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Engineering and Physical Sciences Research Council

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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

- Fibres, 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

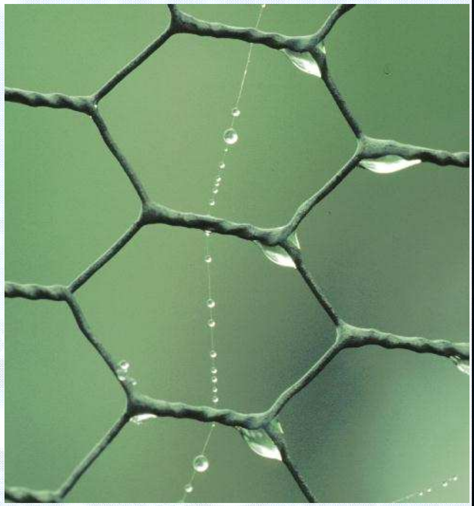
- Liquid Marbles
- Gas Exchange
- Directional Wetting
- Bioadhesion, Ice
- Superwetting, Superspreading, Hemi-wicking, Porosity,
- Interfacial slip
- Surfactants

Basics of Superhydrophobicity

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

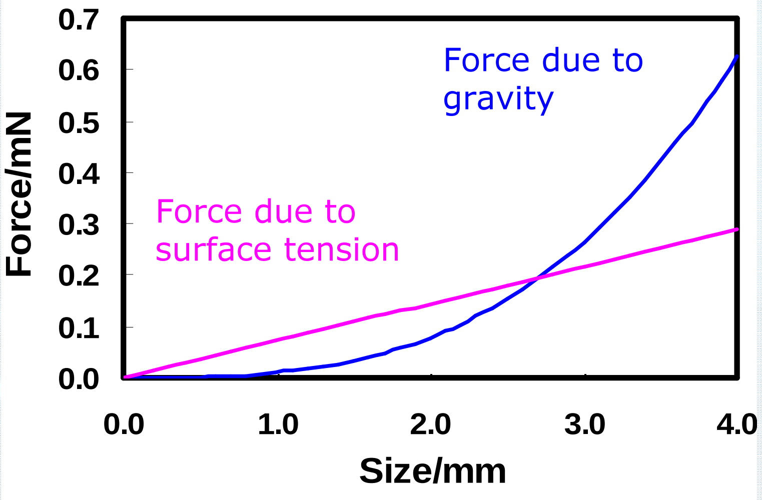
Surface Tension v Gravity

- Surface tension forces scale with length

  e.g. Force~$R\gamma_{LV}$
- Gravity forces scale with length^3

  e.g. Force~$R^3\rho g$
- Small sizes $\Rightarrow$ surface tension wins
- Small means << capillary length= κ^{-1}

  $\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2}$ ~ 2.73mm for water



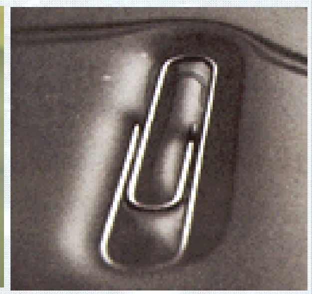
Effects of Surface Tension

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?

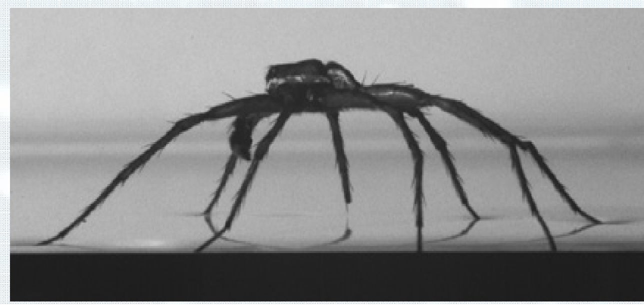
Solids-on-Water

- 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"

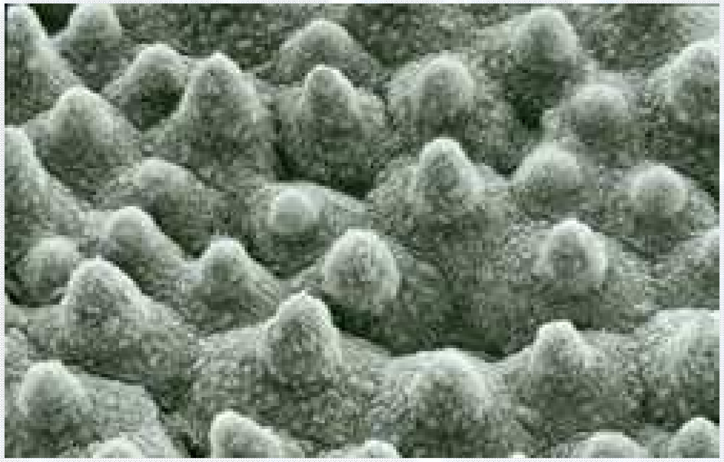


The Sacred Lotus Leaf

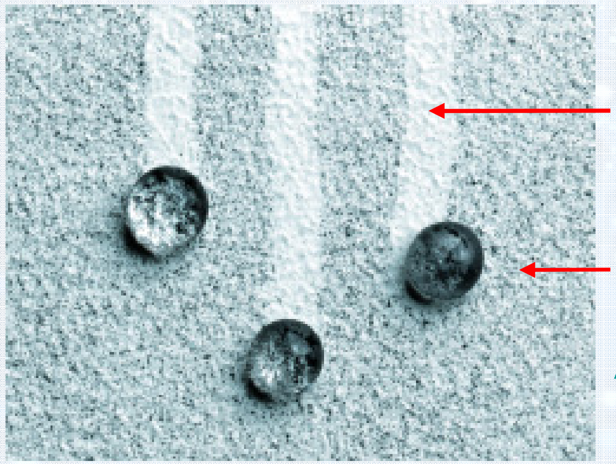
Plants

- 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.

Plants and Leaves

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

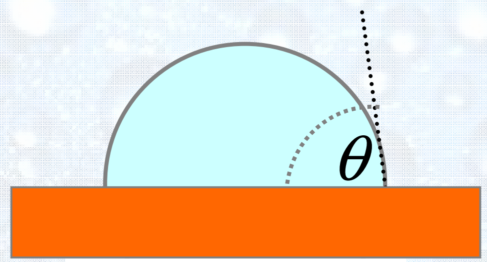
Superhydrophobicity

Water Repellency (Hydrophobicity)

Surface Chemistry

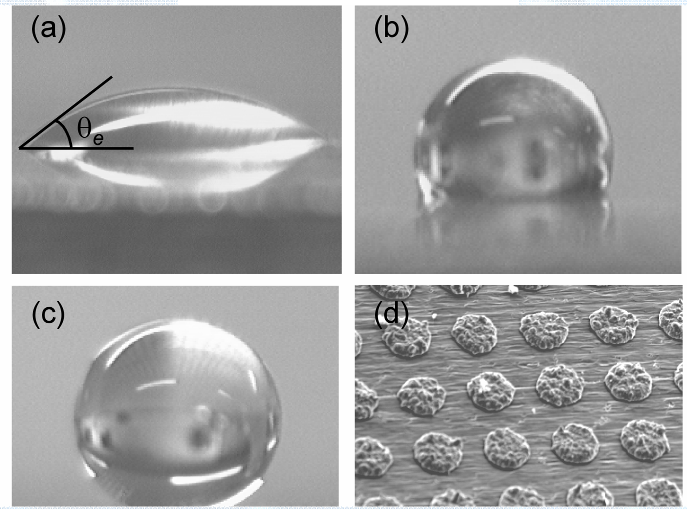
- Terminal group determines whether surface is water hating
- Hydrophobic terminal groups are Fluorine (F) and Methyl (CH_3)

Contact Angles



- Characterize hydrophobicity
- Water-on-Teflon gives ~ 115°
- 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 $\theta > 150°$
(and contact angle hysteresis is low)

