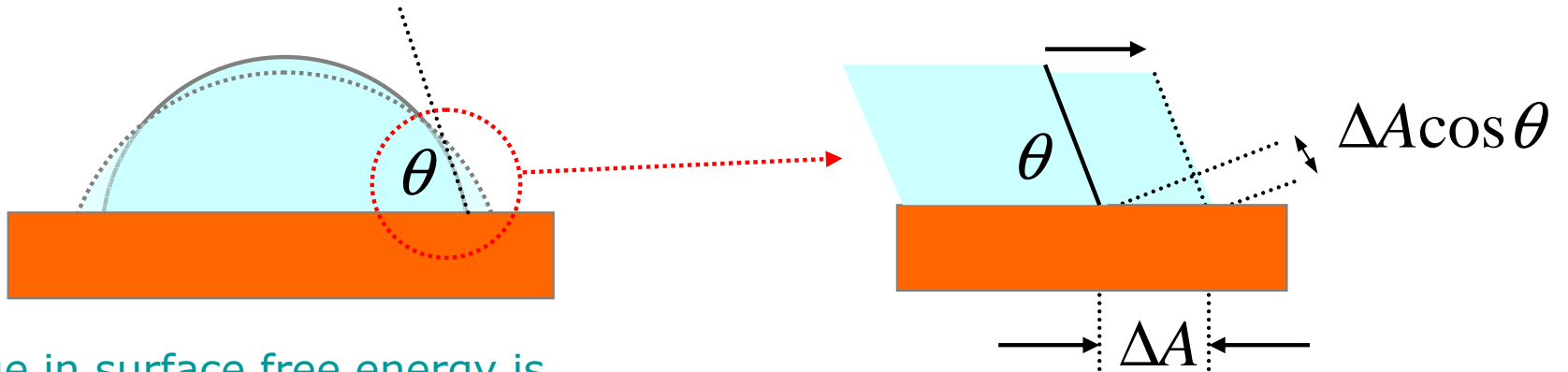
$f_s =$ solid surface fraction

References Cassie, A. B. D.; Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. Wenzel, R. N. Ind. Eng. Chem. 28 (1936) 988-994; J. Phys. Colloid Chem. 53 (1949) 1466-1467.

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 gain of energy per \times substrate unit area area

solid-vapor loss of energy per \times substrate unit area area

liquid-vapor gain of energy per \times liquid-vapor unit area area

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

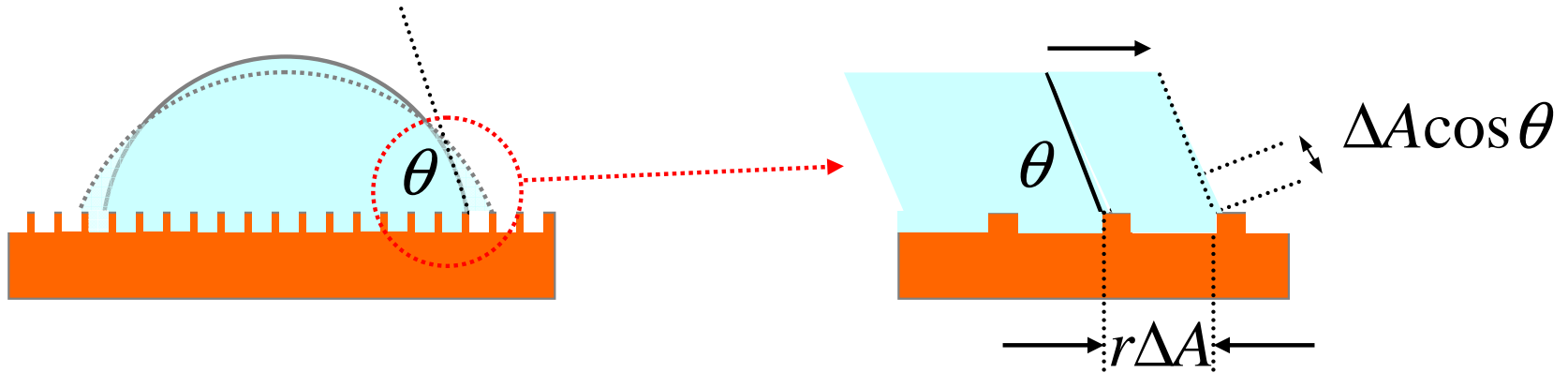
Equilibrium is when $\Delta F = 0 \Rightarrow$

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

Young's Law

Same result as from resolving forces at contact line

Topography 1: Wenzel's Equation



Change in surface free energy is

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

Equilibrium is when $\Delta F = 0 \Rightarrow \cos \theta_W = r(\gamma_{SV} - \gamma_{SL}) / \gamma_{LV}$

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

Wenzel Eq

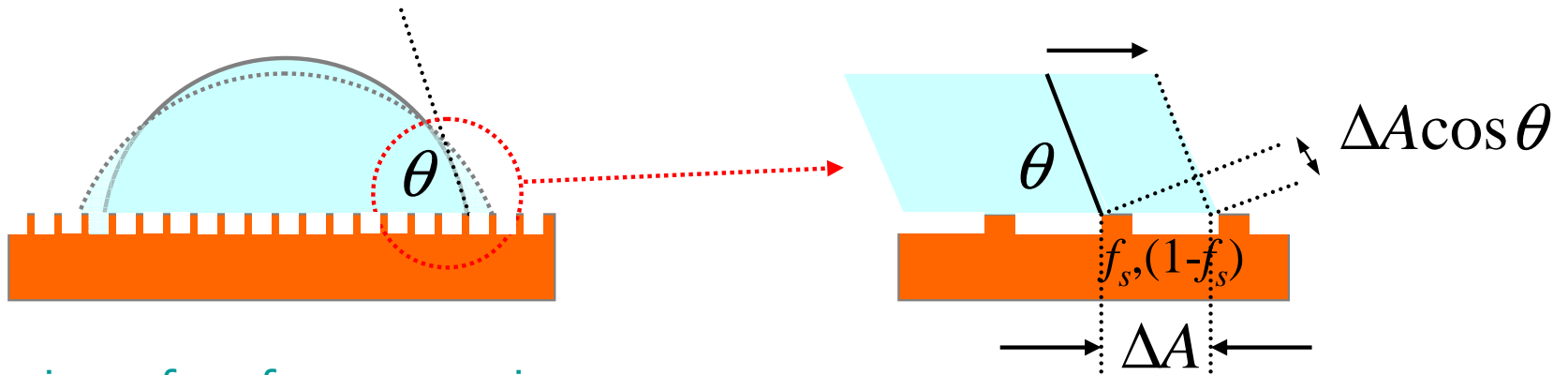
Topography $\Rightarrow r =$ roughness factor

Chemistry \Rightarrow Young's Law θ_e

The derivation is based on contact line changes², i.e. $r=r(x)$ and $\theta(x)$

References Johnson, R.E.; Dettre, R.H. Adv. in Chem. Series 43 (1964) 112-135. Bico, J.; Marzolin, C.;

Topography 2: 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 $\Delta F = 0 \Rightarrow \cos \theta_{CB} = f_s (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} - (1 - f_s)$

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

Cassie-Baxter Eq

Topography $\Rightarrow f_s =$ solid surface fraction

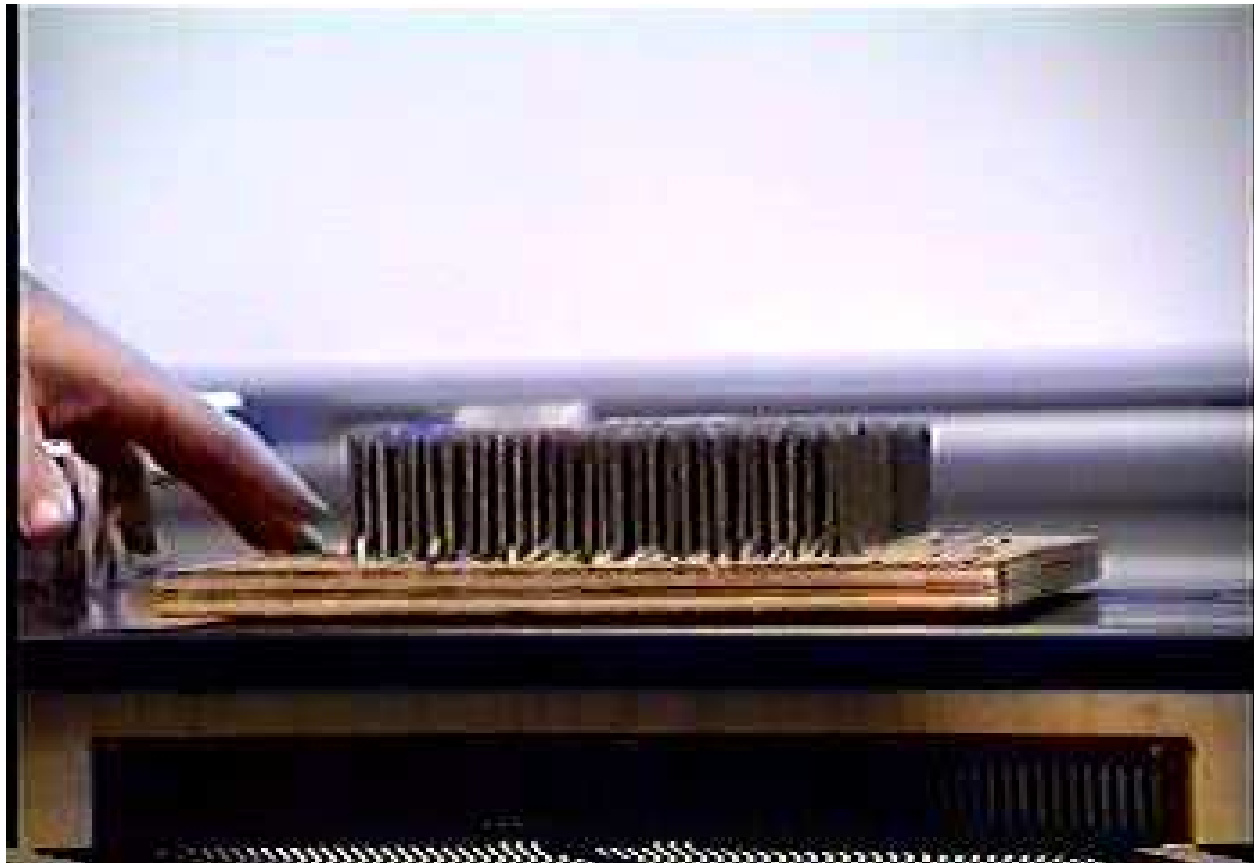
Chemistry \Rightarrow Young's Law θ_e

Air gaps $\Rightarrow \cos(180^\circ) = -1$

Simplistic view: Weighted average using f_s and $(1 - f_s)$

The derivation is based on contact line changes, i.e. $f_s = f_s(x)$ and $\theta(x)$

Fakir's Carpet - "Bed of Nails" Effect



Balloon on a Bed of Nails

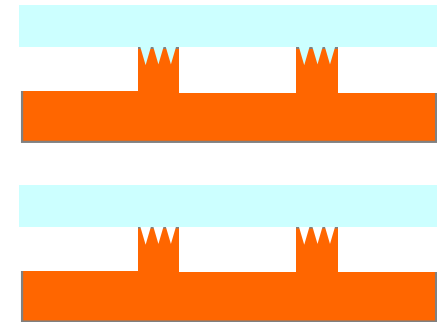
But liquid skin interacts with solid surfaces and "nails" do not need to be equally separated. A useful analogy, but it is not an exact view.

Acknowledgement Wake Forest University

Complex Topography

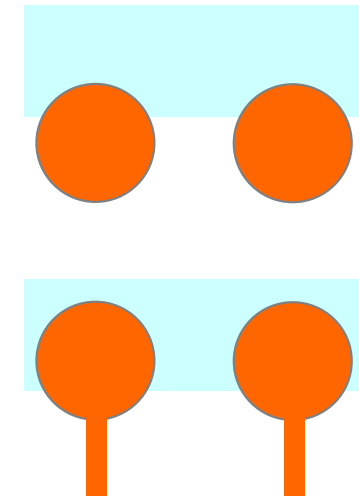
Roughness on Top of Features

- Liquid filled case: Create Wenzel angle and use in Cassie-Baxter equation
- Non-filled case: Create Cassie-Baxter angle for top and use in Cassie-Baxter for large scale structure



Curved Features

- Describes fibers¹, spheres and complex shapes
- Recently described as re-entrant shapes²
- Roughness, $r(\theta_e)$, and solid surface fraction, $f_s(\theta_e)$, become dependent on θ_e
- Surfaces can support droplets even when θ_e is substantially below 90° ³



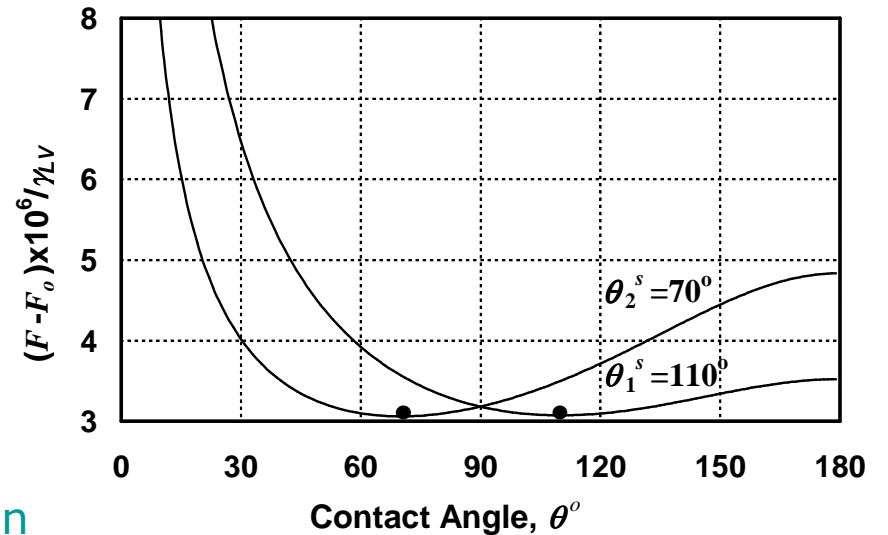
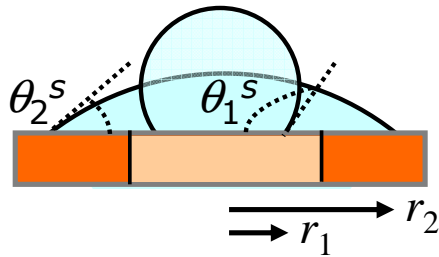
Patterns with Changing Separations

- Roughness, $r(x)$, and solid surface fraction, $f_s(x)$, become dependent on contact line position⁴, x
- Can create gradients in superhydrophobicity⁵

1D Pictures to 2D Cassie-Baxter Surfaces

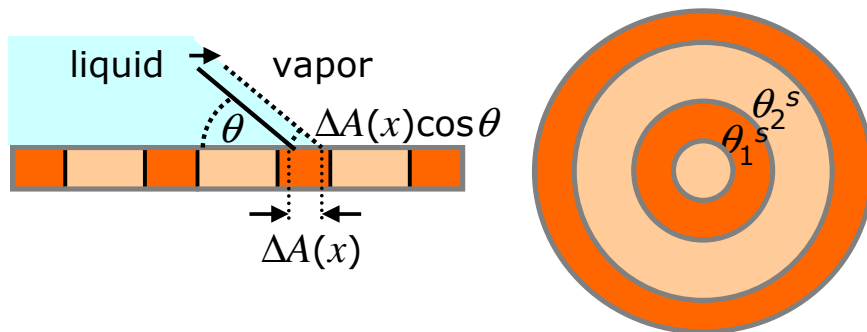
Isolated Defect Surface

Surface has $\theta_1^s = 110^\circ$, $\theta_2^s = 70^\circ$

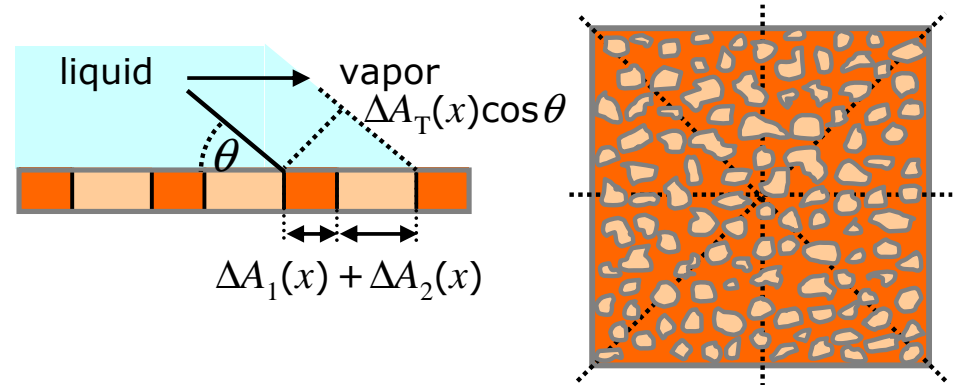


Two droplet configurations exist with min in their local surface free energy corresponding to the same droplet volume

Radial Symmetry



Random Surface

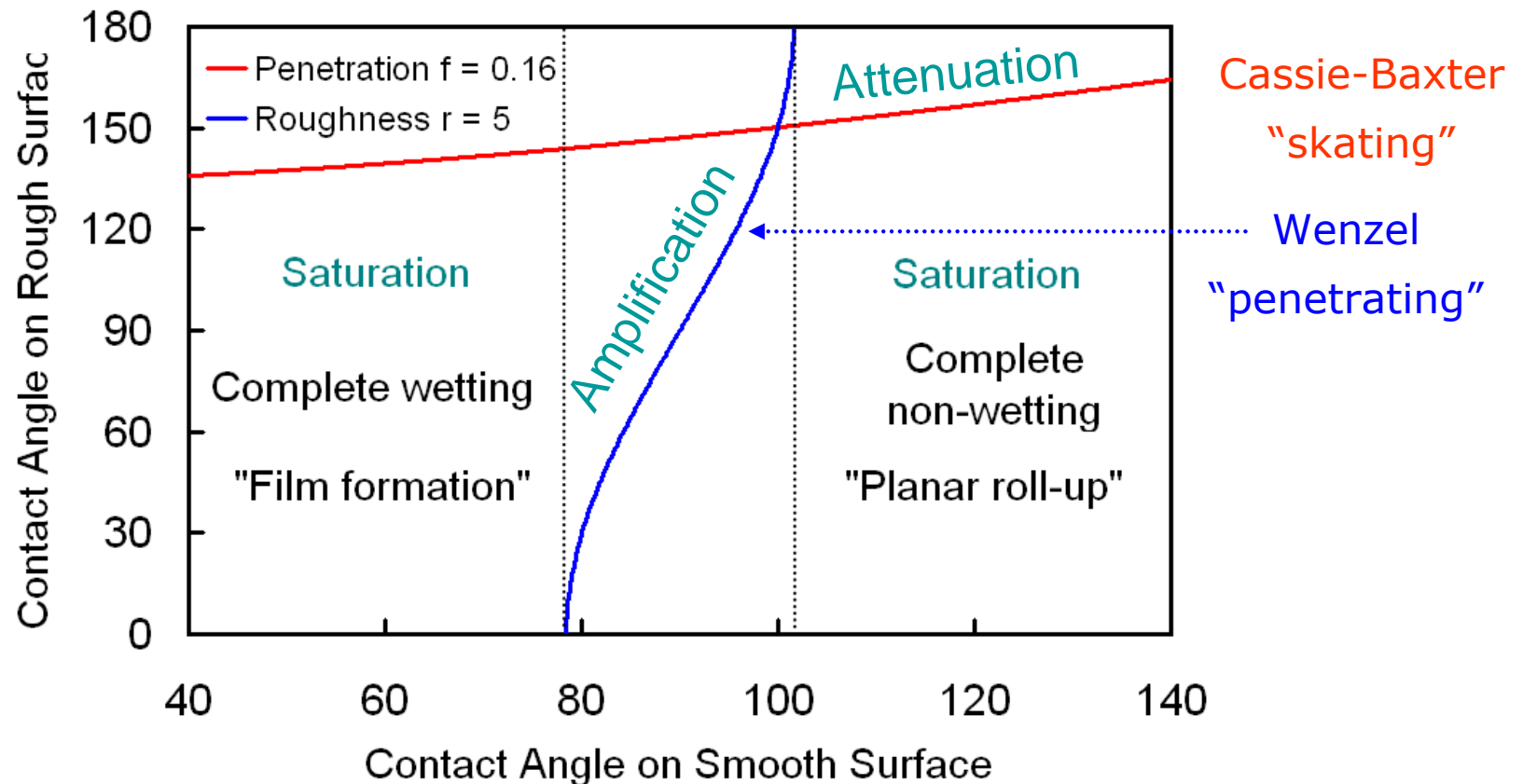


References Gao, L.C.; McCarthy, T.J. *Langmuir* **23** (2007) 3762-3765.
McHale, G. *Langmuir* **23** (2007) 8200-8205.