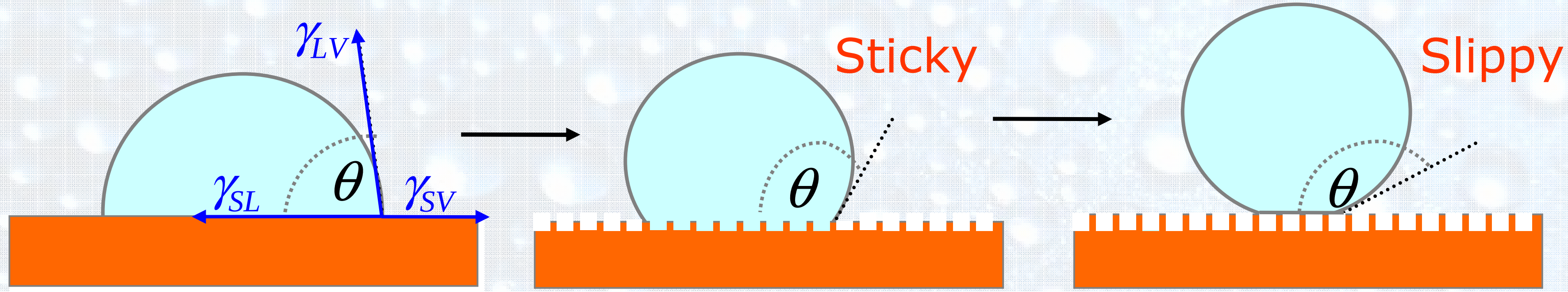
Basics of Superhydrophobicity

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

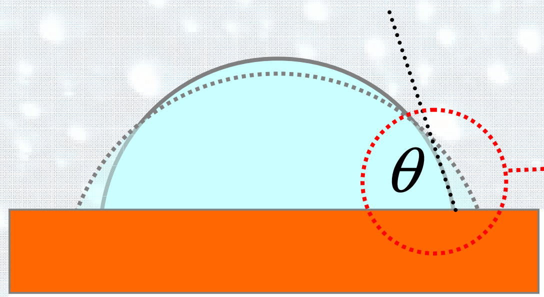
f_s = solid surface fraction

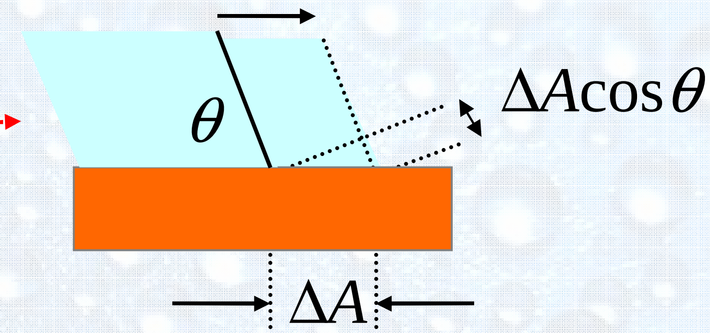
References Cassie, A. B. D.; Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. Wenzel, R. N. Ind. Eng. Chem. 28 (1936) 988-994; J. Phys. Colloid Chem. 53 (1949) 1466-1467.

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

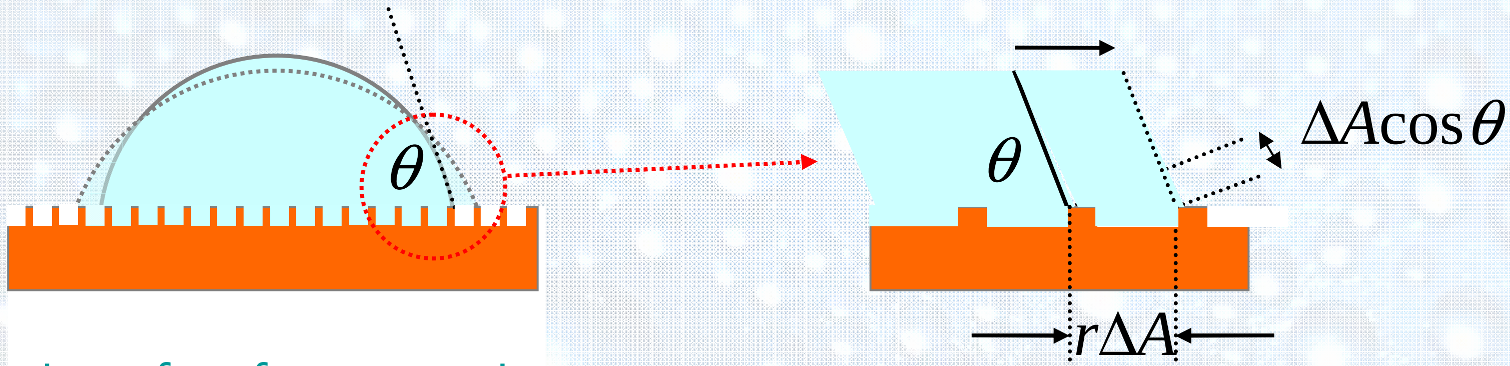
[solid-liquid energy per unit area × gain of substrate area] - [solid-vapor energy per unit area × loss of substrate area] + [liquid-vapor energy per unit area × gain of liquid-vapor area]

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

Equilibrium is when $\Delta F = 0$ $\Rightarrow$ $\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$ Young's Law

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

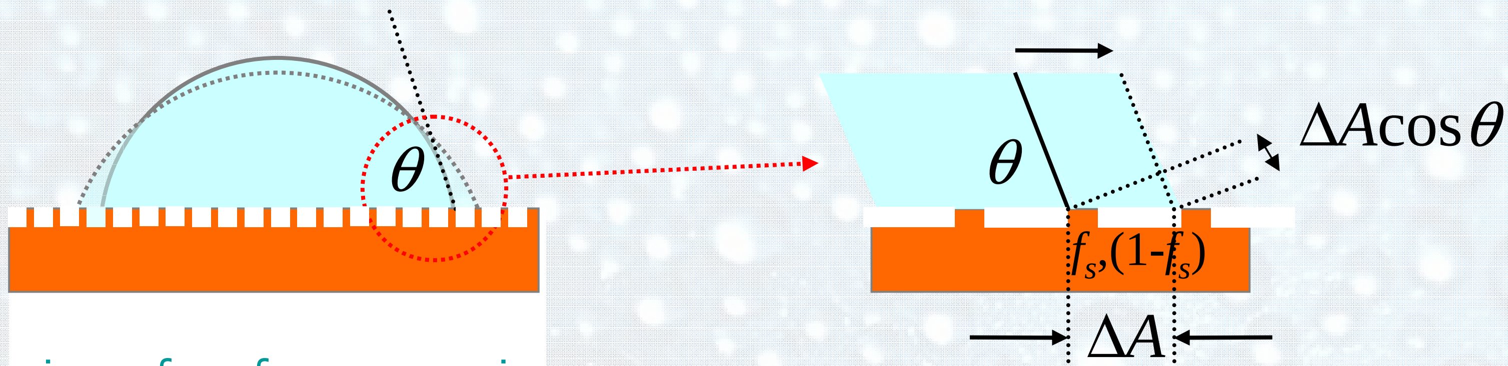
Topography $\Rightarrow$ r = roughness factor

Chemistry $\Rightarrow$ Young's Law θ_e

The derivation is based on contact line changes[2], 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.; Quéré, D. Europhys. Lett. 47 (1999) 220-226. McHale, G., Langmuir 23 (2007) 8200-8205.

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°) = -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

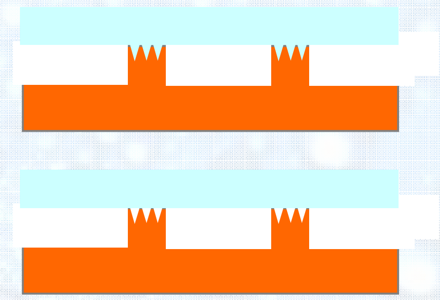
Balloon on a Bed of Nails

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

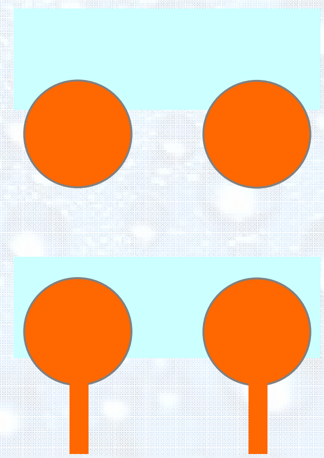
Complex Topography

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 fibers[1], spheres and complex shapes
- Recently described as re-entrant shapes[2]
- 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

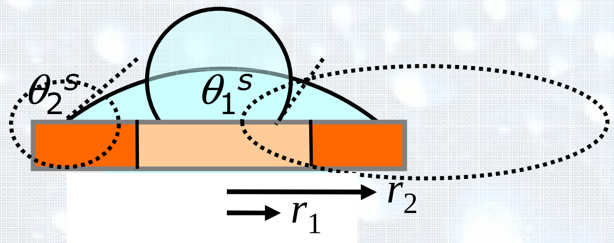
- Roughness, $r(x)$, and solid surface fraction, $f_s(x)$, become dependent on contact line position[4], x
- Can create gradients in superhydrophobicity[5]

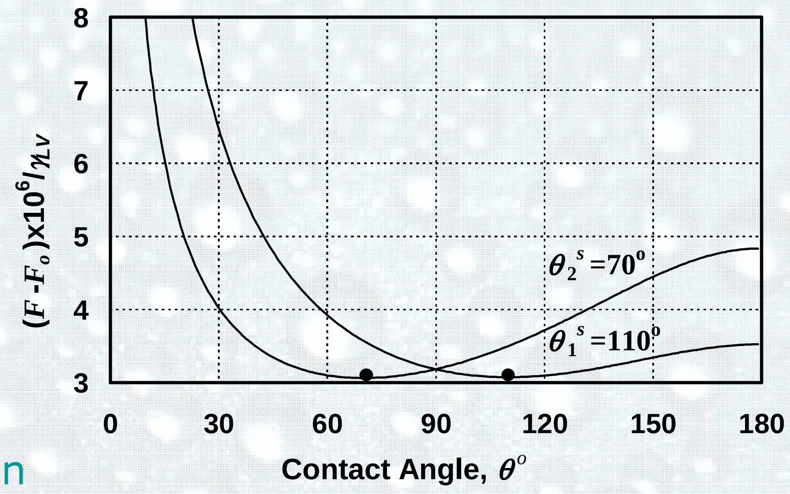
References [1]Cassie, A. B. D.; Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. , [2]Tuteja, A. *et al*., Science 318 (2007) 1618-1622. [3]Shirtcliffe, N.J. *et al.*, Appl. Phys. Lett. 89 (2006) art. 094101. [4]McHale, G., Langmuir 23 (2007) 8200-8205. [5] McHale, G. *et al.*, Analyst 129 (2004) 284-287.

1D Pictures to 2D Cassie-Baxter Surfaces

Isolated Defect Surface

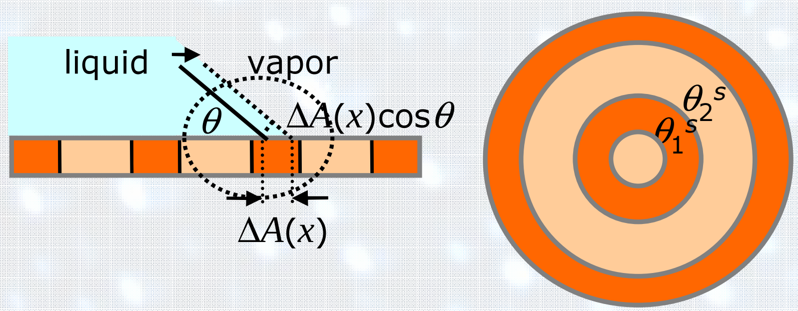
Surface has θ_1^s=110°, θ_2^s =70°



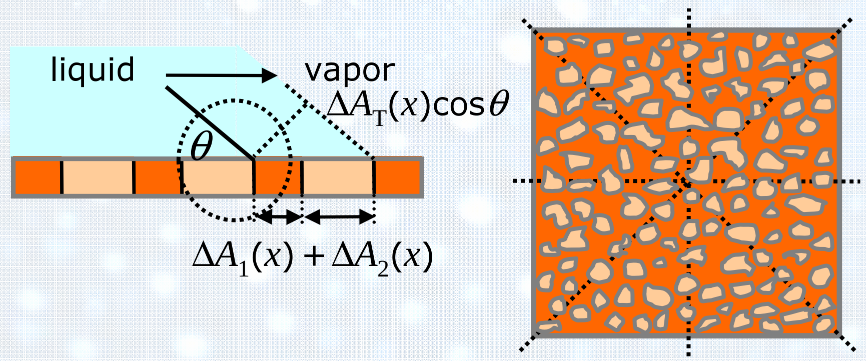


Two droplet configurations exist with min in their local surface free energy corresponding to the same droplet volume

Radial Symmetry



Random Surface

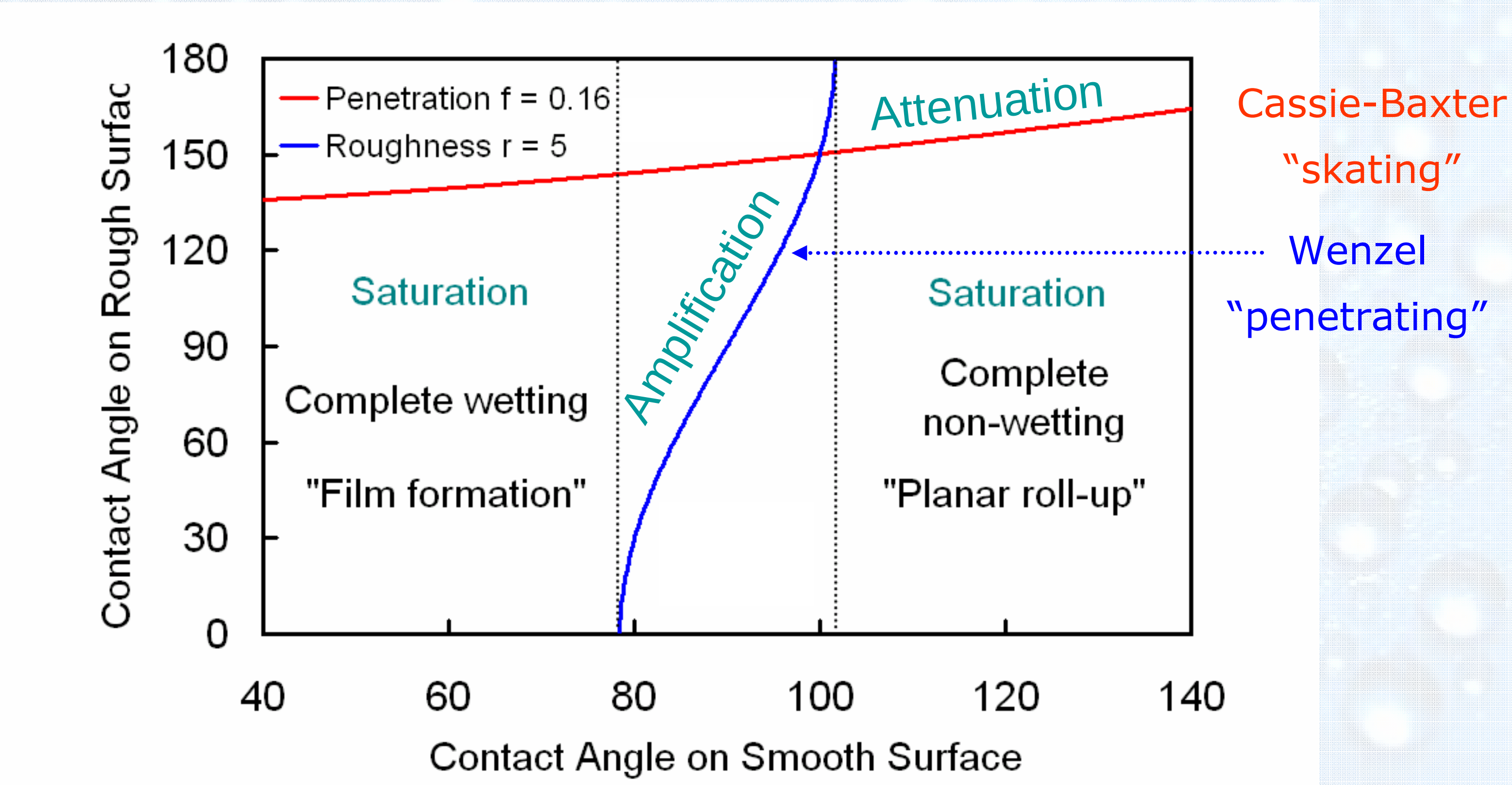


References Gao, L.C.; McCarthy, T.J. Langmuir 23 (2007) 3762-3765.
McHale, G. Langmuir 23 (2007) 8200-8205.

Basics of Superhydrophobicity

Consequences

Theory: Amplification, Attenuation, Saturation



Roughness/Topography

θ_e^s > threshold ⇒ enhances repellence

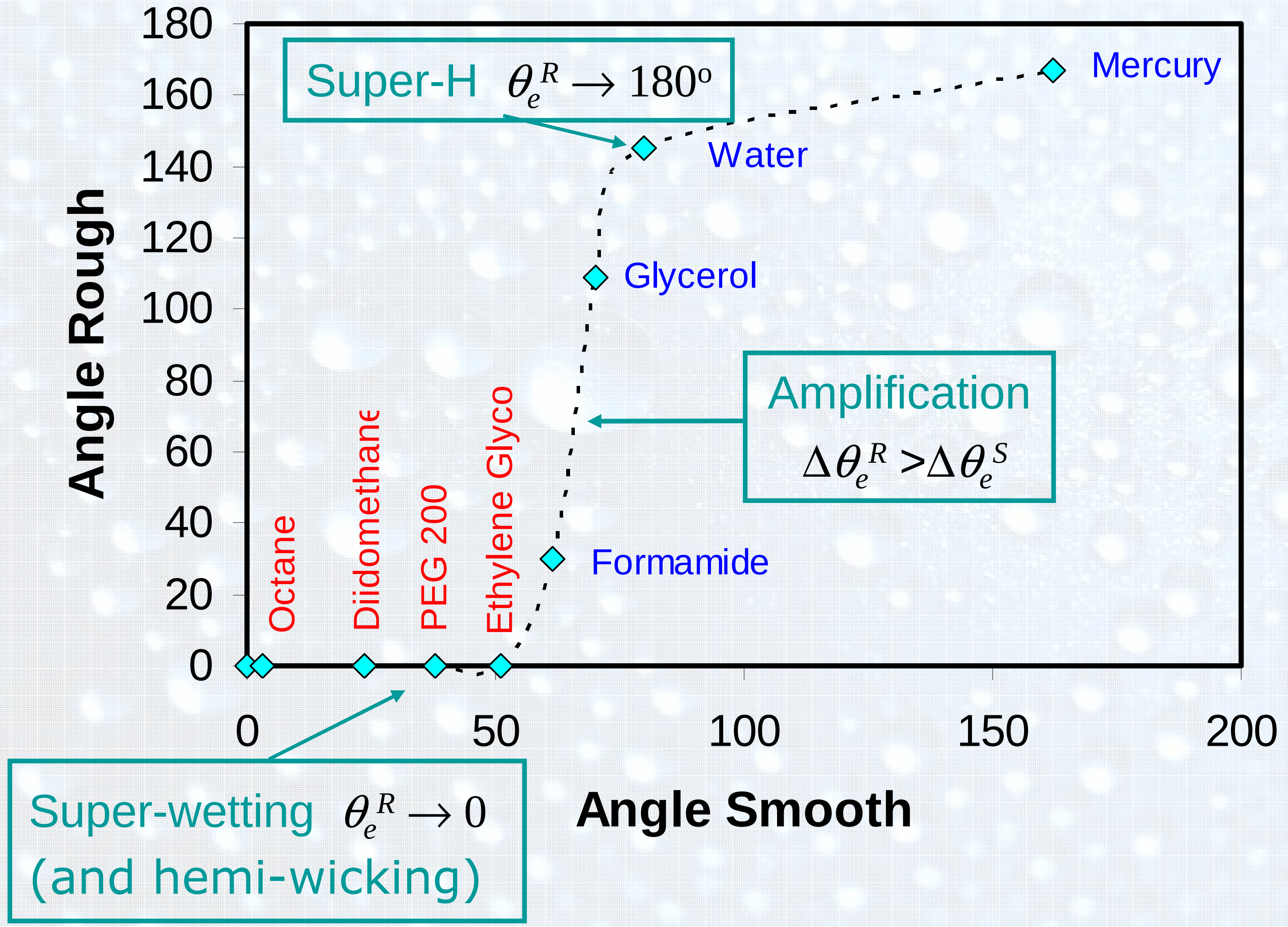
θ_e^s < threshold ⇒ enhances film formation