Basics of Superhydrophobicity

Consequences

Theory: Amplification, Attenuation, Saturation



Roughness/Topography

$\theta_e^s > \text{threshold} \Rightarrow \text{enhances repellence}$

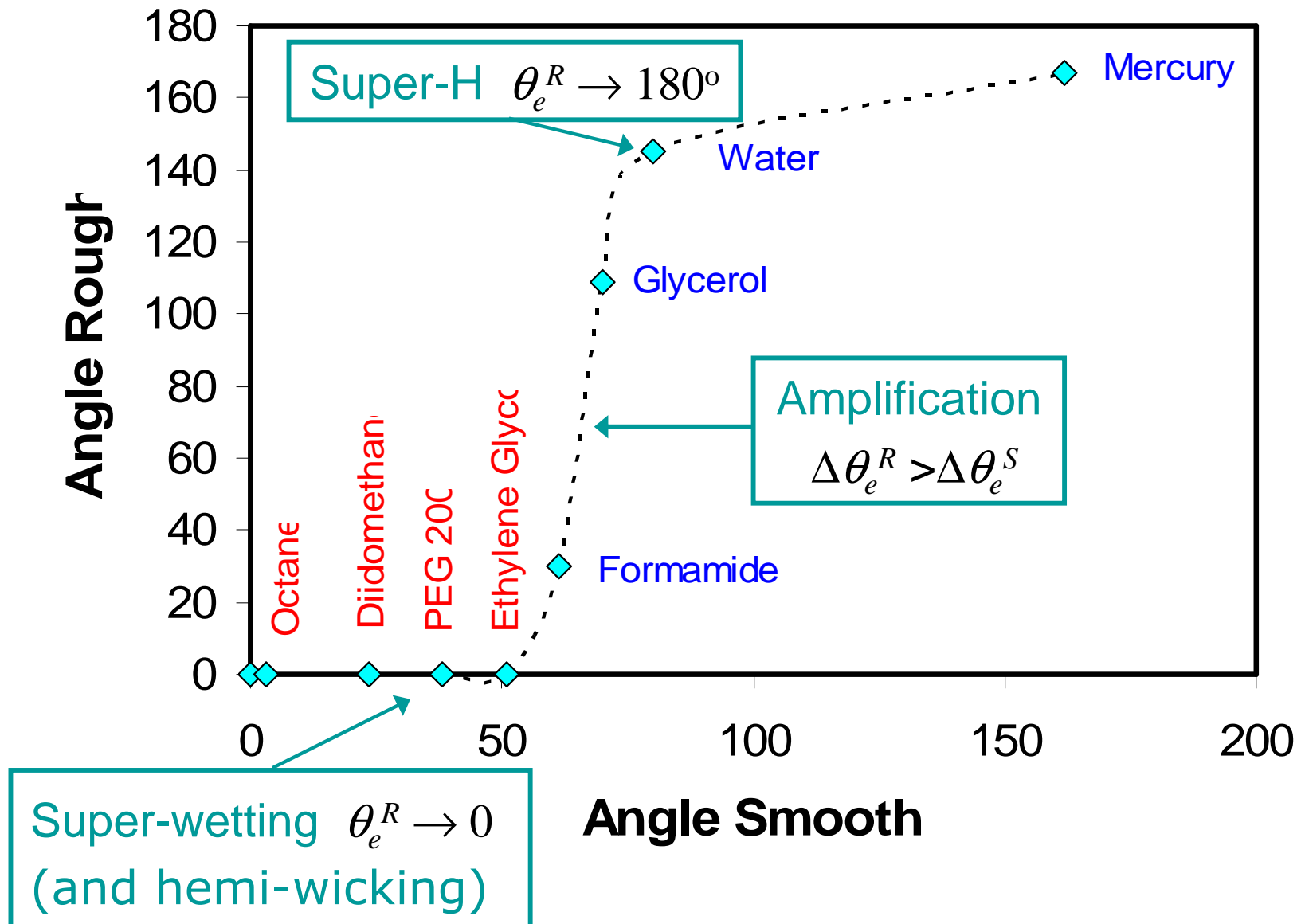
$\theta_e^s < \text{threshold} \Rightarrow \text{enhances film formation}$

Superhydrophobic

"Skating case" \Rightarrow most existing examples

Pressure \Rightarrow transition to penetrating

Liquids on a Superhydrophobic Surface



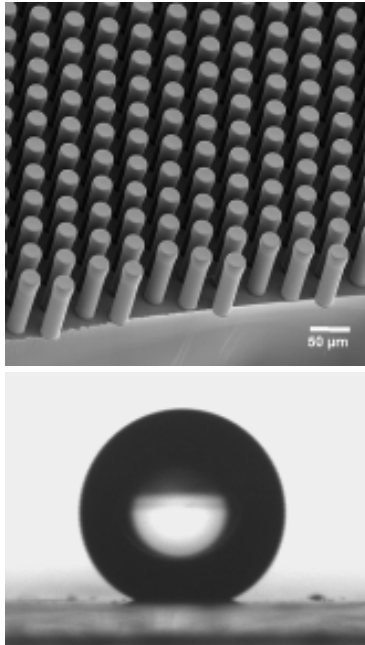
References: McHale, G. et al., *Analyst* **129** (2004) 284-287; *Langmuir* **20** (2004) 10146-10149.

Skating-to-Penetrating Transition

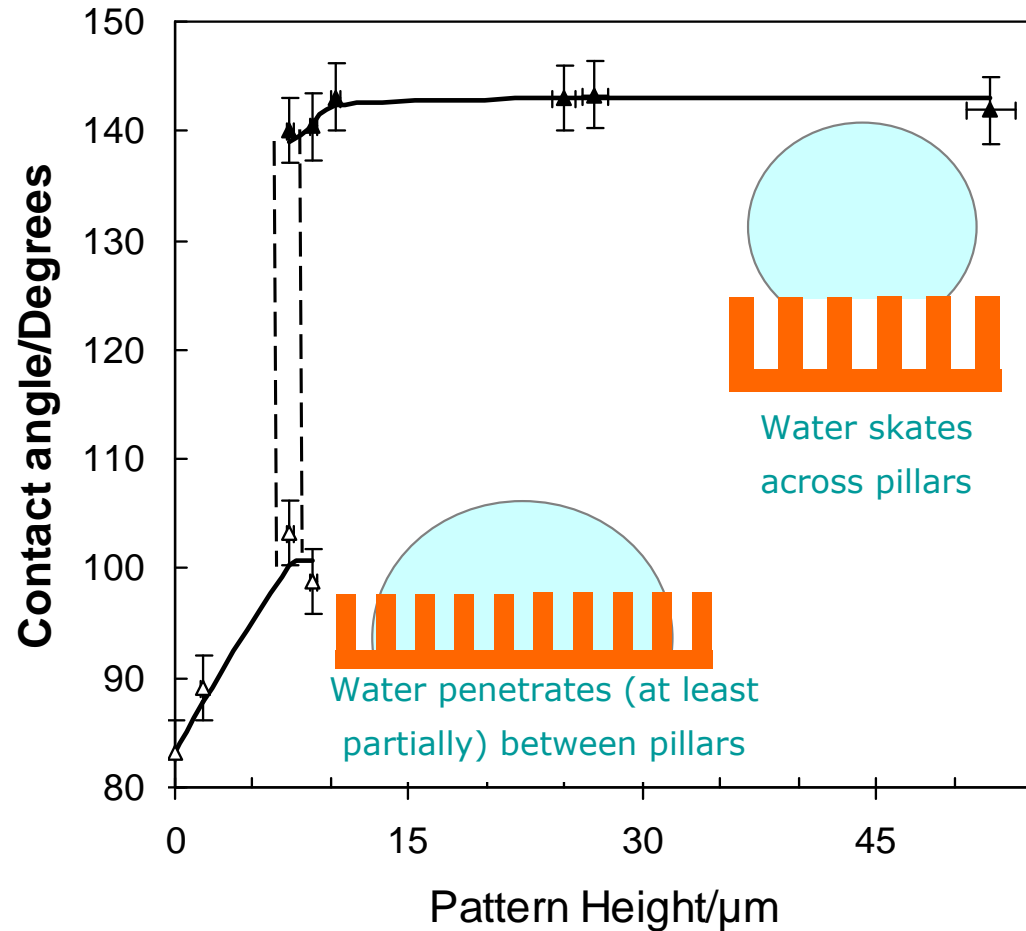
Micro-Structured Surface

SU-8 pillars¹ 15 μm

Hydrophobic treatment



Change of Pillar Height



Quéré Condition

Skating-to-penetrating transition is favoured by surface free energy

considerations when $\theta_W < \theta_{CB}$ (transition may not occur due to sharp features).

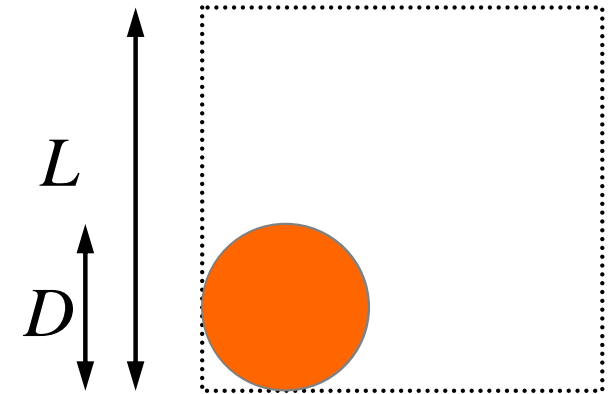
References Shirtcliffe, N.J. *et al.*, J. Micromech. Microeng. 14 (2004) 1384-1389. Bico, J. *et al.*, Coll. Surf.

Texture Example

Circular Pillars

Diameter D , box side L , height h

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



Numerical Example Using $\theta_e^s = 115^\circ$

$L=2D$ and $f_s=0.196$ gives $\theta_{CB}=152^\circ$

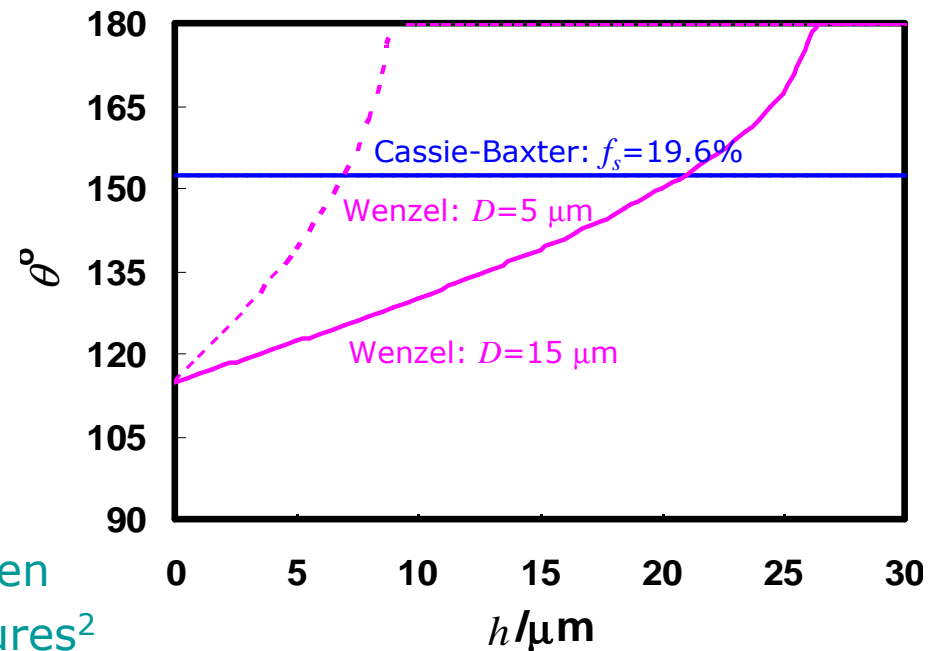
For penetrating transition:

$D=15 \mu\text{m}$ and $h < 21 \mu\text{m}$

$D=5 \mu\text{m}$ and $h < 7 \mu\text{m}$

Ignores sharp features causing metastability¹

Condensing liquid may fill features when droplets may only deposit across features²

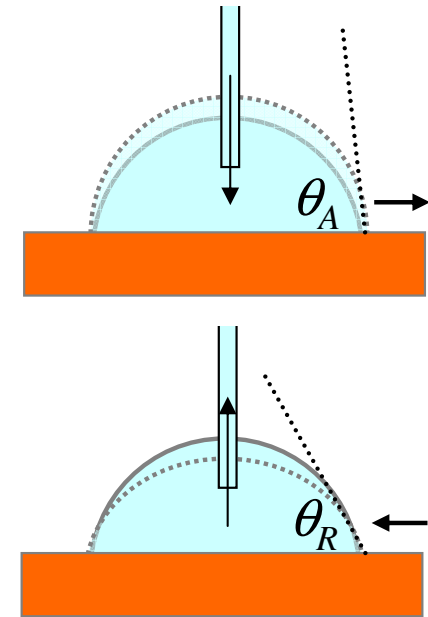


References ¹Bico, J. *et al.*, *Coll. Surf. A* **206** (2002) 41-46. De Gennes, P.G.; Brochard-Wyart, F.; Quéré, D. "Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves" Springer-Verlag (2003). ²Wier, K.A.; McCarthy, T.J. *Langmuir* **22** (2006) 2433-2436.

Contact Angle Hysteresis

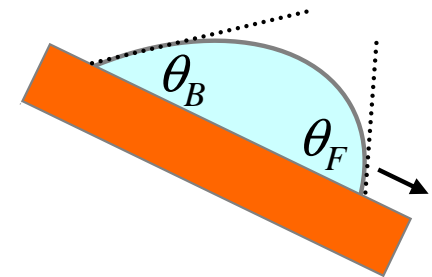
Advancing and Receding Contact Angles

- Largest θ prior to contact line motion as liquid fed in is θ_A
- Smallest θ prior to contact line motion as liquid withdrawn is θ_R
- Difference is contact angle hysteresis $\Delta\theta = \theta_A - \theta_R$
- In some sense characterizes difficulty of moving a droplet on a given “smooth and flat” surface



Tilt and Sliding Angles

- Tilt platform and measure forward, θ_F , and backward, θ_B , contact angles
- At instant before motion assume these give advancing and receding angles
- There is no proof that these are equivalent
- Sliding angle is lowered by superhydrophobicity¹



Reference ¹Miwa, M. *et al.*, *Langmuir* 16 (2000) 5754-5760.

Superhydrophobicity and Hysteresis in θ

Experimental Observations of Contact Angle Hysteresis

- Smaller than on flat for the skating (Cassie-Baxter) state
"Slippy" state¹
- Larger than on flat for the penetrating (Wenzel) state
"Sticky" state¹

Models?

- Different views exist possible factors to be considered include:
Shape of tops of features, contact line length², contact area³ (at perimeter)

Gain and Attenuation View

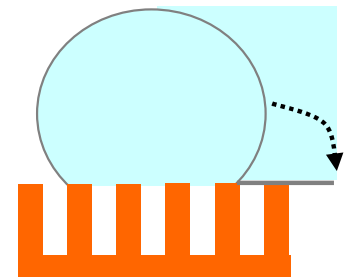
Use CB or W model for θ_A and θ_R
Can work out analytical formulae³
Assumes contact area changes are dominant effect and amplify an intrinsic hysteresis of the surface

2-D Theory World View

CB: To advance must touch next shape and to recede can retract across features⁴

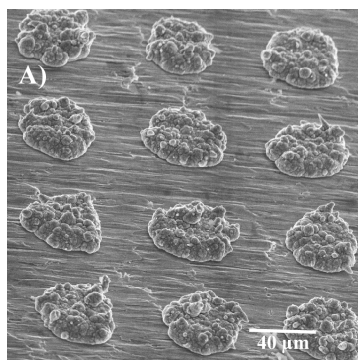
$$\theta_A = 180^\circ \text{ (and } \theta_R = \theta_e^\circ)$$

3-D world is more complex

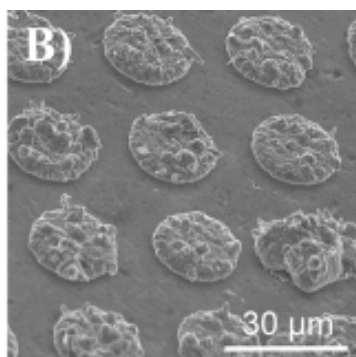
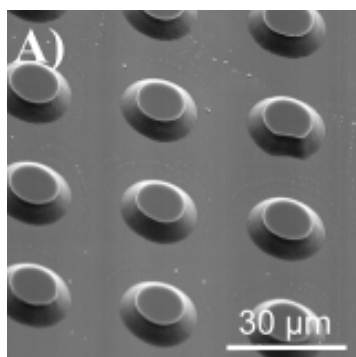
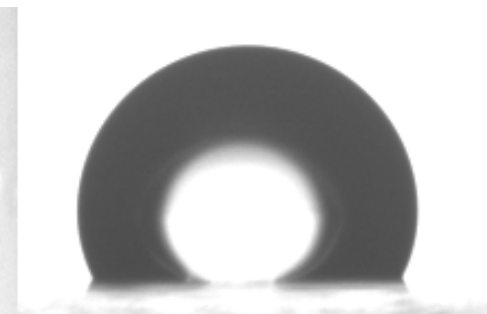
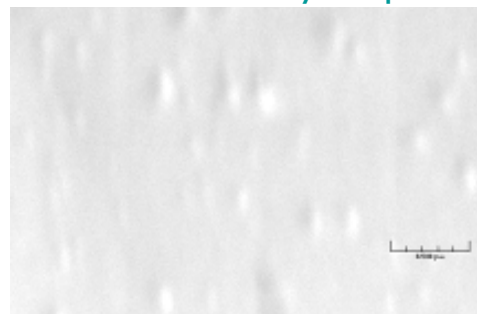


References ¹Quéré, D.; Lafuma, A.; Bico, J. Nanotechnology 14 (2003) 1109-1112. ²Öner, D.; McCarthy, T.J. Langmuir 16 (2000) 7777-7782. ³McHale, G. *et al.*, Langmuir 20 (2004) 10146-10149. ⁴Kusumaatmaja, H.; Yeomans, J.M. Langmuir 23 (2007) 6019-6032.

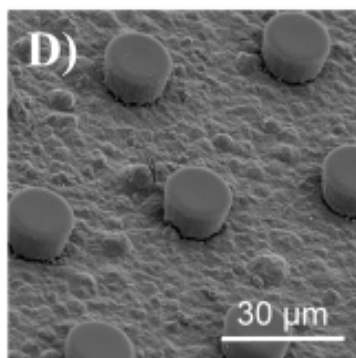
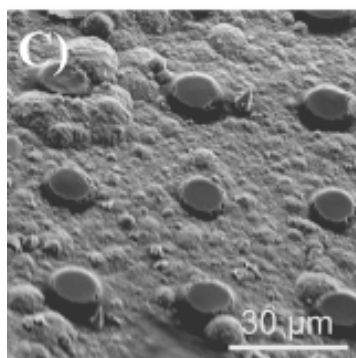
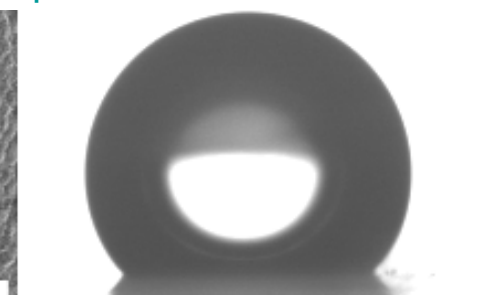
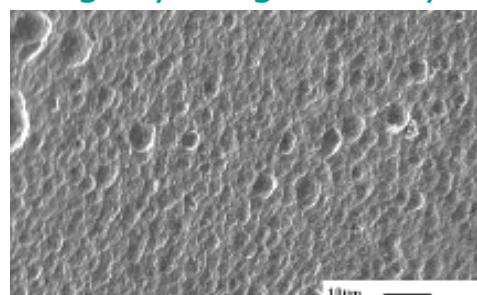
Double Length Scale Systems



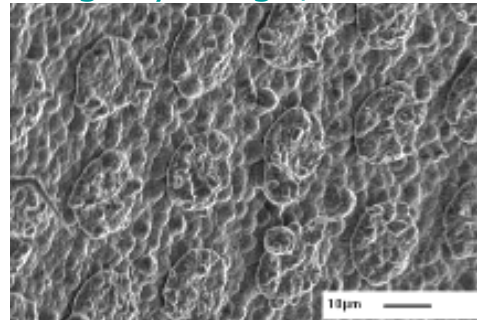
Two length scales is extremely effective
Smooth and hydrophobised: 115°



Slightly rough and hydrophobised: 136°



Slightly rough, textured and hydrophobised: 160°



References Shirtcliffe, N.J. *et al.*, *Adv. Mater.* **16** (2004) 1929-1932 (see also: Patankar, N.A. *Langmuir* **20** (2004) 8209-8213.

Path Definition & Self-Actuated Motion

Gradients in Contact Angle

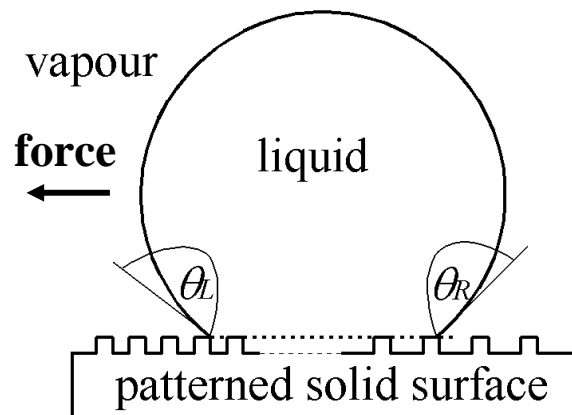
Make contact angle depend on position and surface chemistry $\theta(x, \theta_e^s)$

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

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

Idea

Droplet experiences different contact angles



$$\begin{aligned} \text{Driving force} &\sim \gamma_{LV}(\cos \theta_R - \cos \theta_L) \\ &\sim \gamma_{LV}(f_R - f_L)(\cos \theta_e + 1) \end{aligned}$$

Experiment

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



Electrodeposited copper – fractal to overcome hysteresis

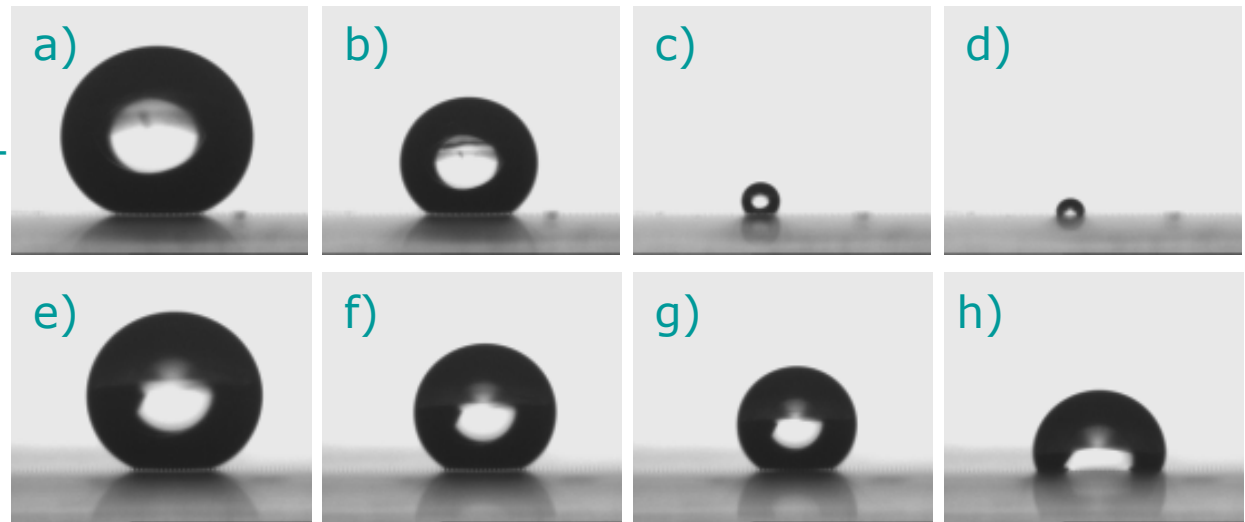
References McHale, G. *et al.*, *Analyst* **129** (2004) 284-287; *Langmuir* **20** (2004) 10146-10149.
McHale *et al.*, to be submitted; Quéré *unpublished*.

Evaporation and Droplet Collapse

Experiments

Panels a)-d) Late stage collapse from the Cassie-Baxter state. Abrupt/rapid change.¹

Panels e)-h) Mid-stage collapse into Wenzel state. Subsequently, contact line is pinned.¹



Theory/Simulation

Yeomans² suggests three processes during evaporation:

1. the contact line retreats inwards across the surface
2. the free energy barrier to collapse vanishes and the drop moves smoothly down the posts (long posts)
3. the drop touches the base of the surface patterning and immediately collapses (short posts) – critical curvature of droplet $\propto b^2/h$, where b =gap width and h =post height

3D simulation suggests the drop can depin from all but the peripheral posts, so that its base resembles an inverted bowl.

References ¹McHale, G. *et al.*, *Langmuir* 21 (2005) 11053–11060. ² Kusumaatmaja, H. *et al.*, *Euro. Phys. Lett.* 81 (2008) art. 36003. Reyssat, M.; Yeomans, J.M.; Quéré, D. *Euro. Phys. Lett.* 81 (2008) art. 26006. Moulinet, S.; Bartolo, D. *Euro. Phys. J.* E24 (2007) 251-260. Bartolo D., *et al.*, *Europhys. Lett.* 74 (2006) 299-305.

Materials Methods for Surface Fabrication

Basic Approach

- Create ordered or disordered surface structures
- Keep solid surface fraction low
- Keep size scale for gaps \ll capillary length
- Use intrinsically hydrophobic material or apply a hydrophobic surface chemistry
- Use single, double or multiple length scales
- For optical transparency keep length scales $\ll \mu\text{m}$
- Choose material for desired properties: transparent, hard, durable, electrically conducting, insulating, etc
- Choose method for size of piece and level of technological complexity
- Huge number of possible methods – an extensive list of recipes exist
- Following is based in recent materials focused review by our group:

Roach, P., Shirtcliffe, N.J. and Newton, M.I., *Soft Matter* 4 (2008) 224-280

- Original references are in the review

Fibers, Textiles and Fabrics

- Take woven or non-woven cloth and make hydrophobic – **original 1930's work**
- **1945 patent** (D. Parker, US Pat. 2386259) applied to polyester in 2006
- Modern versions include perfluorocarbon coated cotton, surface treated nylon and many other materials
- Electrospun fiber mats allow fiber diameters to be **sub-micron** (e.g. 50 nm) and **non-circular** cross-sectional shapes
- Can obtain **conductive and magnetic properties** with carbon nano-fibers
- **Hydrophilic** polymers can form **superhydrophobic surfaces**
- **Superoleophobic** properties possible
- Can also add roughness to fiber

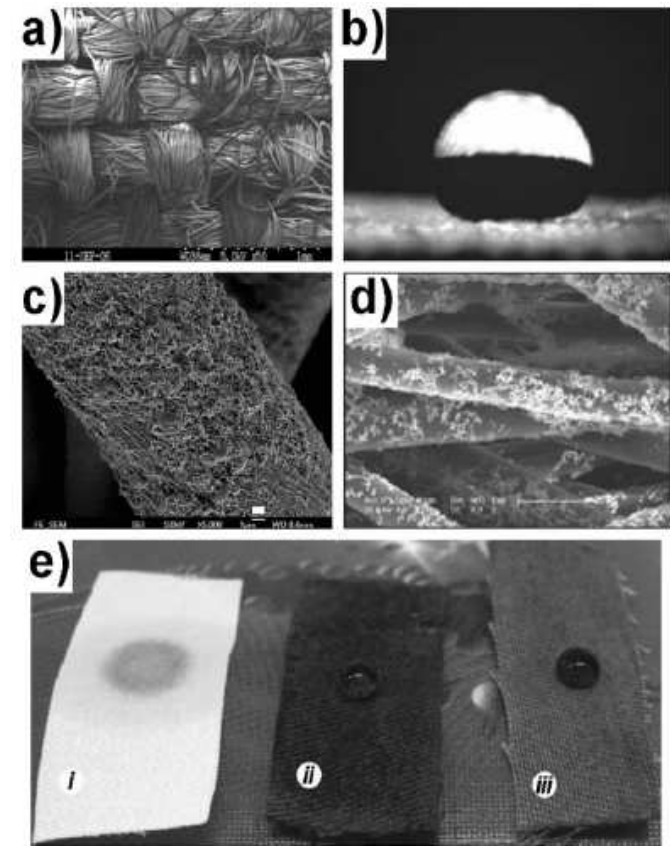


Fig. 3 Woven superhydrophobic surfaces (a) multifilament woven fabric,¹⁵ (b) droplet resting on surface shown in (a), (c) CNT-treated cotton fibre,¹⁶ (d) cloth surface impregnated with gold particles,¹⁷ and (e) water droplets on¹⁶ i) untreated woven cotton sheet, ii) CNT-treated woven cotton sheet shown in (c) and iii) poly(butyl acrylate)-CNT-treated woven cotton sheet. Images reprinted with permission from (a) and (b) American Chemical Society, Copyright 2007, (c) (d) and (e) The Royal Society of Chemistry, Copyright 2007.

Fibers, Textiles and Fabrics

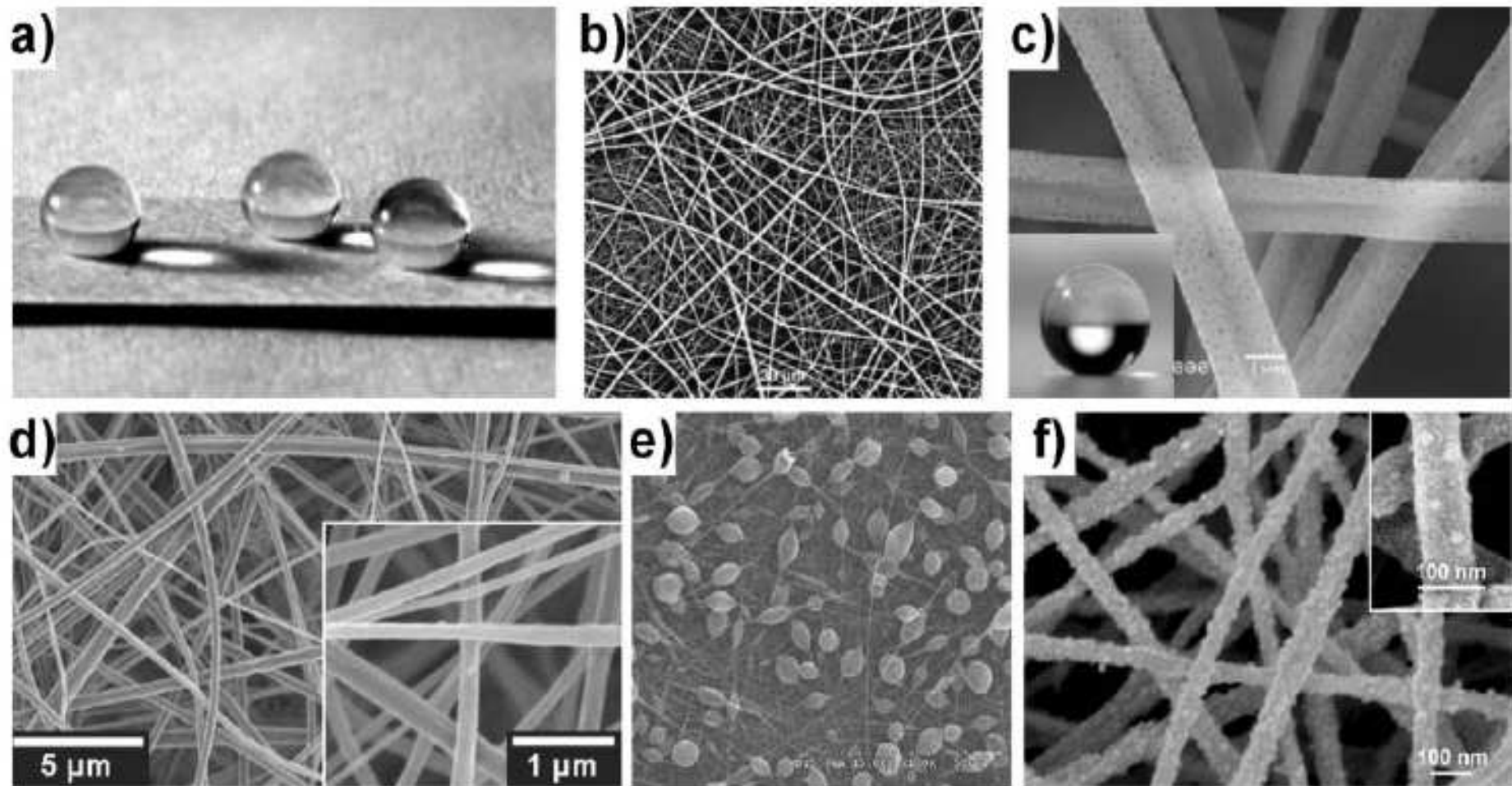


Fig. 4 Superhydrophobic fibre surfaces (a) water droplets on a block copolymer electrospun fibre mat,²³ (b) electrospun fluoropolymer mat,²⁴ (c) porous electrospun fluorinated fibres,²⁵ (d) cellulose acetate fibrous membrane,²⁶ (e) micro-bead connected fibres by electrospinning.²⁷ Images reprinted with permission from (a) American Chemical Society, Copyright 2005, (b) (c) and (f) Copyright Wiley-VCH Verlag GmbH & Co. KGaA, (d) Institute of Physics, Copyright 2007, and (e) Elsevier, Copyright 2007.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* 4 (2008) 224-280.