Superhydrophobic

"Skating case" ⇒ most existing examples

Pressure ⇒ transition to penetrating

Liquids on a Superhydrophobic Surface



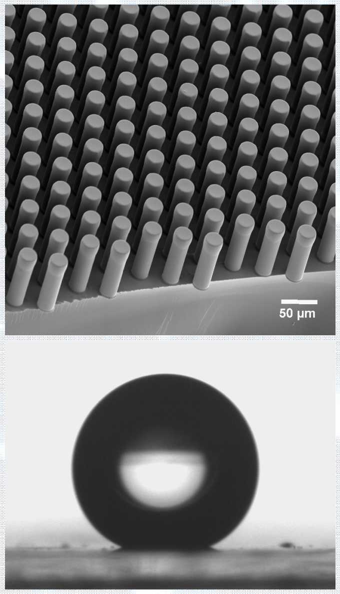
References McHale, G. *et al.*, Analyst 129 (2004) 284-287; Langmuir 20 (2004) 10146-10149.

Skating-to-Penetrating Transition

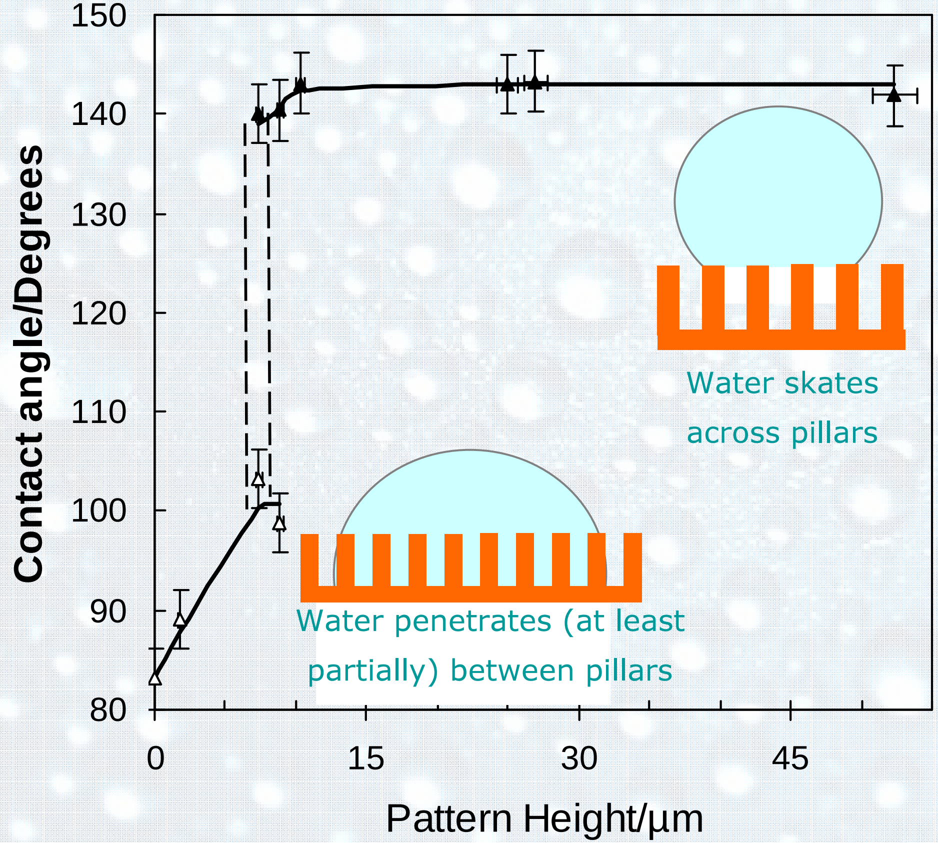
Micro-Structured Surface

SU-8 pillars[1] 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*).

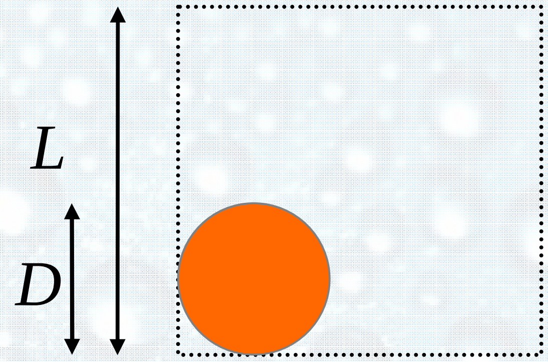
References Shirtcliffe, N.J. *et al.*, J. Micromech. Microeng. 14 (2004) 1384-1389. Bico, J. *et al.*, Coll. Surf. A206 (2002) 41-46. Quéré, D. Physica A313 (2002) 32-46; Ishino, C.; Okumura, K.; Quéré, D. Europhys. Lett. 68 (2004) 419-425.

Texture Example

Circular Pillars

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

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



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

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

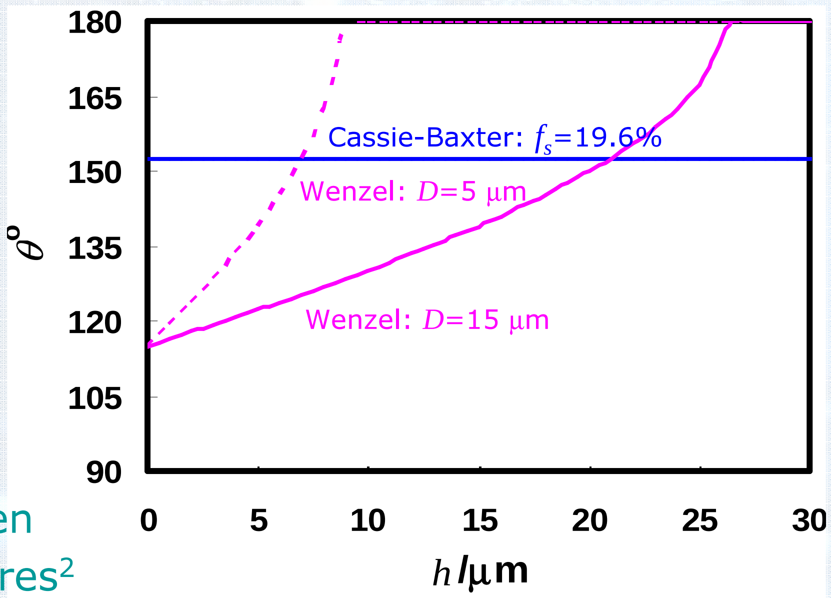
For penetrating transition:

$D=15$ μm and $h<21$ μm

$D=5$ μm and $h<7$ μm

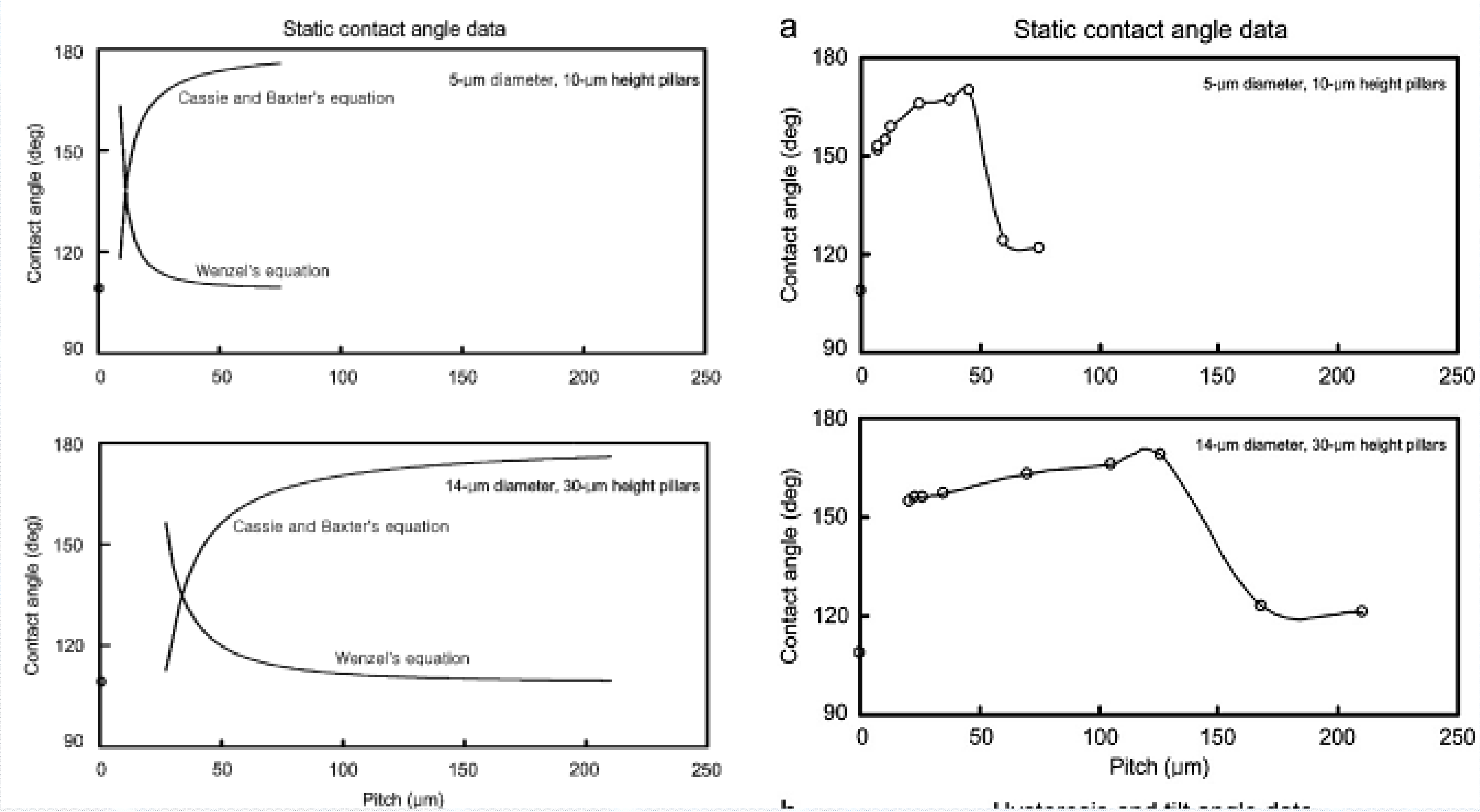
Ignores sharp features causing metastability[1]

Condensing liquid may fill features when droplets may only deposit across features[2]



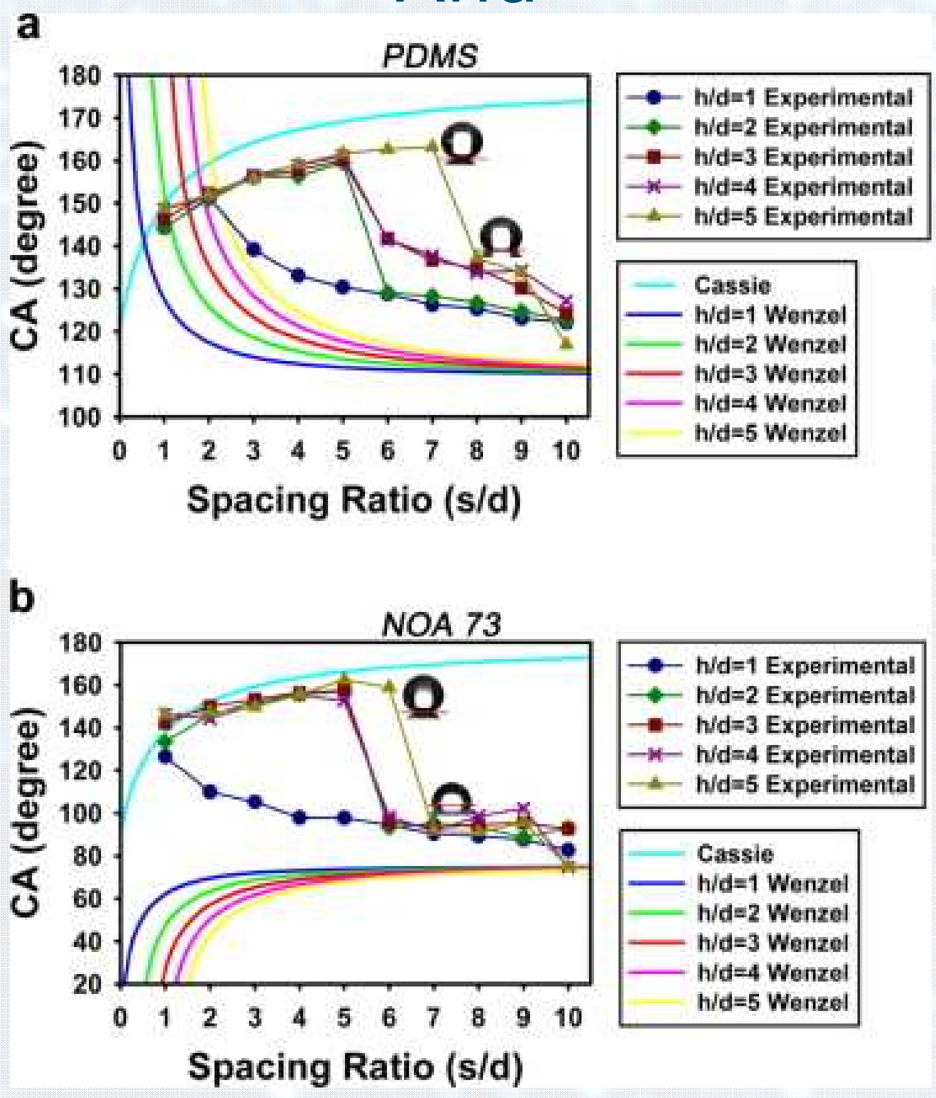
References [1]Bico, J. *et al.*, Coll. Surf. A 206 (2002) 41-46. De Gennes, P.G.; Brochard-Wyard, F.; Quéré, D. "Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves" Springer-Verlag (2003). [2] Wier, K.A.; McCarthy, T.J. Langmuir 22 (2006) 2433-2436.

But



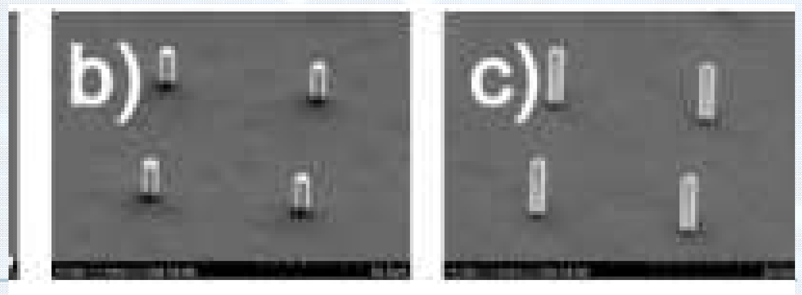
B. Bhushan, Y. Chae Jung / Ultramicroscopy 107 (2007) 1033–1041

And



Curves follow below C-B and then drop to above Wenzel, discrepancy greater for the more hydrophobic surface

Both this and previous slide suggest far lower height to spacing than suggested in our work. This is because the meniscus bows down and has capillary waves, so the size of features is important.



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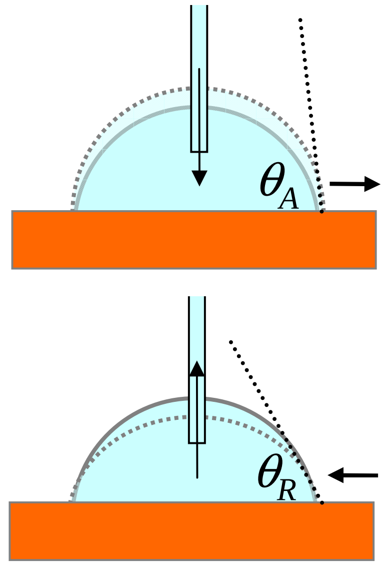
Contact Angle Hysteresis

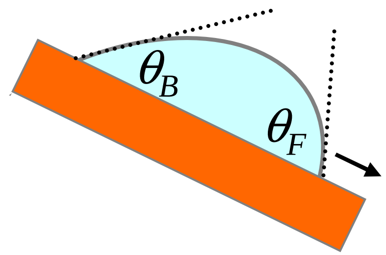
Advancing and Receding Contact Angles

- 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 superhydrophobicity[1]



Reference [1]Miwa, 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" state[1]

- Larger than on flat for the penetrating (Wenzel) state

  "Sticky" state[1]

Models?