Lithographic Techniques

- Create designer surfaces: many **identical copies** from a master design
- **Testing of theory**: bespoke cross-sectional shape of features, height, separation and repeat pattern
- Tests of Cassie-Baxter and Wenzel theory and of contact angle hysteresis
- Recent work on **hydrophobic/hydrophilic regions**
- Techniques: Inked stamp, nano-imprint lithography (NIL), photolithography with UV, X-ray, e-beam, etc, direct mechanical cutting/grooving
- Materials: Silicon processing, photoresists (thin film and thick-film, e.g. SU-8), metals, ...
- Designs can be used as masters themselves for casting in other materials
- Used with electrowetting-on-dielectric (**EWOD**)

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Lithographic Techniques

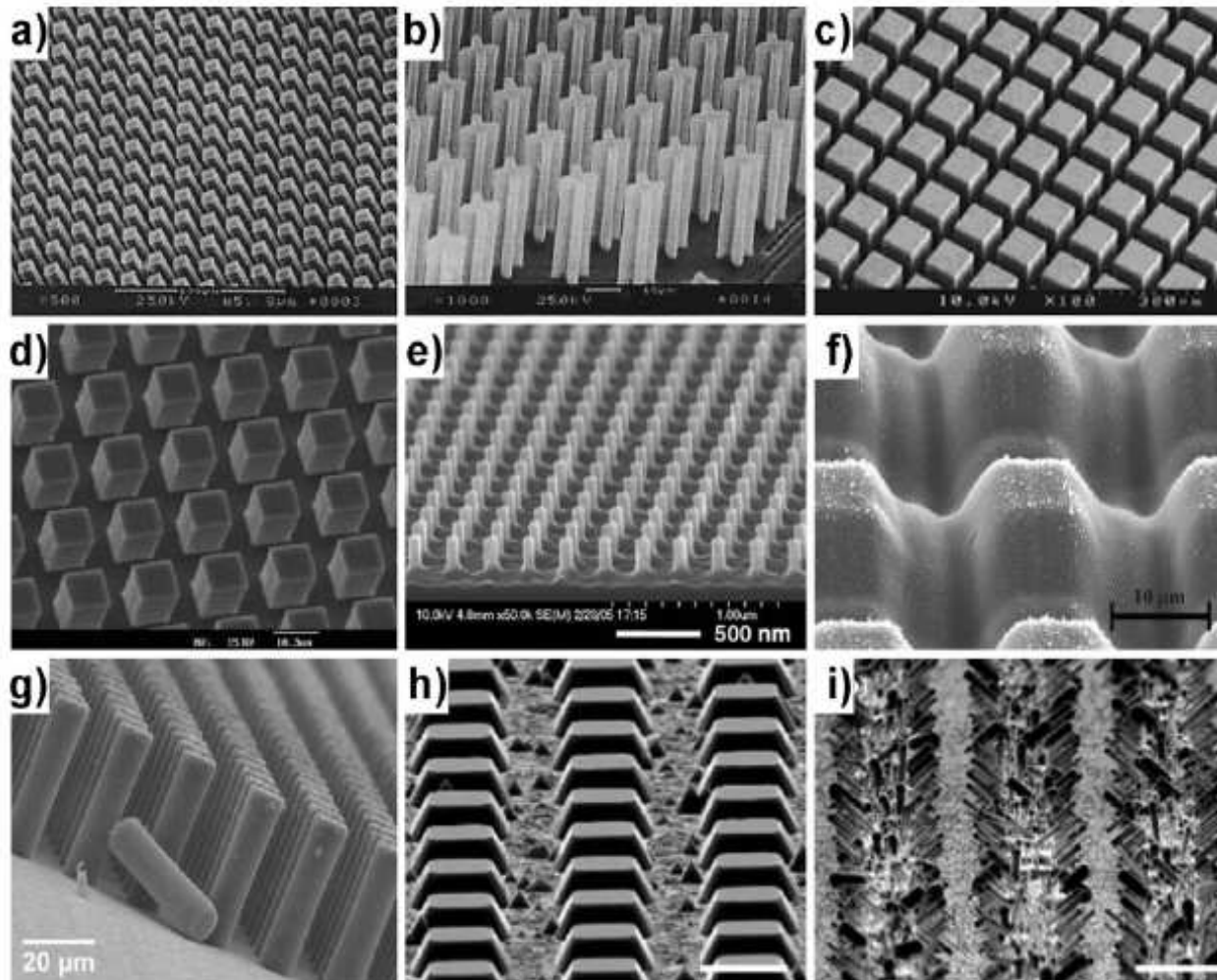


Fig. 9 Lithographic surface modification (a) photolithographic towers and (b) indented square posts,¹¹⁴ (c) diced silicon wafer,¹¹⁵ (d) photolithographic towers,¹¹⁶ (e) silicon nano-towers,¹¹⁷ (f) laser-modified SU8 surface,¹¹⁸ (g) SU8 towers,^{8b} (h) silicon islands and (i) silicon nano-wires grown on those silicon islands.¹¹⁹ Images reprinted with permission from (a), (b), (c), (f), (h) and (i) American Chemical Society, Copyright 2000, 2002, 2006 and 2007, (d) Elsevier, Copyright 2006, and (e) and (g) Institute of Physics, Copyright 2006 and 2004, respectively.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Aggregation and Assembly of Particles

- Colloidal particles can form close-packed assemblies on surfaces
- Methods: Spin-coating, dip-coating or reverse-dip coating
- Arrays of particles are also **photonic crystals** and display optical properties
- Particle **coating is conformal**
- Roughness on scales from **nm to μm**
- Si particles form hexagonally close packed arrays with particle sizes nm- $100\mu\text{m}$
- Polymer spheres or polymer spheres with attached Si nanoparticles or CNTs
- Aggregations can give **“raspberry”** structures
- Random rather than ordered close-packed structures is possible
- **Low cost and large surface areas**

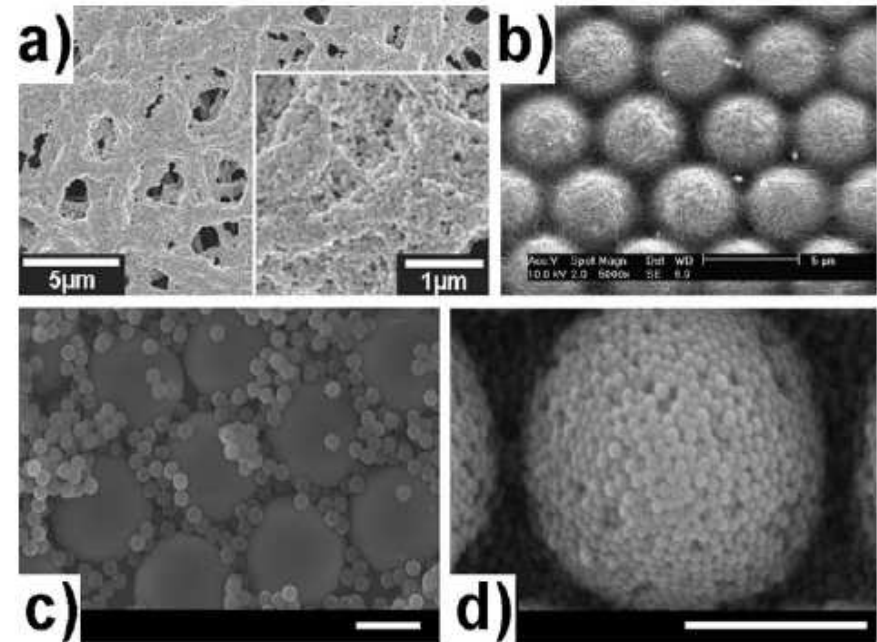


Fig. 10 Particle aggregation (a) layer-by-layer deposition of TiO_2 particles on fibres,²⁶ (b) CNT-coated polystyrene-sphere array,¹²⁸ (c) silica-sphere array with additional smaller sphere aggregates (scale bar = $5\ \mu\text{m}$) and (d) micron-sphere array produced from 300 nm particles silica nano-spheres (scale bar = $5\ \mu\text{m}$).¹²⁹ Images reprinted with permission from (a) Institute of Physics, Copyright 2007, (b) American Chemical Society, Copyright 2007, (c) and (d) Elsevier, Copyright 2007.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Templating

- **Pattern** or shape, either 2D or 3D, can be **replicated** using a templating method
- Material is printed, pressed or grown against the voids of a template
- **Fast, very low cost and reproducible** - widely used method for polymeric surfaces
- Any surface can be used as a template, such as biological, colloidal, lithographic and woven materials
- **Lotus** and other leaf structures, **butterfly wings**, etc have been reproduced

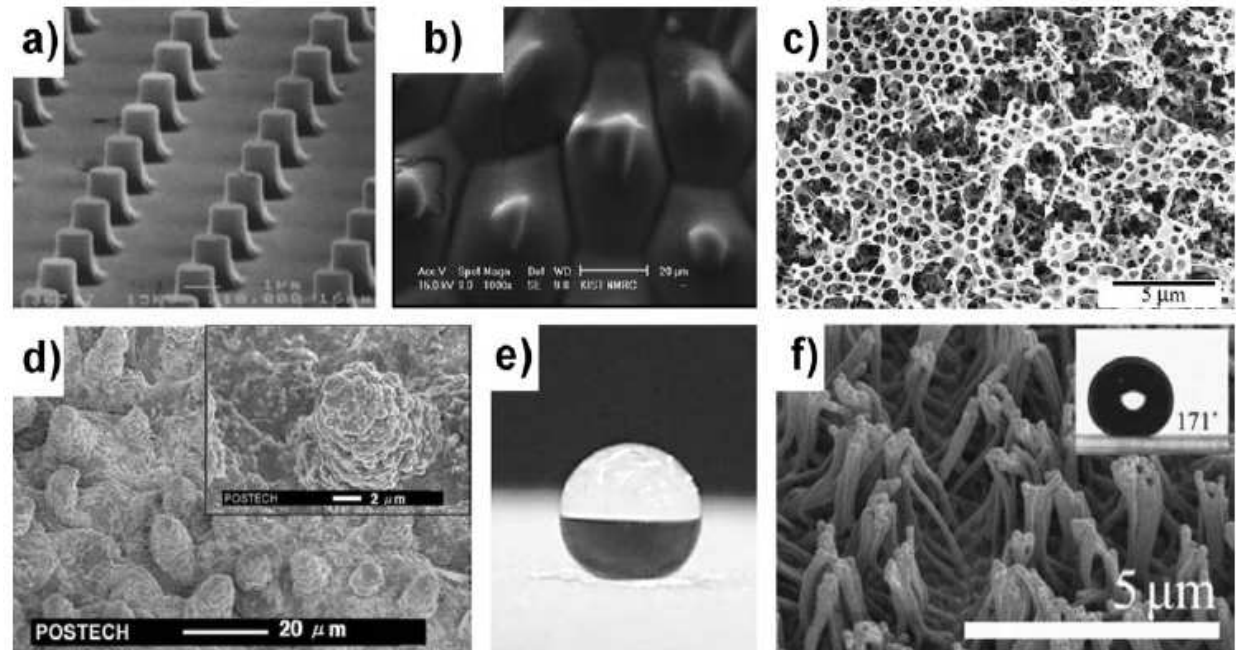


Fig. 11 Replica surfaces produced by templating (a) micro-posts,¹⁴³ (b) PMMA replica of *Colocasia*-like leaf surface,¹⁴⁴ (c) a polyvinylidene fluoride inverse opaline structure,¹⁴⁵ (d) photoresist replica of lotus leaf by UV-NIL,¹²⁷ (e) water droplet resting on a polymer hot-press transferred pattern,¹⁴⁶ and (f) polymer hairs grown through an AAO template with insert showing water droplet resting on surface.¹⁴⁷ Images reprinted with permission from (a) EDP sciences, Copyright 1999, (b) and (c) Elsevier, Copyright 2007 and 2006, respectively, (d) Institute of Physics, Copyright 2007, and (e) and (f) American Chemical Society, Copyright 2006.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* 4 (2008) 224-280.

Phase Separation

- Multicomponent mixture become unstable (e.g. via cooling or pressure), one component solidifies before other, remove other as a liquid.
- If solid component is continuous can get a **porous 3D structure** with **controllable pore size**.
- Low cost, easy production, **flexible shapes by casting or coating**
- Bicontinuous structures have been used for many years as filters and chromatography stationary phases - now as superhydrophobic surfaces
- Polypropylene, polyvinyl chloride, polycarbonate, polystyrene, some fluoropolymers, sol-gel derived materials, block co-polymers
- **Optically transparent** silica sol-gel and poly(acrylic acid) materials
- Structures tend to have **one length scale**
- Superhydrophobic properties are **renewable by abrasion**

Phase Separation

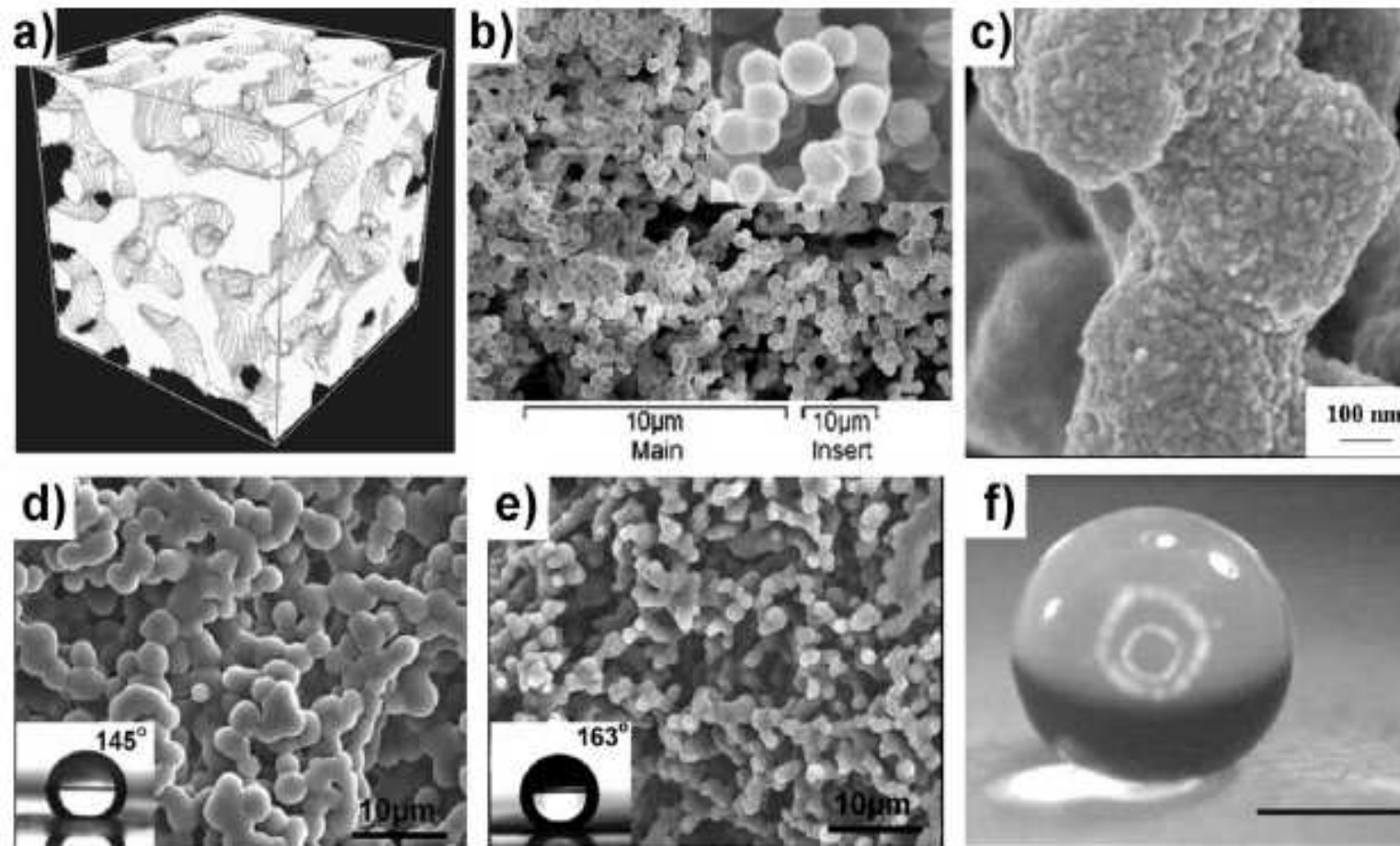


Fig. 5 Examples of phase separation, (a) model of a bicontinuous structure,³⁹ (b) sol-gel foam produced using acetone as co-solvent,⁴⁰ (c) superhydrophobic PVC film,⁴¹ (d) and (e) phase-separated block copolymer films,⁴² (f) water droplet on an organic xerogel (scale bar = 1 mm)⁴³ Images reprinted with permission from (a) American Physical Society, Copyright 2001, (b) and (c) from Elsevier, Copyright 2007 and 2006, respectively, (d) and (e) from American Chemical Society, Copyright 2005, and (f) The Royal Society of Chemistry, Copyright 2006.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Porous and Etched Systems

- Al_2O_3 layers can be grown on Al under anodic potentials in acid forms **nano-pores** in a hexagonal array sizes determined by the potential used
- **Differential etching** roughens often due to the relative rates of etching of different crystal planes or of the matrix compared to crystalline region
- Plasma and ion etching or laser ablation of polymers (e.g. PTFE, PP, PET, PS, transparent PMMA). **Fast and large sample sizes**
- Wet chemical etching of polycrystalline metals (e.g. Al, Zn and Cu)
- TiO_2 layer etched using a RF plasma using CF_4 as etchant
- Steel, copper and titanium alloys have been wet etched
- Femtosecond laser to create micro/nanoscale roughness on a silicon wafer
- **Etching time** determines height of features
- Etching process can be tailored to produce two-tiers of length scale
- Etching can be combined with masking techniques

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Porous and Etched Systems

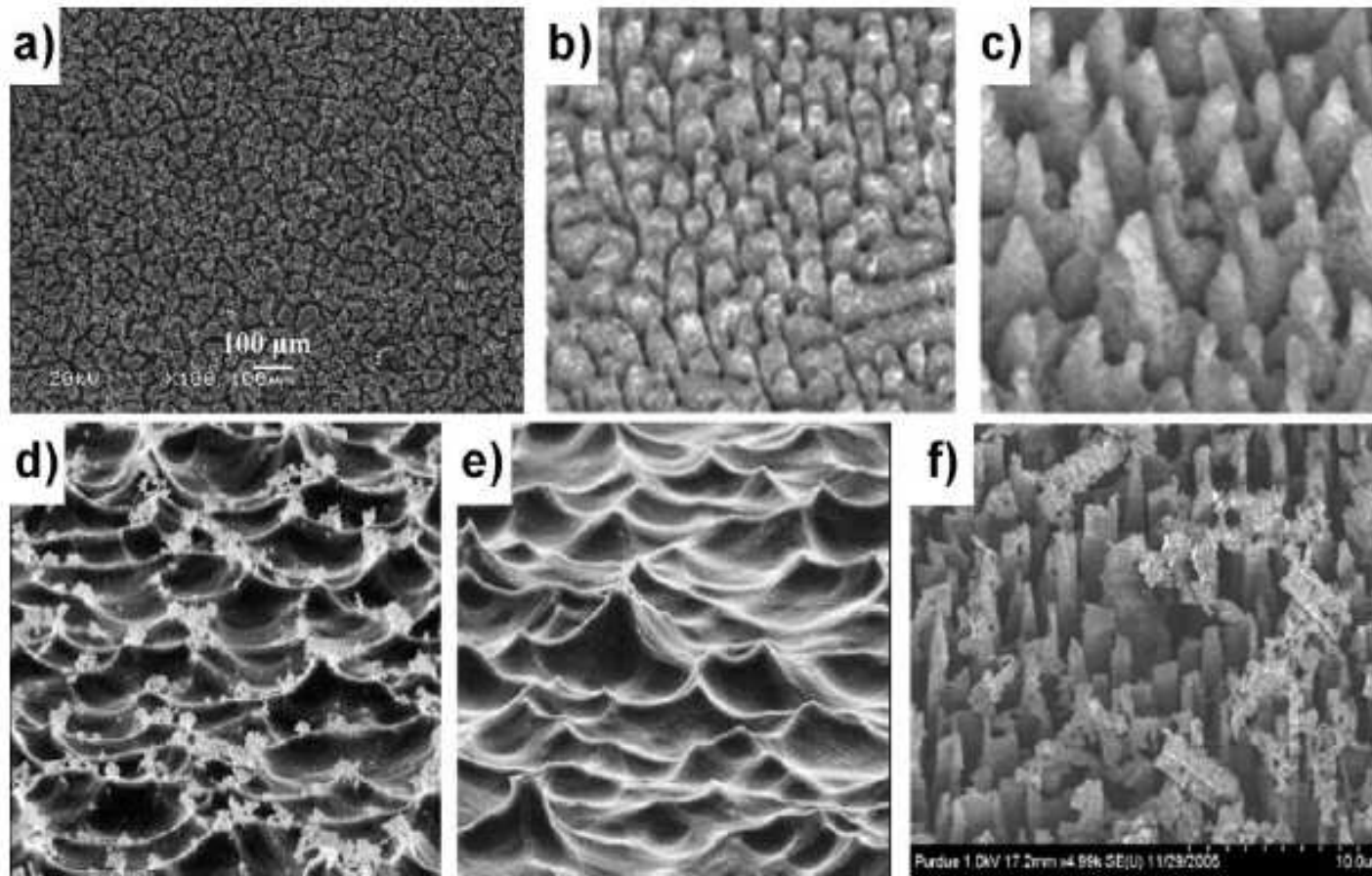


Fig. 7 Etching (a) roughened aluminium alloy,⁷⁹ (b) laser-etched silicon surface in SF_6 3.2 kJ m^{-2} and (c) using 5 kJ m^{-2} ,⁸⁰ (d) silicon wafer/ photoresist layer over-etched by an inductively-coupled SF_6 plasma before cleaning,⁸¹ and (e) after ultrasonication to remove residual photoresist, and (f) submicron pillar structures in p-type silicon after buffered oxide etching.⁸² Images reprinted with permission from (a), (d) and (e) Elsevier, Copyright 2006 and 2005, and (b), (c) and (f) American Chemical Society, Copyright 2006 and 2007.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Crystal Growth

- Complex patterns: rough and **fractal** are possible
- Cooling of alkyl ketene dimer (AKD) (a waxy paper sizing agent), fractal triglyceride surfaces and random crystallisation of n-hexatriacontane,
- Stretching a thin sheet of Teflon causes fibrous crystals separated by voids
- Fractal aluminium oxide surfaces formed by anodic oxidation
- PECVD surfaces of silica and aluminium, which are both **hard and transparent**
- **Semiconductors** which are superhydrophobic in the dark, but hydrophilic in the light, e.g. ZnO and SnO₂ nano-rod surfaces and photocatalytic metal oxides (e.g. TiO₂) – **photo-switchable superhydrophobicity**
- Growth of crystal face parallel to surface from distributed nucleation centres to create **nano-columns** e.g. ZnO from solution phase or vapour deposition
- Nanostructured flower-like crystals (e.g. SnO₂, polyethylene from xylene)
- Catalysed growth via sputtered array of metal particles and then gas phase reactants: **very high aspect ratios**, e.g. CNT nanograss/nano-forests

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Crystal Growth

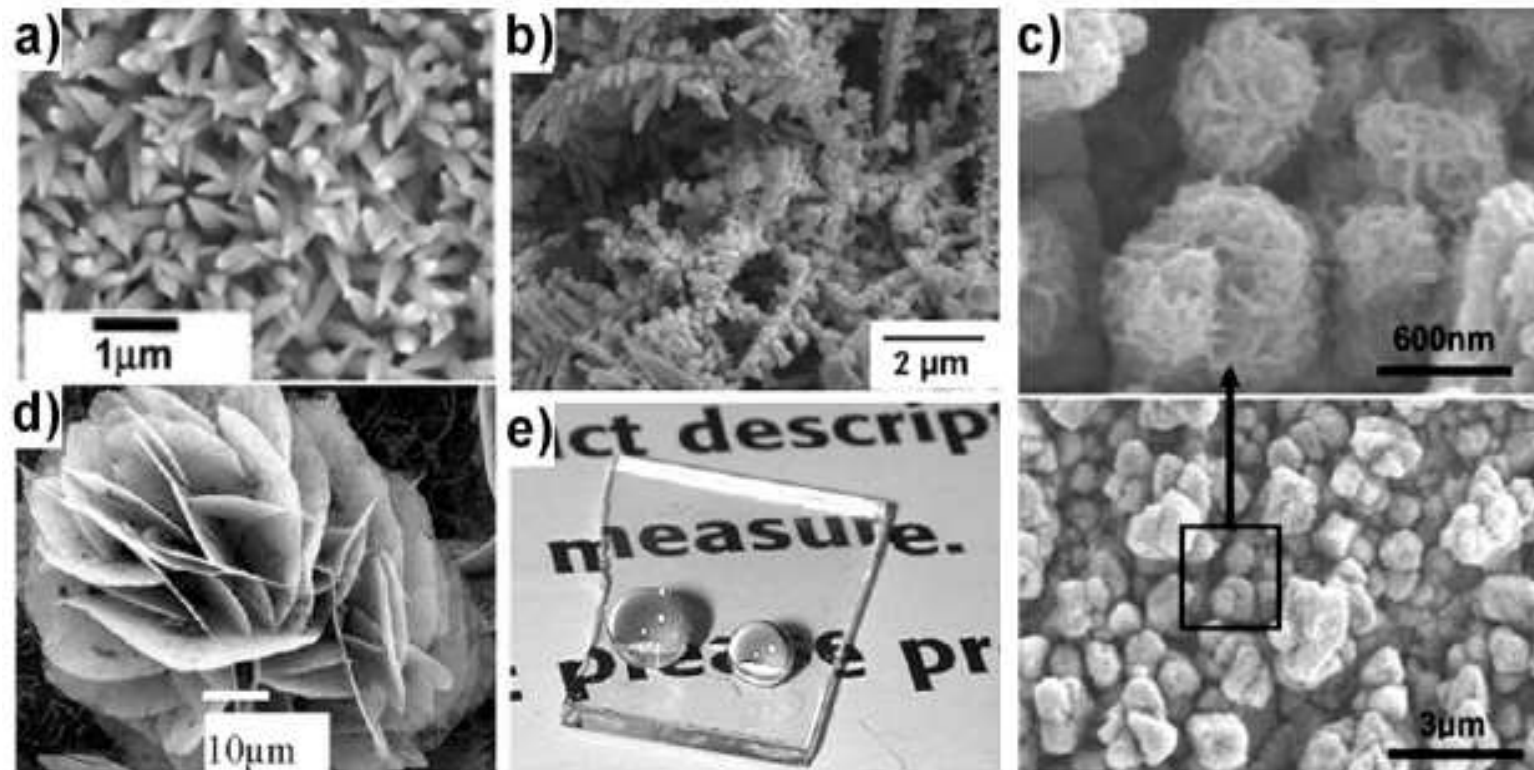


Fig. 6 Rough surfaces by crystal growth (a) cobalt hydroxide crystalline nano-pins (brucite-type) with diameter of 6.5 nm,⁵³ (b) silver aggregates deposited on a silicon wafer,⁵⁴ (c) CuS-coated copper oxide; enlargement shows nanostructure,⁵⁵ (d) flower-like tin oxide structure,⁵⁶ and (e) transparent superhydrophobic alumina-silica composite film.⁵⁷ Images reprinted with permission from (a) and (b) American Chemical Society, Copyright 2005 and 2006, respectively, (c) and (d) The Royal Society of Chemistry, Copyright 2005 and 2004, respectively, and (e) Institute of Physics, Copyright 2007.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* 4 (2008) 224-280.

Diffusion Limited Growth

- Rate of deposition is only dependent upon the flux of material – **diffusion-controlled deposition**
- Growth concentrated at protuberances so roughness generated by chance increases rapidly.
- As the structures get larger growth occurs on their sides, generating a branching structure with **fractal character** – cauliflower florets
- Fractal so highly hydrophobic, some quite strong, but most are easily damaged and few are transparent as the **fractal patterns have many length scales**
- Electro-deposition and gas-phase deposition, e.g. plasma deposited polymers (technical coatings on high value or small components)
- Electrodeposition of metals and metal oxides (e.g. Zn, Cu, Au, Ti)
- **Conducting polymers** can be used and are **switchable** from conducting and hydrophilic to **non-conducting** and hydrophobic
- **Industrial** type processes

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Diffusion Limited Growth

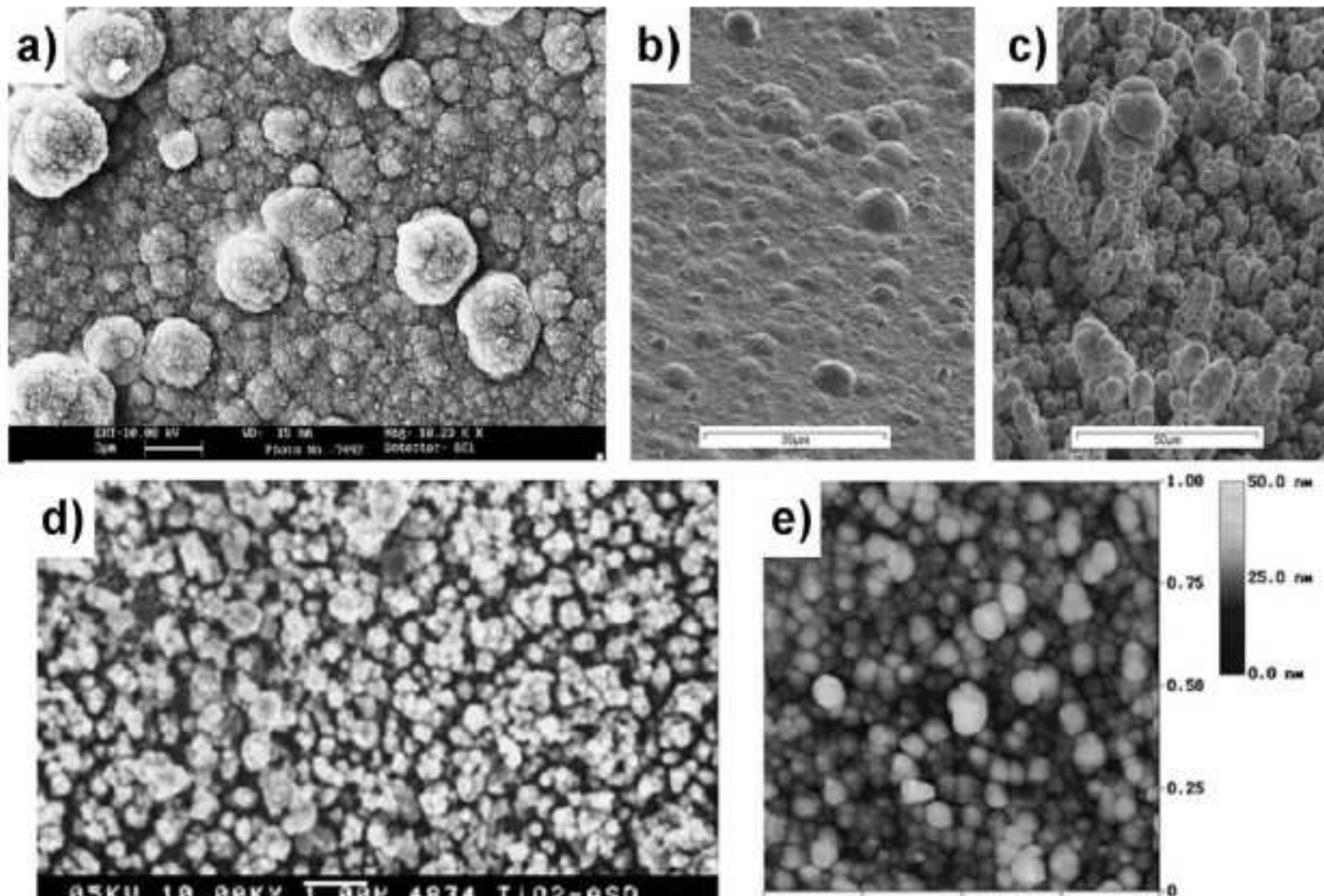


Fig. 8 Diffusion-limited growth on surfaces (a) plasma-deposited Teflon structures,⁹⁶ (b) electrochemically deposited copper at 100 mA cm⁻², and (c) 200 Ma cm⁻²,⁸ (d) an electrodeposited amorphous TiO₂ thin film,⁹⁷ and (e) HMDS plasma-deposited polymer.⁹⁸ Images reprinted with permission from (a), (d) and (e) Elsevier, Copyright 2007, 2005 and 2001, respectively, and (b) and (c) American Chemical Society, Copyright 2005.

Reference Roach, P., Shirtcliffe, N.J., Newton, M.I., *Soft Matter* **4** (2008) 224-280.

Beyond Simple Superhydrophobicity

Unexpected superhydrophobicity?

Leidenfrost Effect

Perfect Superhydrophobicity?

Cassie-Baxter with solid fraction $f_s=0$

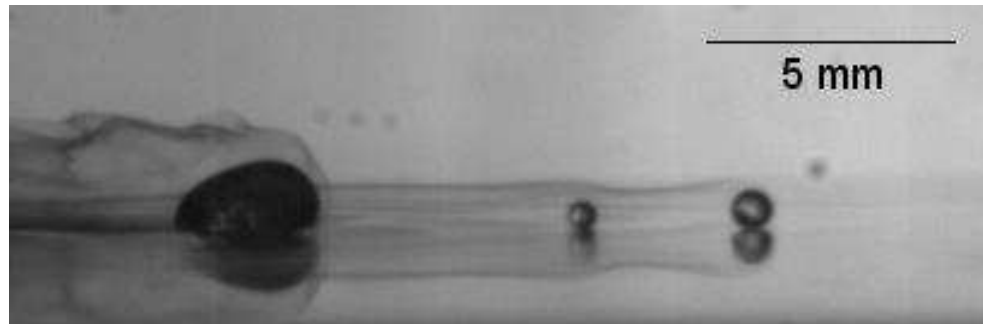
Droplet floats on a layer of vapor: $\cos\theta_{CB}=0 \times \cos\theta_e - (1-0) \Rightarrow \theta_{CB}=180^\circ$

Droplet of water deposited onto a hot surface ($\sim 200^\circ\text{C}$)

Thin vapor layer forms and insulates rest of droplet (only slowly evaporates)

Droplet is completely non-wetting and mobile

Leidenfrost Droplets



Liquid nitrogen poured on water at ambient temperature slides on an "air cushion" over the liquid surface

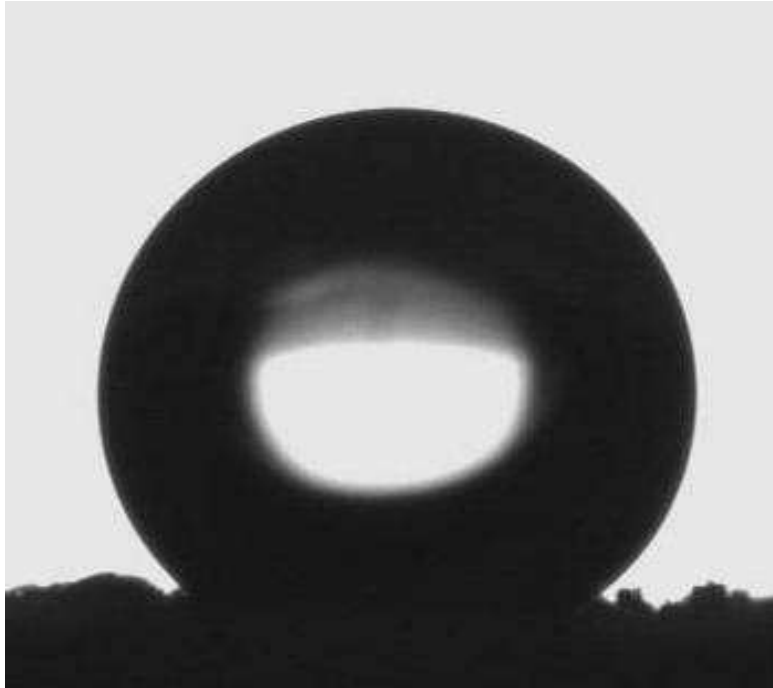
Leidenfrost Puddle



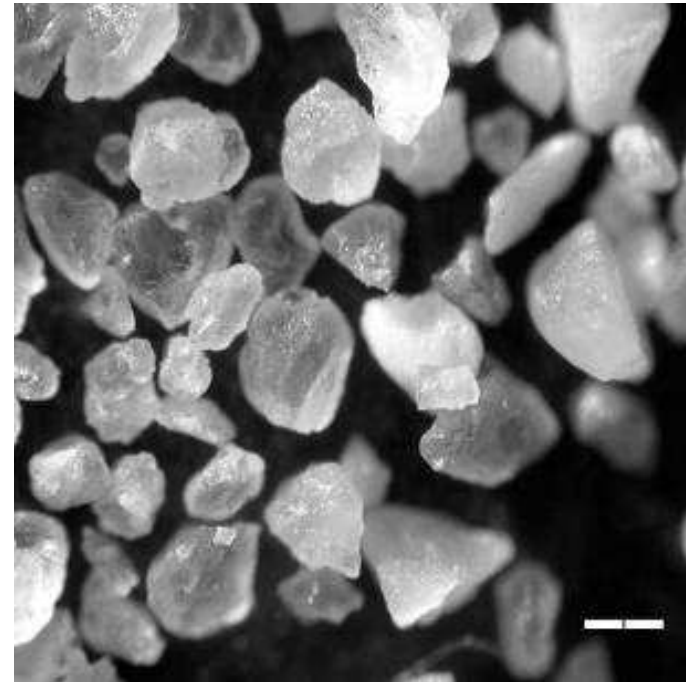
FIG. 2. Large water droplet deposited on a silicon surface at 200°C .

Super Water-Repellent Sand/Soil

Sand with 139°



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)

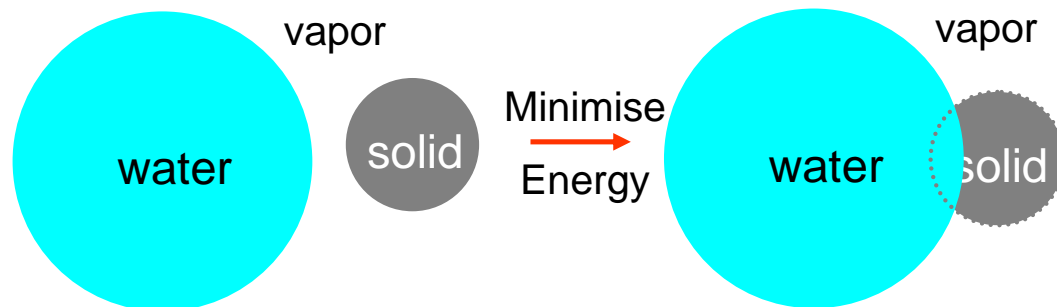
References McHale, G. *et al.*, *Eur. J. Soil Sci.* 56 (2005) 445-452; *Hydrol. Proc.* 21 (2007) 2229-2238.