- Different views exist ..... possible factors to be considered include:

  Shape of tops of features, contact line length[2], contact area[3] (at perimeter)

Gain and Attenuation View

Use CB or W model for θ_A and θ_R

Can work out analytical formulae[3]

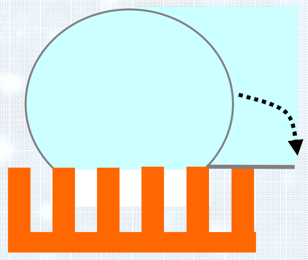
Assumes contact area changes are dominant effect and amplify an intrinsic hysteresis of the surface

2-D Theory World View

CB: To advance must touch next shape and to recede can retract across features[4]

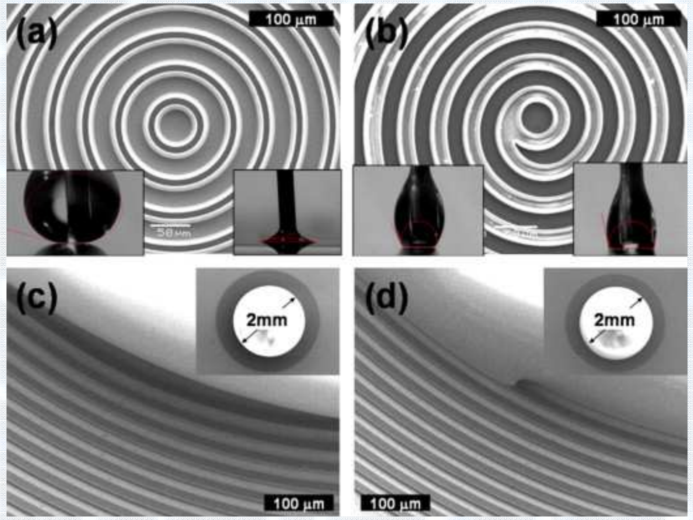
$\theta_A = 180^o$ (and $\theta_R = \theta_e{}^o$)

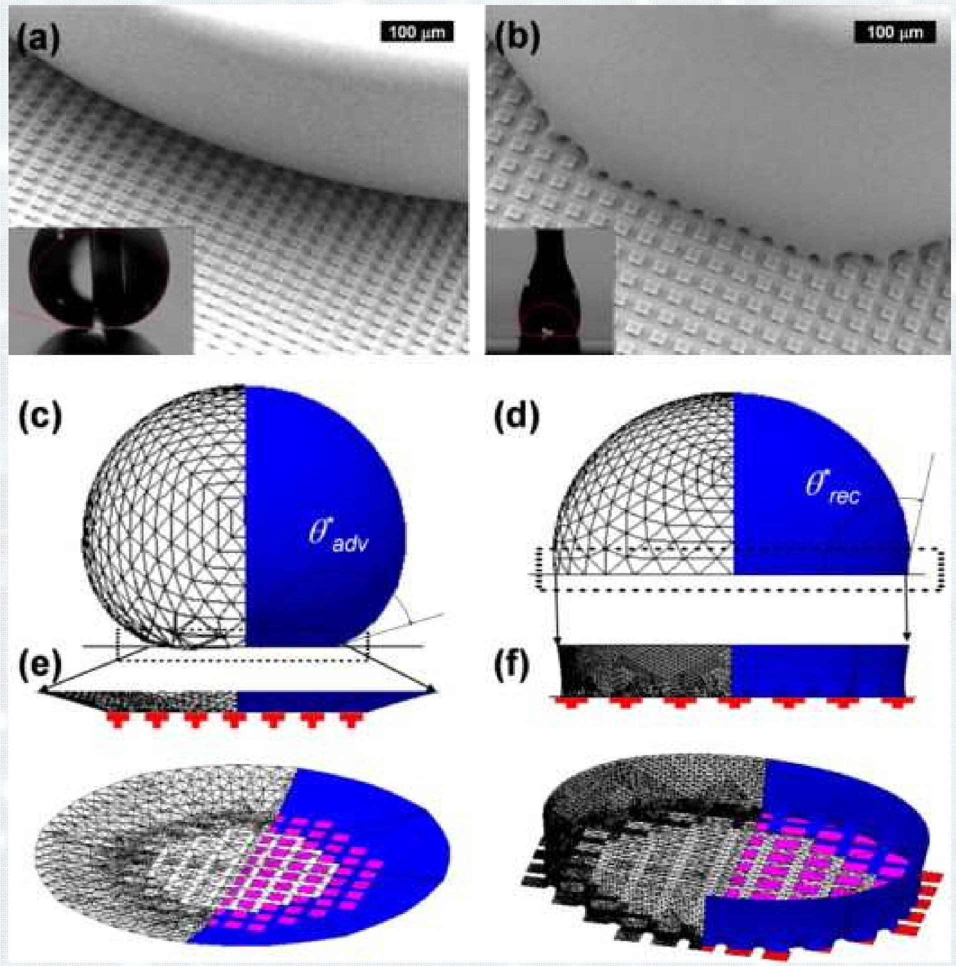
3-D world is more complex



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

More Recently





The advancing/receding angles on a concentric surface are far more different than on a spiral surface where zipping "must" occur and the defect energy of one step must be paid anyway

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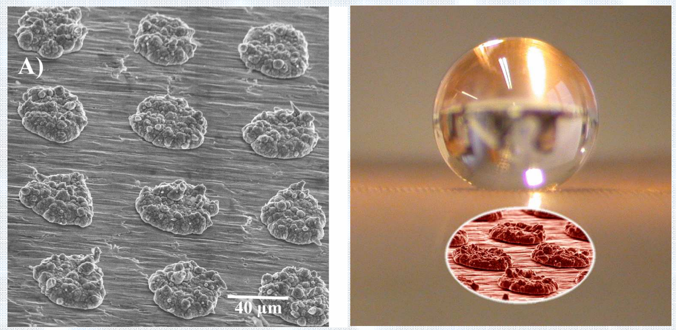
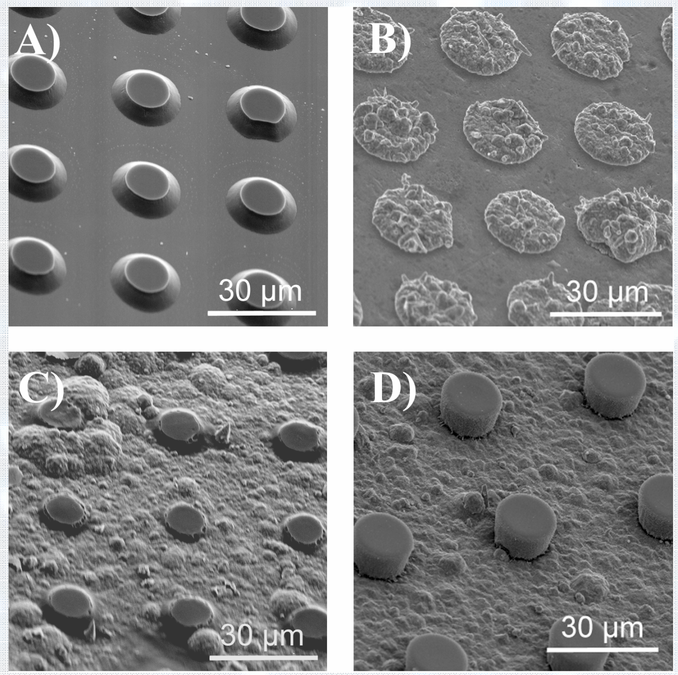
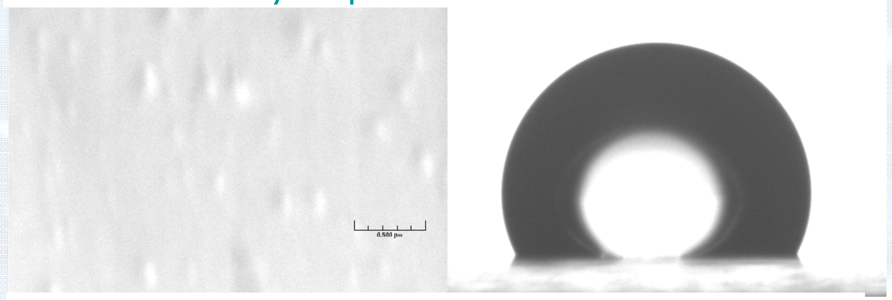
Double Length Scale Systems



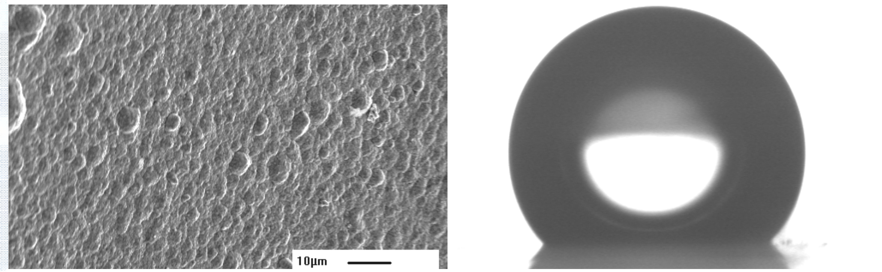


Two length scales is extremely effective

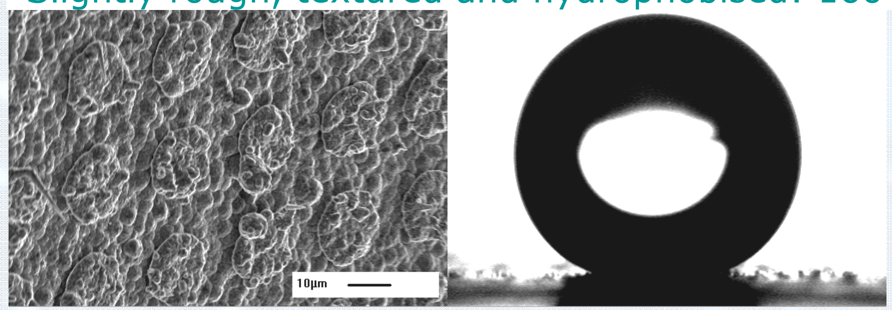
Smooth and hydrophobised: 115°



Slightly rough and hydrophobised: 136°

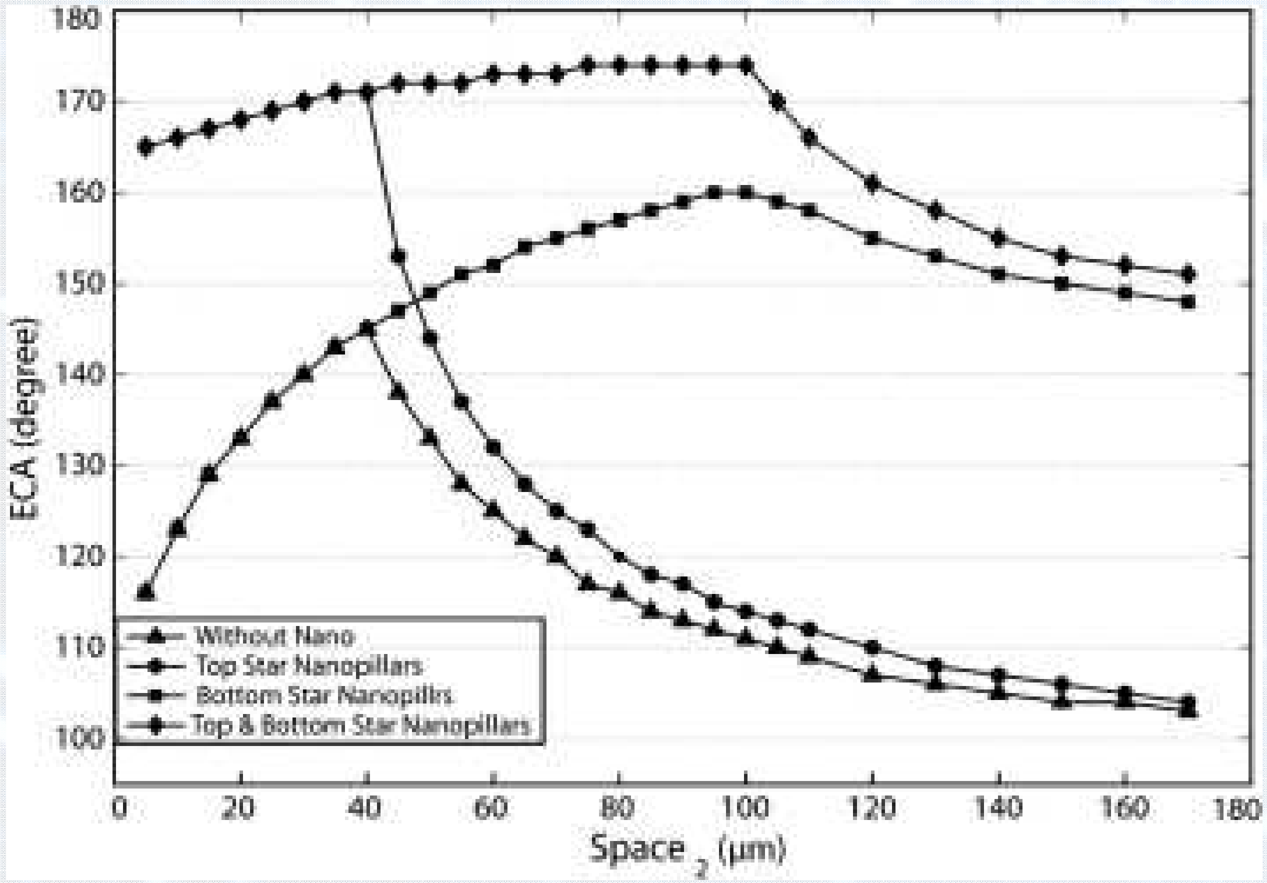


Slightly rough, textured and hydrophobised: 160°



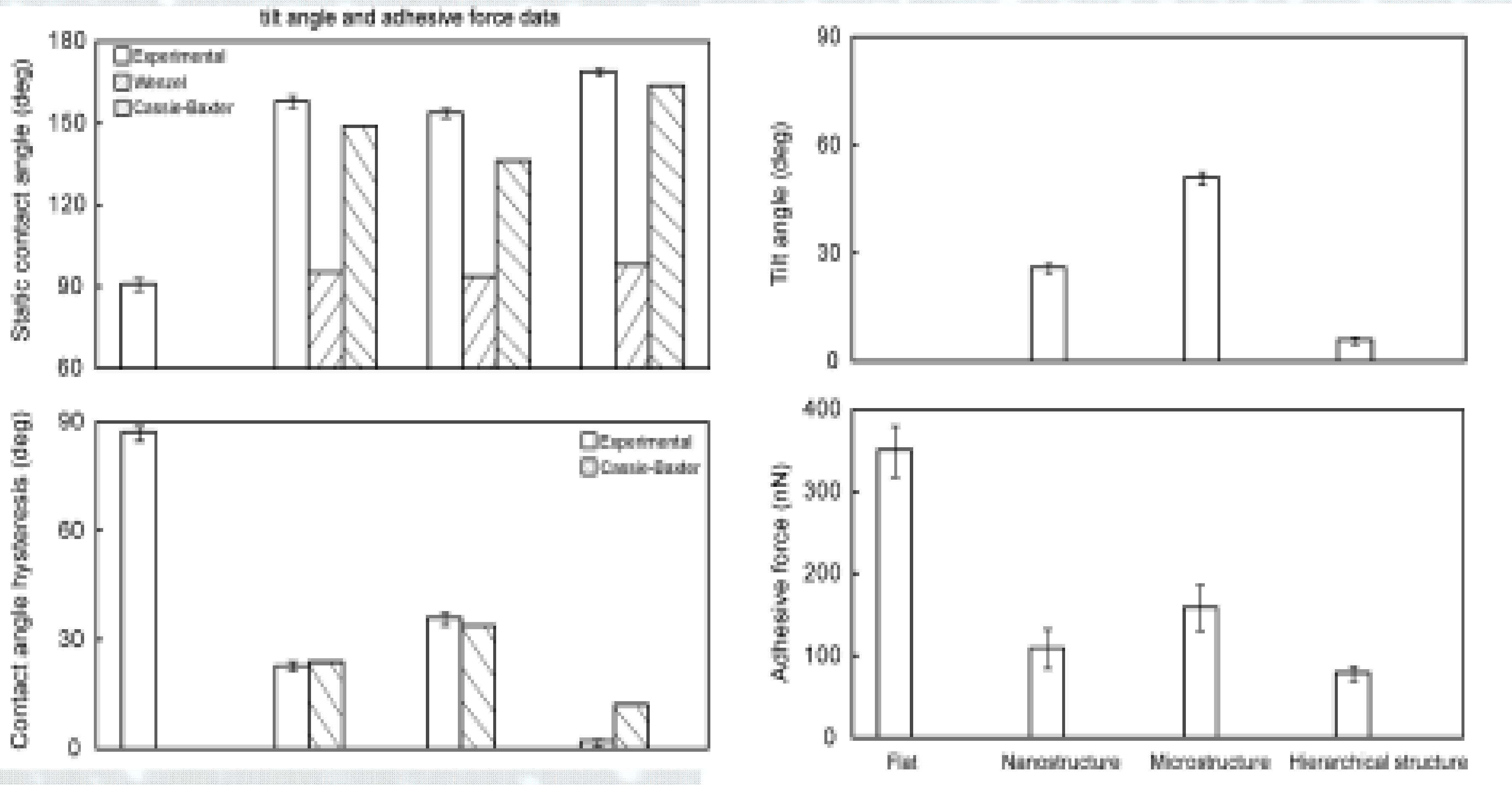
References Shirtcliffe, N.J. *et al.*, Adv. Maters. 16 (2004) 1929-1932 (see also: Patankar, N.A. Langmuir 20 (2004) 8209-8213.