Liquid Marbles

Loose Surfaces

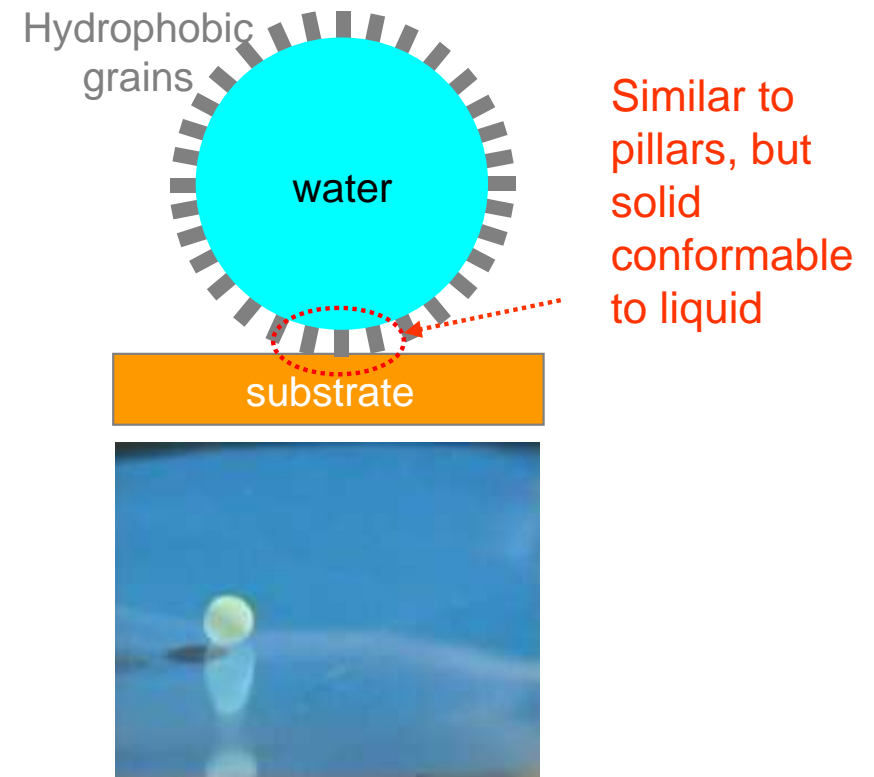
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

Hydrophobic Grains and Water



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

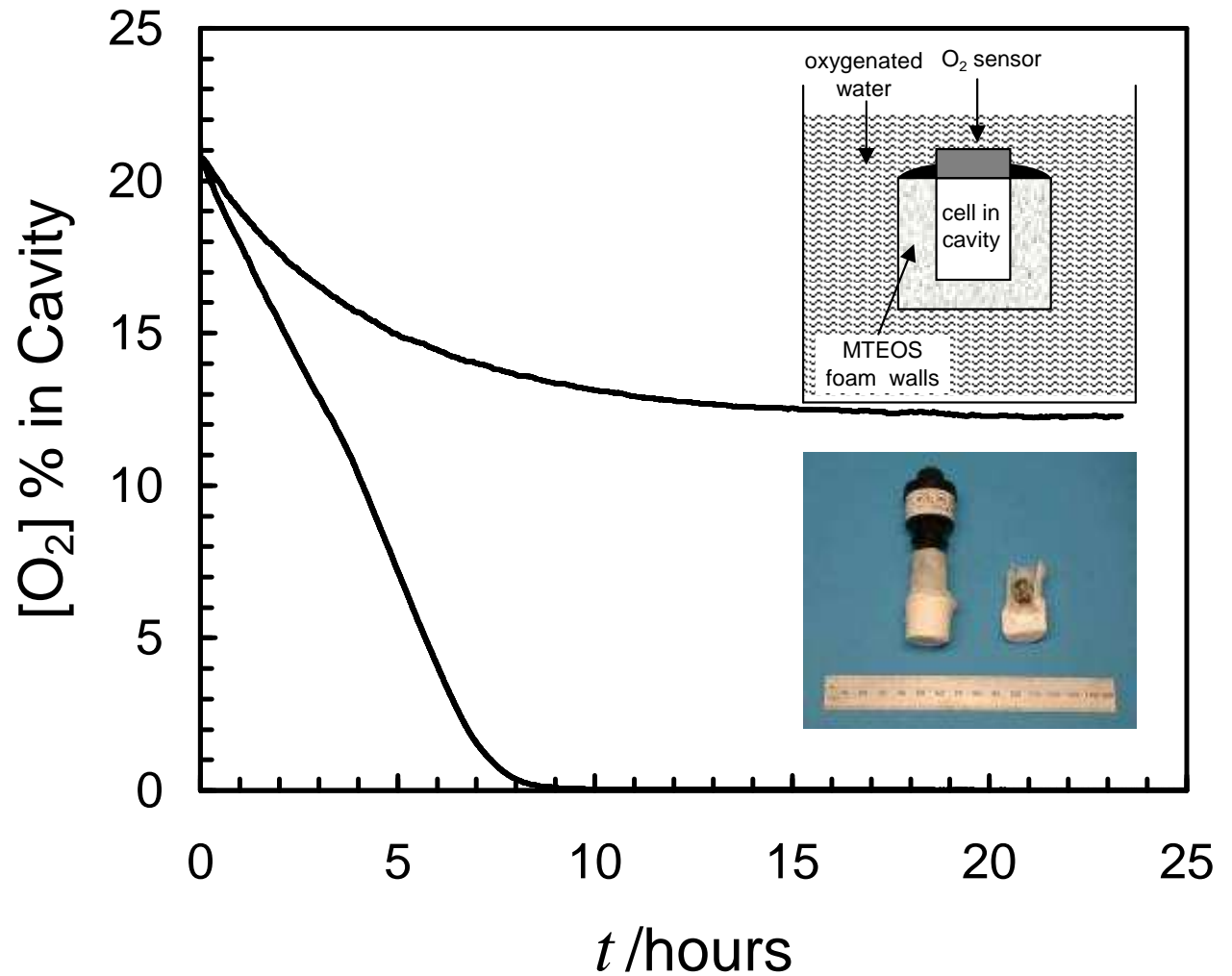
Energy is always reduced on grain attachment



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

Superhydrophobicity: Plastron Respiration

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



References Shirtcliffe, N.J. *et al.*, *Appl. Phys. Lett.* **89** (2006) art 104106. Ege, R. *Z Allg. Physiol.* **17** (1915) 81-124. Thorpe, W.H.; Crisp, D. J. *Exp. Biol.* **24** (1947) 227-269. Bush, J.W.M.; Hu, D.L.; 48
Prakashc, M.; *Adv. Insect Physiol.* **34** (2008) 117-192.

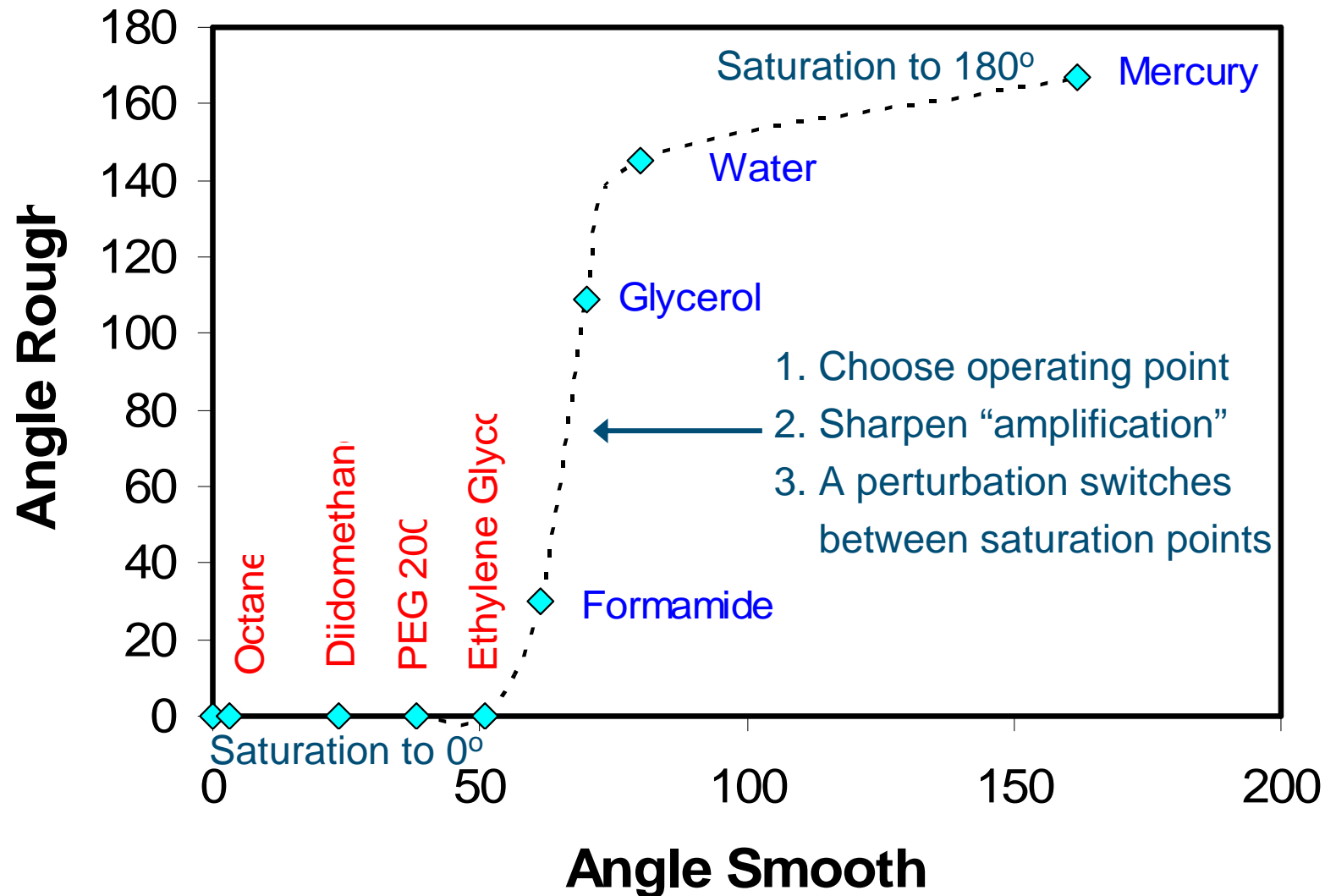
15 May 2009



Beyond Simple Superhydrophobicity

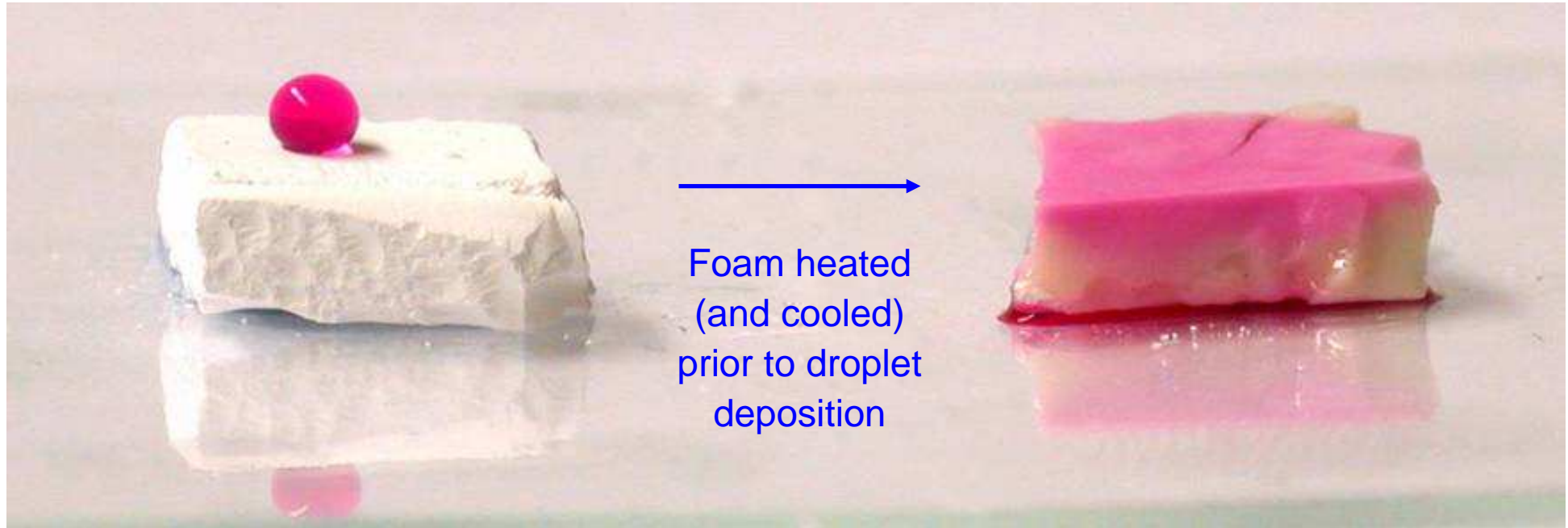
*Superwetting, Superspreading,
Hemi-wicking and Porosity*

Digital Switching



Reference: McHale, G. *et al.*, *Analyst* **129** (2004) 284-287. Shirtcliffe, N.J. *et al.*, *Chem. Comm.* (25) (2005) 3135-3137. Sun, T.L. *et al.*, *Ange. Chemie-Intl. Ed.* **43** (2004) 357-360. Krupenkin, T.N. *et al.*, *Langmuir* **20** (2004) 3824-3827. Herbertson, D.L. *et al.*, *Sens. Act.* **A130** (2006) 189-193.

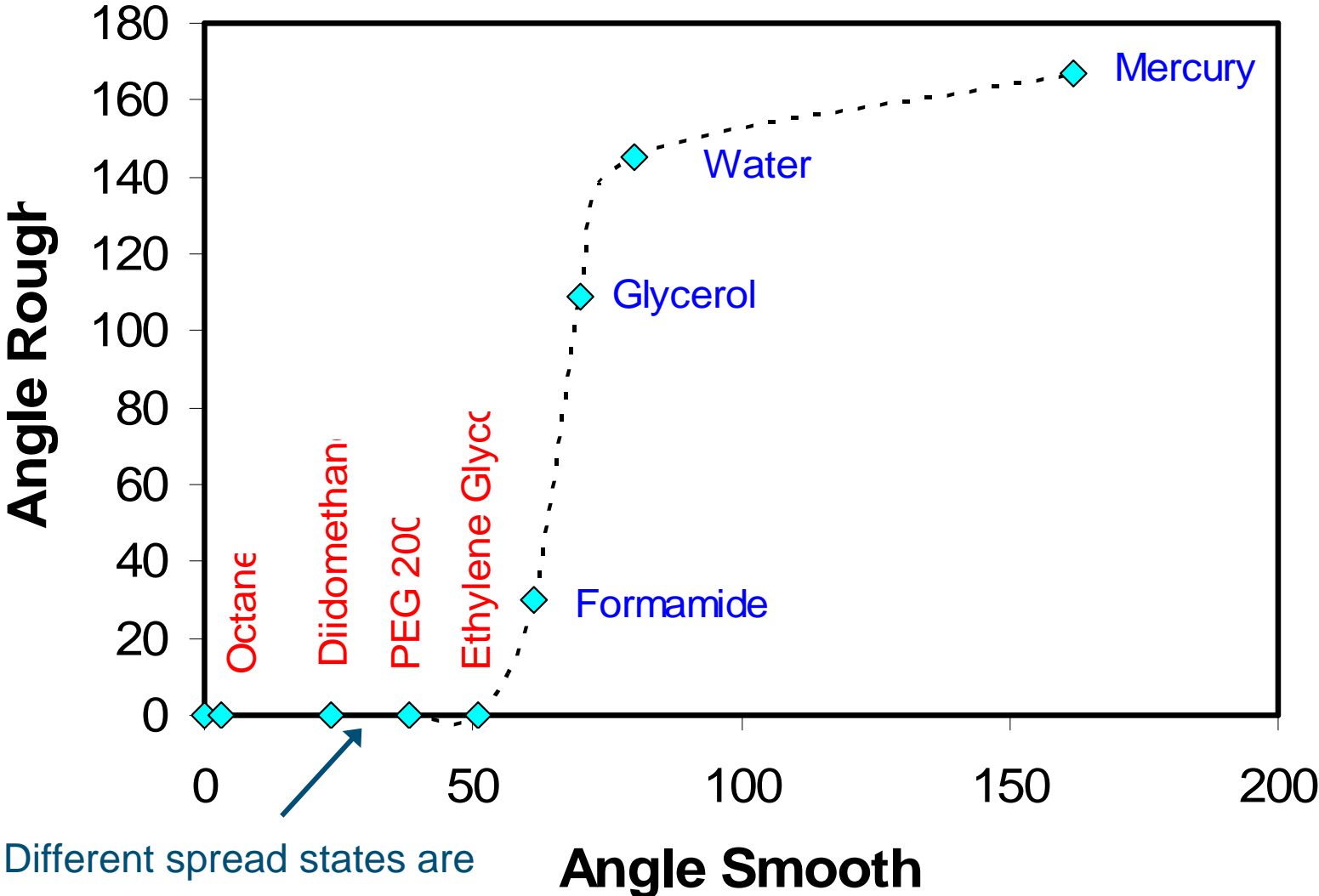
Sol-Gel: Switching off Superhydrophobicity



Mechanisms for Switching

- Temperature history of substrate
- Surface tension changes in liquid (alcohol content, surfactant, ...)
- "Operating point" for switch by substrate design

Super-spreading



Different spread states are approached at different rates

References McHale, G. et al., Analyst 129 (2004) 284-287; Phys. Rev. Lett. 93 (2004) art. 036102.



Driving Forces for Spreading

Drop spreads radially until contact angle reaches equilibrium

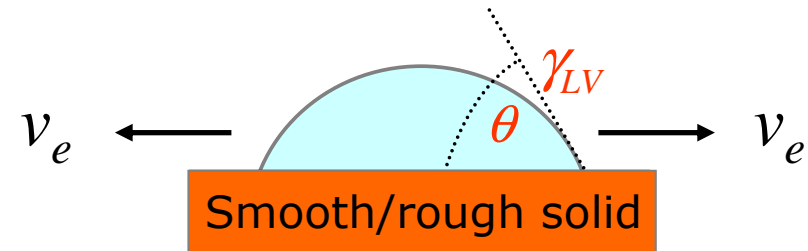
Horizontally projected force $\gamma_{LV} \cos \theta$

Smooth Surface

Driving force $\sim \gamma_{LV}(\cos \theta_e^s - \cos \theta)$

Cubic drop edge speed

$$\Rightarrow v_E \propto \theta \gamma_{LV}(\theta^2 - \theta_e^{s2})$$



Wenzel Rough Surface

Driving force $\sim \gamma_{LV}(r \cos \theta_e^s - \cos \theta)$

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:

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

Reference McHale, G.; Newton, M.I. Colloids & Surfaces, A206 (2002) 193-201.

Superspreading of PDMS on Pillars

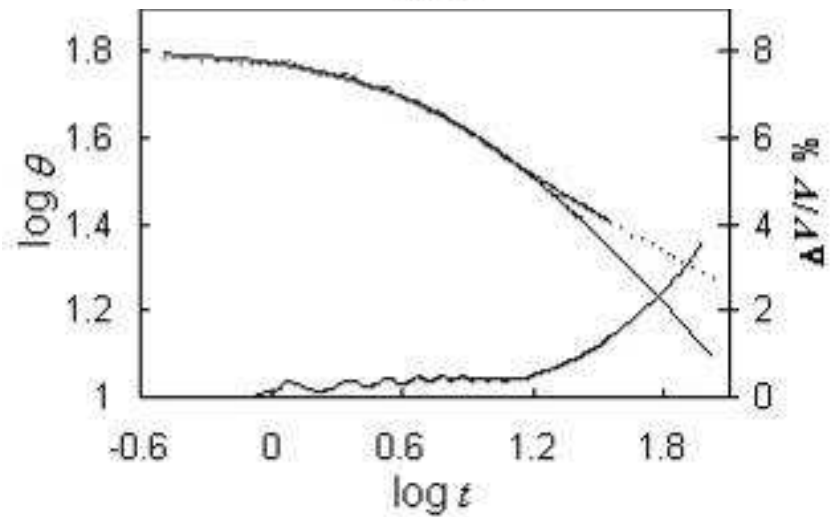
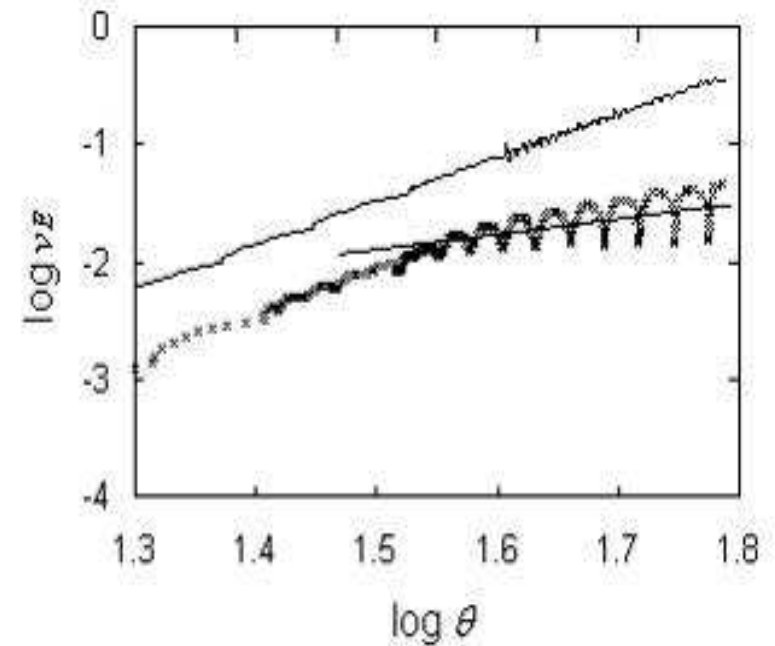
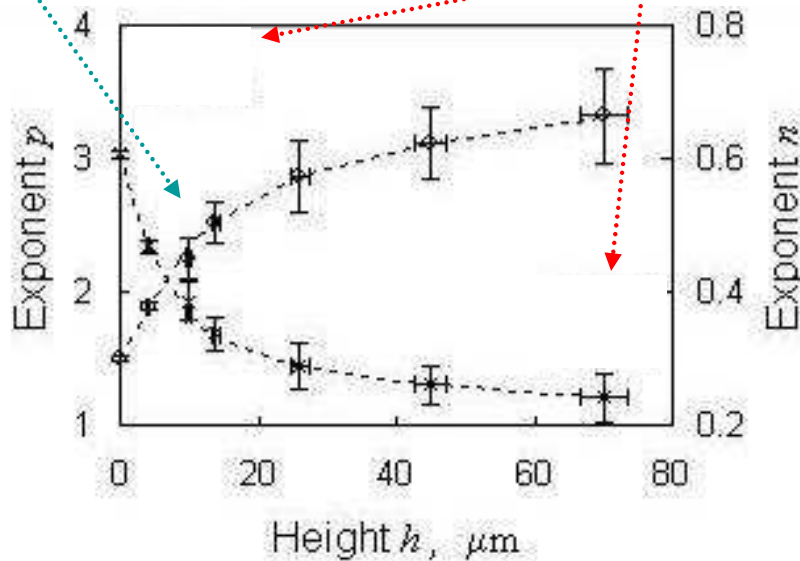
Tanner's Law exponents p and n

(cubic to linear transition)

$$v_E \propto v^* \theta^p \quad \theta \propto \left(\frac{V^{1/3}}{v^*} \right)^n \frac{1}{(t + t_0)^n}$$

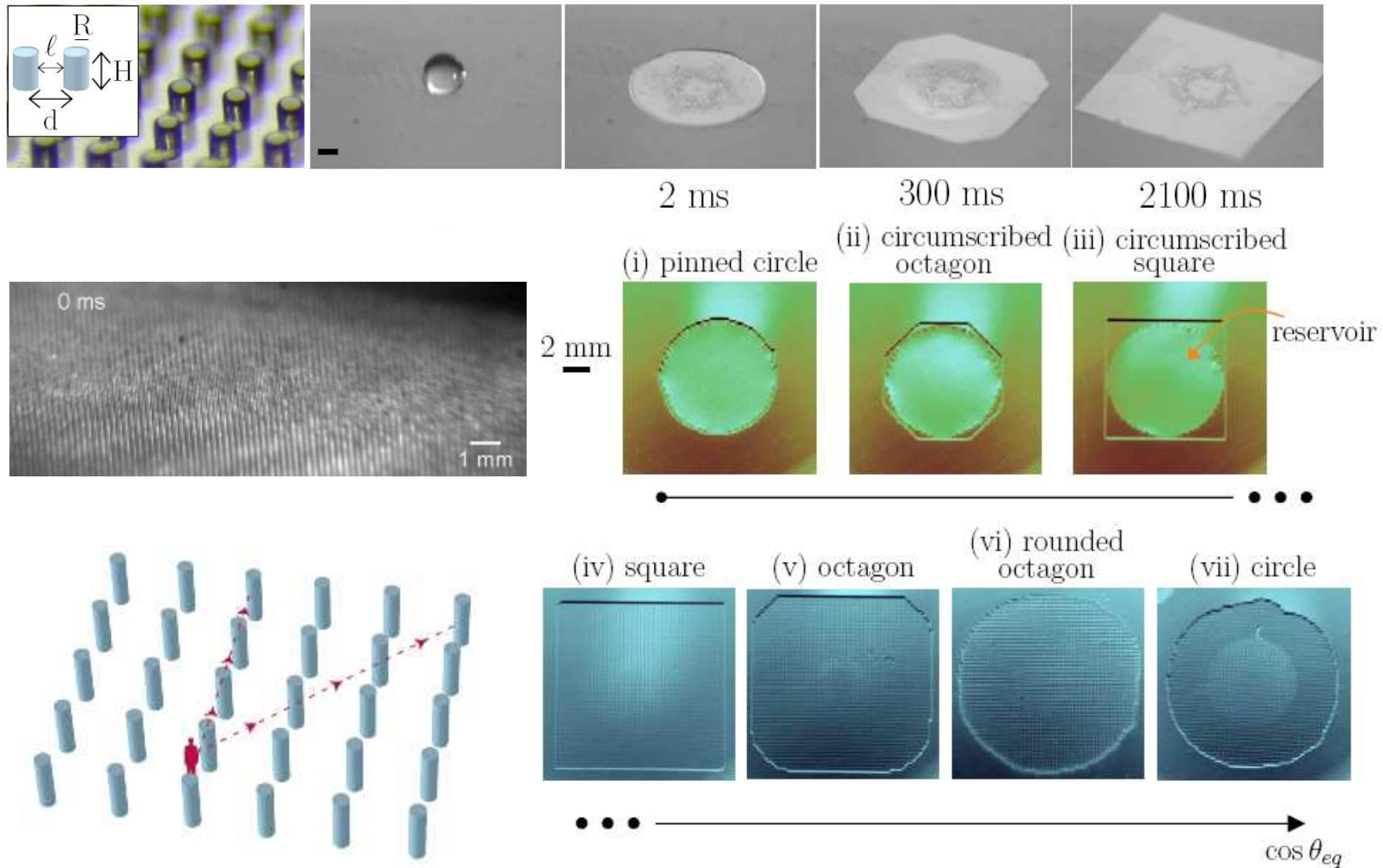
Effect of substrate on PDMS

Effect of substrate on water



Reference McHale, G. et al., Phys. Rev. Lett. 93 (2004) art. 036102.

Topography Induced Wetting: Hemi-Wicking



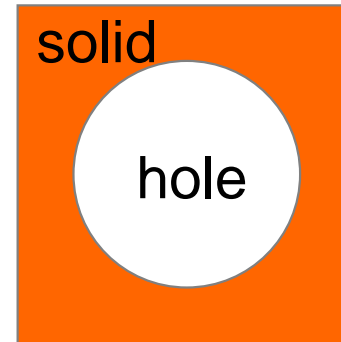
References Bico, J. *et al.*, *Coll. Surf. A* **206** (2002) 41-46. Quéré, D. *Physica A* **313** (2002) 32-46. Courbin *et al.*, *Nature Materials*. **6** (2007) 661-664; McHale, **6** (2007) 627-638.

Cylindrical Model for Capillary Infiltration

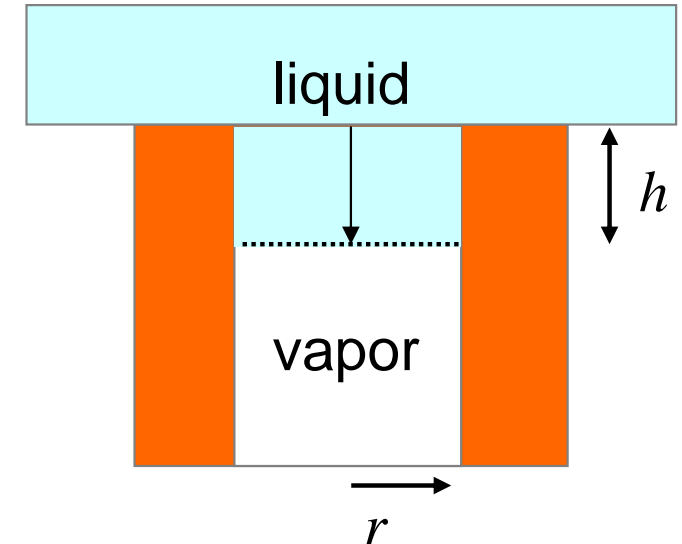
Assumptions

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

Top View



Side View



Change in surface free energy	=	solid-liquid energy per unit area	×	gain of wall area	minus	solid-vapor energy per unit area	×	loss of wall area
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$$\Delta F = (\gamma_{SL} - \gamma_{SV})2\pi r \Delta h \quad \xrightarrow{\text{Young's Law}} \quad \Delta F = -\gamma_{LV} \cos\theta_e 2\pi r \Delta h$$

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

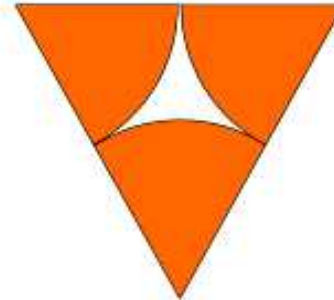
Same result for wetting down sides of posts on a superhydrophobic surface

Transition from Wetting to Porosity

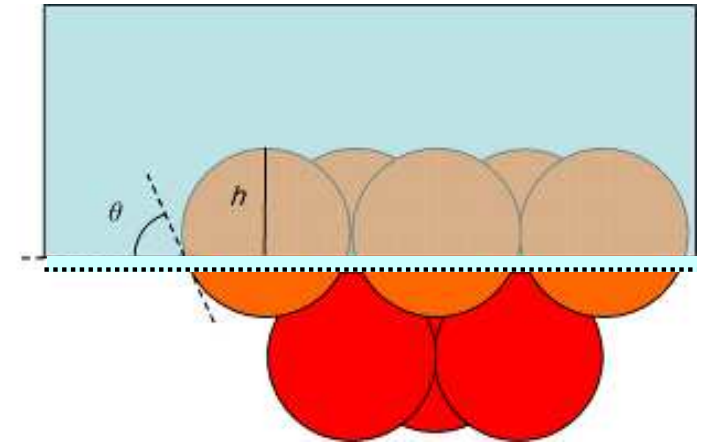
Assumptions

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^{1,2}

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

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

$$\theta_c = 50.73^\circ$$

Creating superhydrophobic surfaces with curved features allows liquids to be supported even when $\theta_e < 90^\circ$ – so-called re-entrant surface features³

References ¹Shirtcliffe, N.J. *et al.*, Appl. Phys. Lett. **89** (2006) art. 094101. ²Bán, S.; Wolfram, E.; Rohrsetzher, S. 22 (1987) 301-309. ³Tuteja, A. *et al.*, Science **318** (2007) 1618-1622.

Summary

1. Basics of Superhydrophobicity

- Well developed conceptual models
- Often over-simplified use of Cassie-Baxter and Wenzel equations
- Can design applications to take advantage of the effects

2. Materials Methods

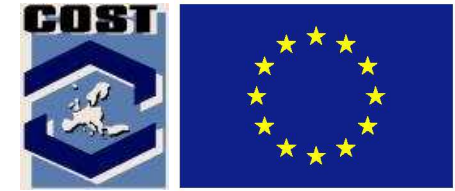
- Large recipe book exists
- Simple and inexpensive methods can be used
- Other properties of surface can be chosen

3. Beyond Simple Superhydrophobicity

- Many other systems (e.g. soil) can be viewed as superhydrophobic
- Wetting, spreading, wicking and porous systems are of future interest
- Functional properties are starting to be investigated

The End

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Internal Collaborators

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 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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EP/C509161/1 – Extreme soil water repellence
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EP/E063489/1 – Exploiting the solid-liquid interface
Dstl via EPSRC/MOD JGS, Kodak European Research
EU COST Action D19 - Chemistry at the nanoscale
EU COST Action P21 - Physics of droplets



Engineering and Physical Sciences
Research Council



Appendices

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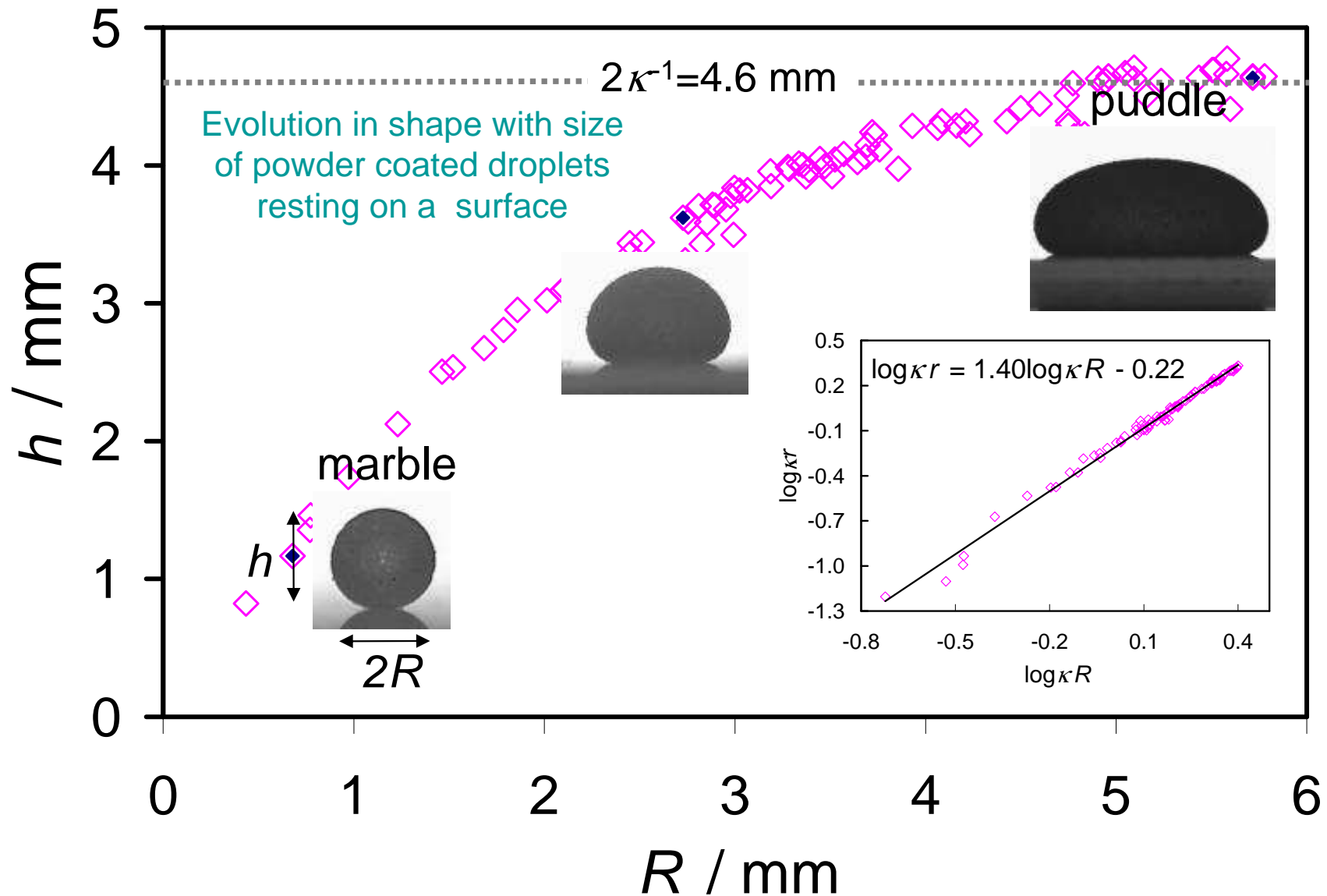
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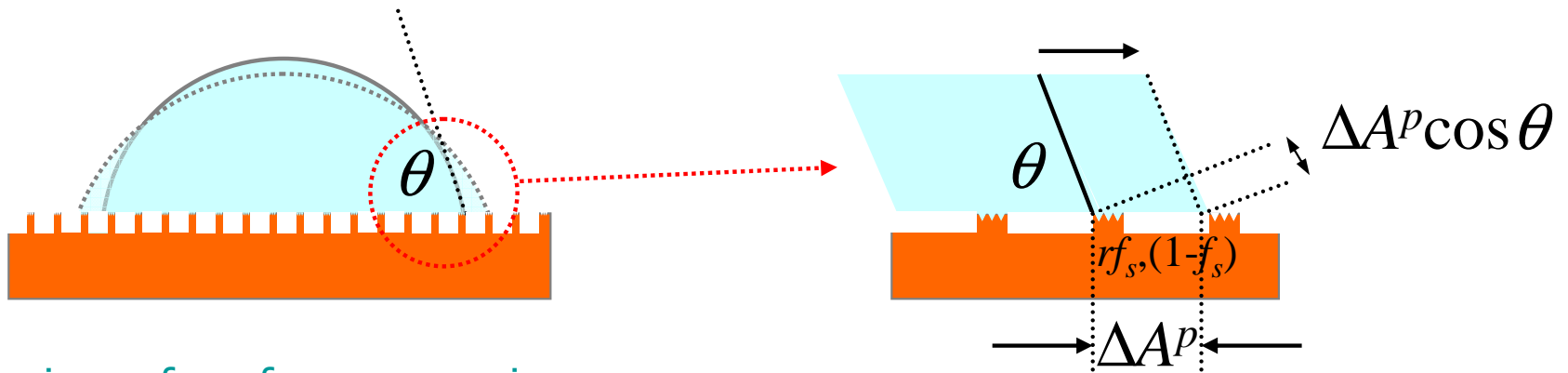
"Transformation of a simple plastic into a superhydrophobic surface", Erbil, H.Y.; Demirel A.L.; *et al.* *Science* 299 (2003) 1377-1380.

Liquid Marble Size Data (Lycopodium)



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 McHale G., et al. 23 Langmuir (2007) 918-924. Newton, M.I., et al. J. Phys. D40 (2007) 20-24.

Topography 4: Top-Filled Dual Scale Surfaces



Change in surface free energy is

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

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

$$\cos \theta_{Obs} = f_s r \cos \theta_e - (1 - f_s)$$

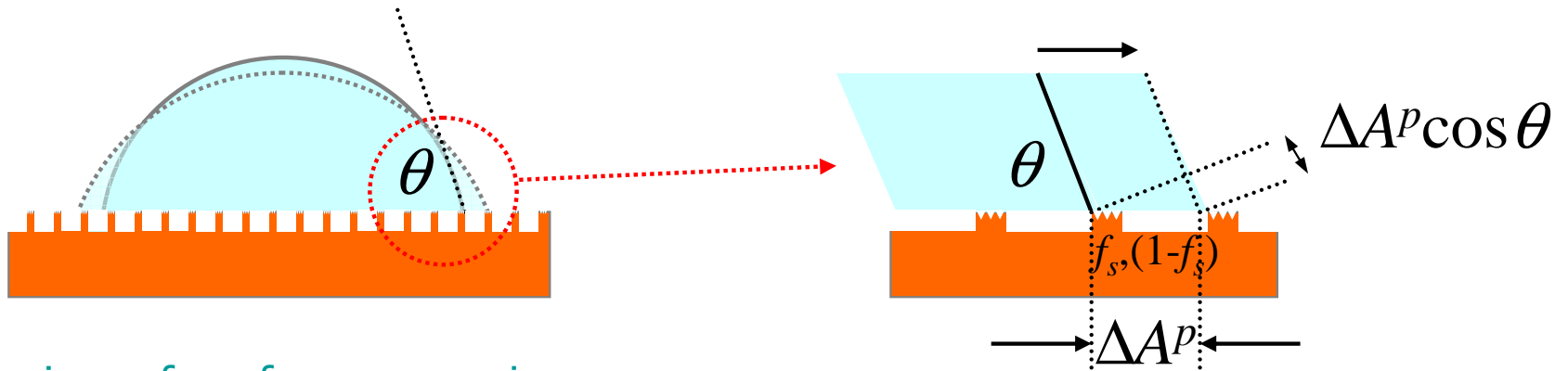
Topography $\Rightarrow f_s = \Delta A_{SL}^P / (\Delta A_{SL}^P + \Delta A_{LV}^P) =$ solid surface fraction from planar projections

$$r = \Delta A_{SL} / \Delta A_{SL}^P = \text{roughness of "tops" of features}$$

Simple view: Transformation via Wenzel law and then by Cassie-Baxter equation

$$\theta_e \rightarrow \theta_W (\theta_e) \rightarrow \theta_{CB} (\theta_W)$$

Topography 5: Top-Empty Dual Scale Surfaces



Change in surface free energy is

$$\Delta F = (\gamma_{SL} - \gamma_{SV}) f_s^{large} f_s^{small} \Delta A^P + \gamma_{LV} [(1 - f_s^{large}) \Delta A^P + f_s^{large} (1 - f_s^{small}) \Delta A^P] + \gamma_{LV} \Delta A^P \cos \theta$$

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

$$\cos \theta_{Obs} = f_s^{large} [f_s^{small} \cos \theta_e - (1 - f_s^{small})] - (1 - f_s^{large})$$

Topography $\Rightarrow f_s^{small}$ = solid surface fraction for small scale structure

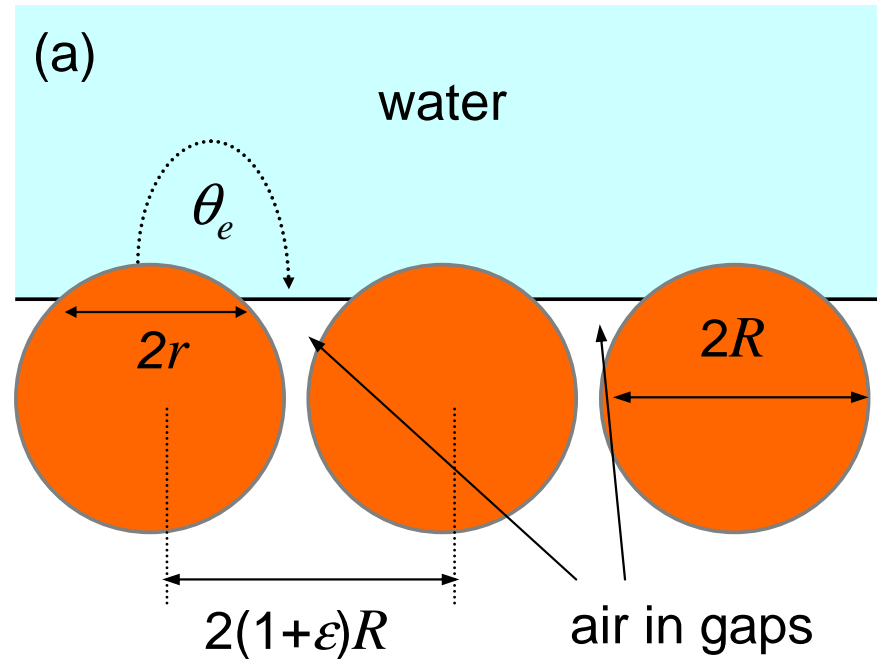
f_s^{large} = solid surface fraction for large scale structure

Simple view: Transformation via Cassie-Baxter and then by Cassie-Baxter again

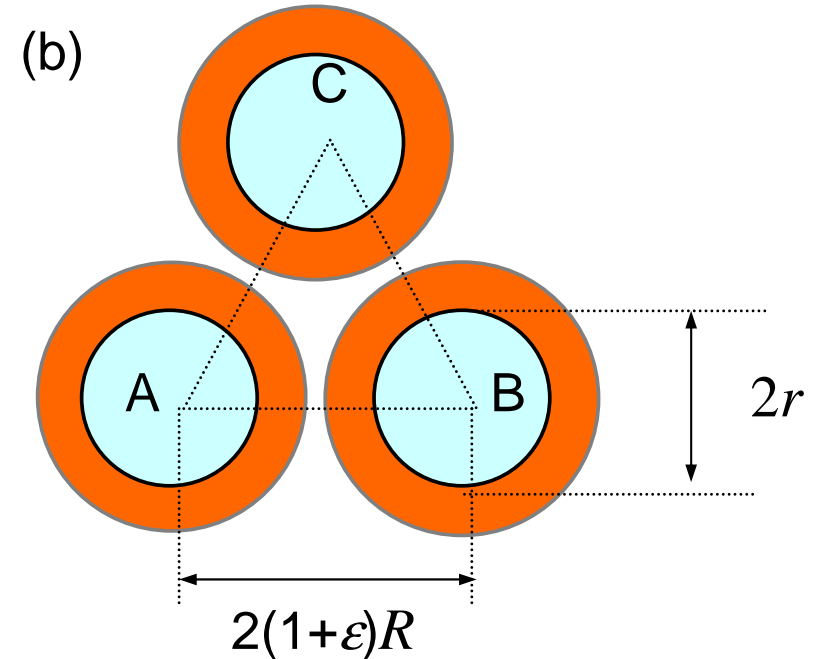
$$\theta_e \rightarrow \theta_{CB} (\theta_e) \rightarrow \theta_{CB} (\theta_{CB})$$

Model of Bead Pack/Soil

Side View



Top View



Assumptions

1. Uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges air gaps horizontally between spheres
3. Capillary (surface tension) dominated size regime of gaps $\ll \kappa^{-1} = 2.73$ mm

Bead Pack/Soil Model Calculations

Surface Free Energy Considerations

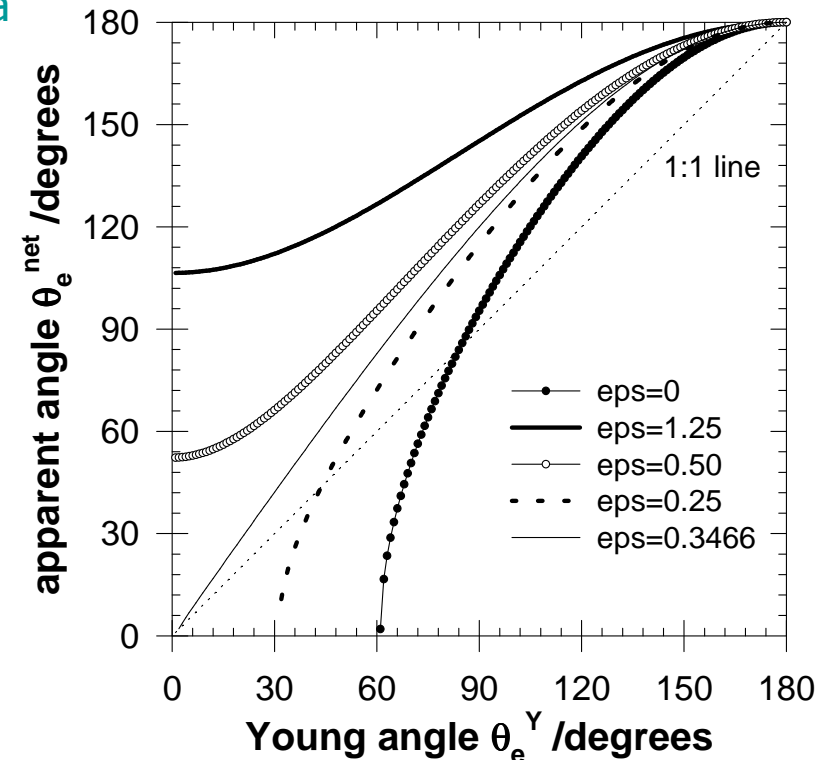
1. the curved bead surface effectively gives a roughness factor, r_s
2. the planar projection of the bead and the gap between beads forms a Cassie-Baxter system with a solid surface fraction, f_s
3. both r_s and f_s depend on the chemistry (via Young's law)
4. Young's contact angle is converted to a Wenzel contact angle and then to a Cassie-Baxter contact angle

Equations

$$\theta_e \xrightarrow{\text{Wenzel}} \theta_W \xrightarrow{\text{Cassie-Baxter}} \theta_{CB}$$

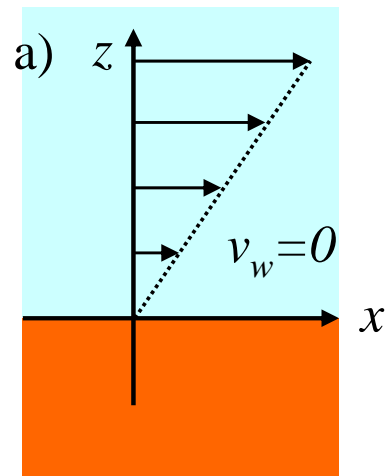
$$\cos \theta_e^{net} = f_s r_s \cos \theta_e - (1 - f_s)$$

$$f_s = \frac{\pi \sin^2 \theta_e}{2\sqrt{3}(1 + \epsilon)^2} \quad r_s = \frac{2(1 + \cos \theta_e)}{\sin^2 \theta_e}$$

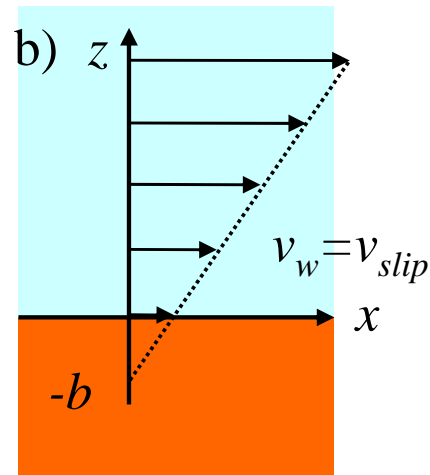


Slip by Simple Newtonian Liquids

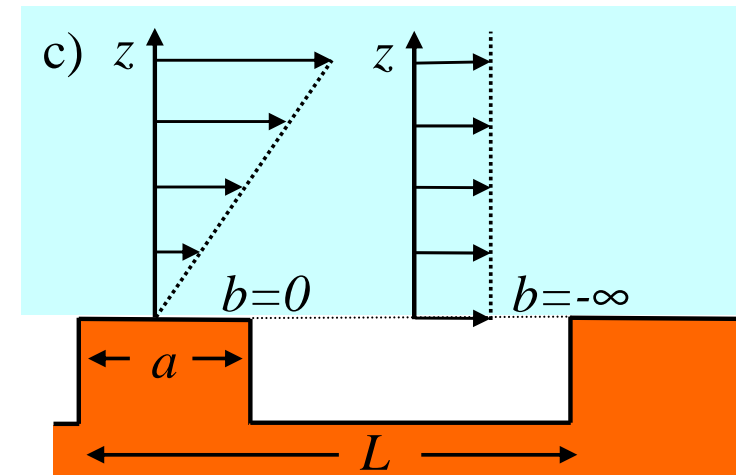
No Slip



Slip



Mixed



Experimental Evidence – Steady Flow

1. Theory^{1,2} supported by simulations suggests $b=L f(\phi_s)/2\pi$
2. Micro-PIV experiments detailing flow profiles³ ($h=1-7 \mu\text{m} \Rightarrow b=0.28L$)
3. Cone-and-plate rheometer experiments⁴ – drag reduction > 10%
4. Hydrofoil in a water tunnel experiments⁵ – drag reduction of 10%

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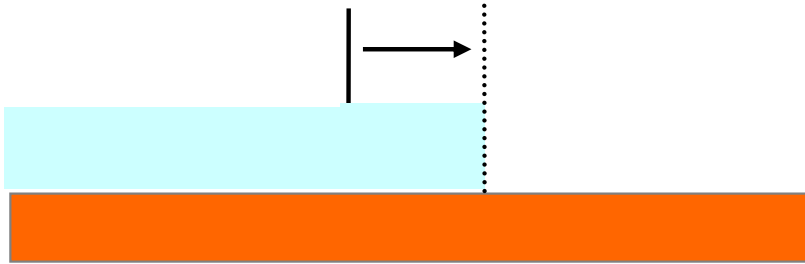
15 May 2009

³Joseph *et al.*, *Phys. Rev. Lett.* **97** (2006). ⁴Choi & Kim, *Phys. Rev. Lett.* **96** (2006).

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Hemi-Wicking: Theory

Flat Surface



Change in surface free energy is

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

liquid is assumed to be infinitesimally thin

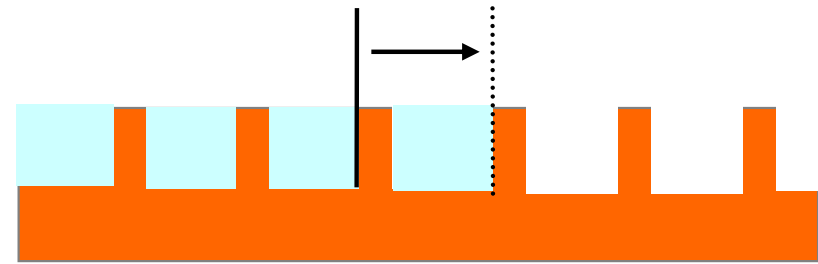
Spreading is when $\Delta F < 0 \Rightarrow$

$$\boxed{(\gamma_{SL} - \gamma_{SV}) / \gamma_{LV} > 1}$$

i.e. critical angle is

$$\cos \theta_c = (\gamma_{SL} - \gamma_{SV}) / \gamma_{LV} = 1 \Rightarrow \theta_e = 0^\circ$$

Textured Surface



Change in surface free energy is

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

extra surface area excluding tops of features

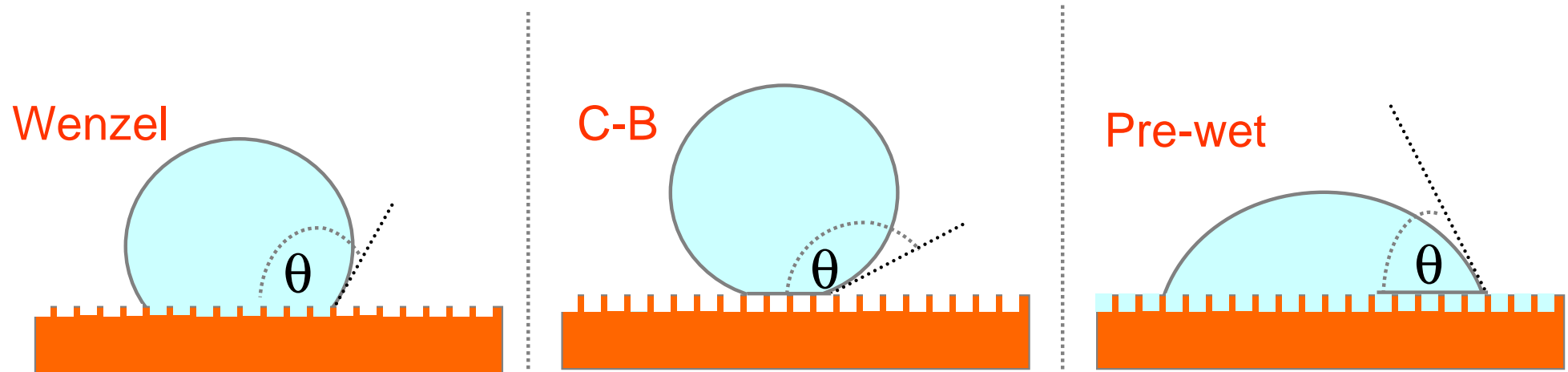
Imbibition is when $\Delta F < 0 \Rightarrow$

$$\boxed{\theta_e < \theta_c \text{ where } \cos \theta_c = (1 - f_s) / (r - f_s)}$$

i.e. critical angle is between 0° and 90°

(usual porous media is equivalent to $r \rightarrow \infty$)

Pre-existing Wetness



Weighted average of fractions f_s and $(1-f_s)$ with θ_e

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

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

*sign has been switched to
+ve from -ve*

A Selection of Topics Not Covered

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