More Recently



Journal of Colloid and Interface Science
Volume 344, Issue 2, 15 April 2010, Pages 575-583

Multiple scale helps sliding/hysteresis B. Bhushan et al. / Ultramicroscopy 109 (2009) 1029–1034



Path Definition & Self-Actuated Motion

Gradients in Contact Angle

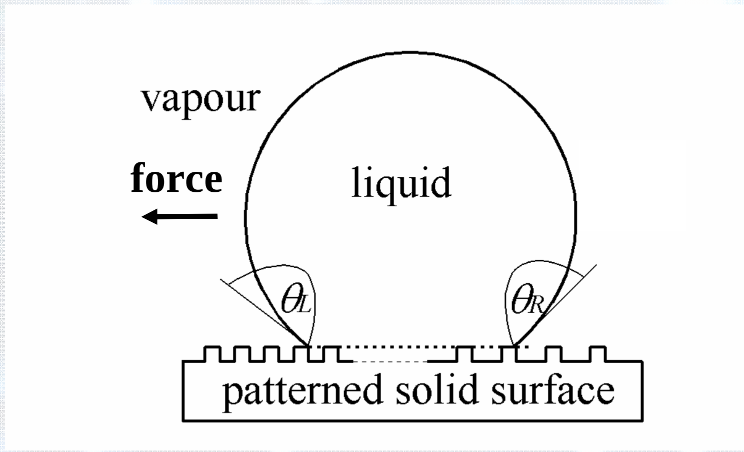
Make contact angle depend on position and surface chemistry $\theta(\underline{x}, \theta_e^s)$

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

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

Idea

Droplet experiences different contact angles



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

~ $\gamma_{LV}(f_R - f_L)(\cos\theta_e + 1)$

Experiment

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

Electrodeposited copper – fractal to overcome hysteresis

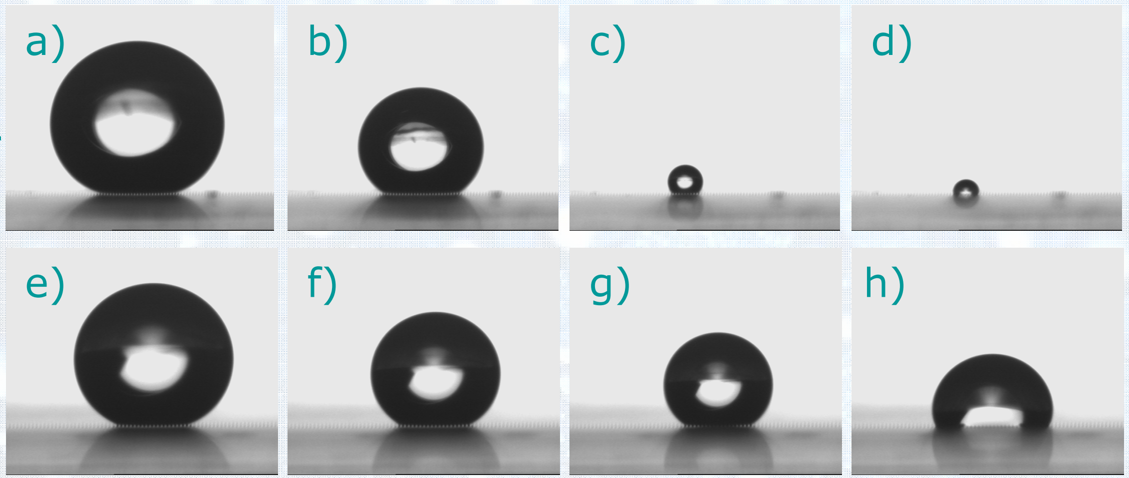
References McHale, G. *et al.*, Analyst 129 (2004) 284-287; Langmuir 20 (2004) 10146-10149. McHale *et al*, to be submitted; Quéré *unpublished*.

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

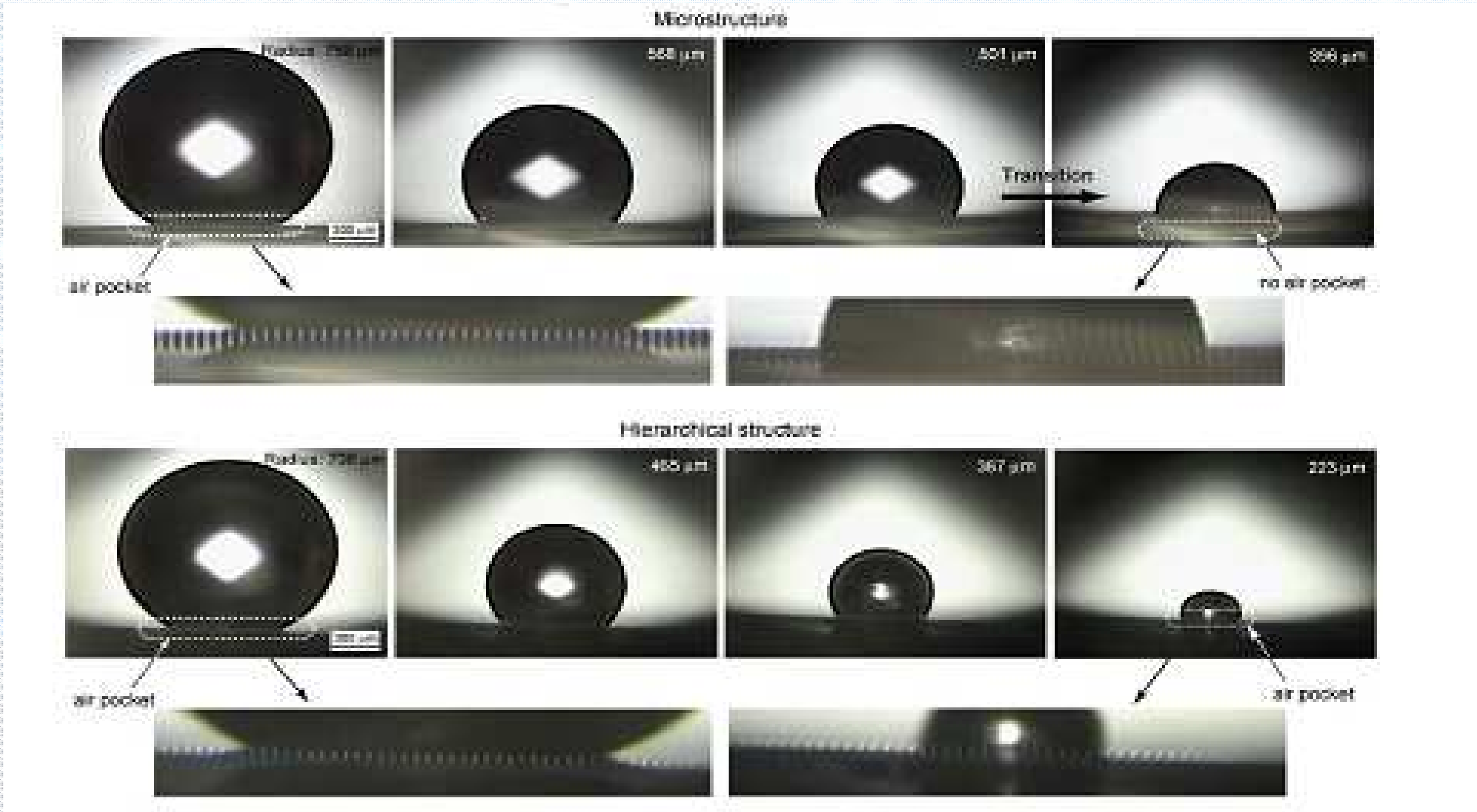
Yeomans[2] suggests three processes during evaporation:

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.

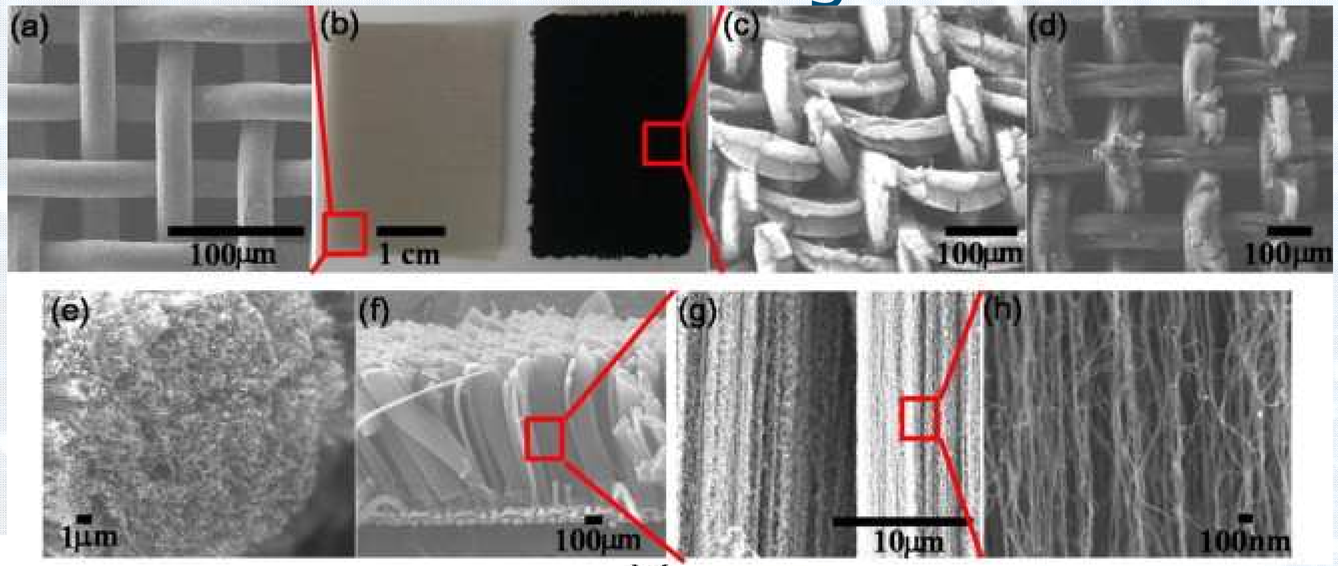
References [1]McHale, G. *et al.*, Langmuir 21 (2005) 11053–11060. [2] Kusumaatmaja, H. *et al.*, Euro. Phys. Lett. 81 (2008) art. 36003. Reyssat, M.; Yeomans, J.M.; Quéré, D. Euro. Phys. Lett. 81 (2008) art. 26006. Moulinet, S.; Bartolo, D. Euro. Phys. J. E24 (2007) 251-260. Bartolo D., *et al.*, Europhys.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

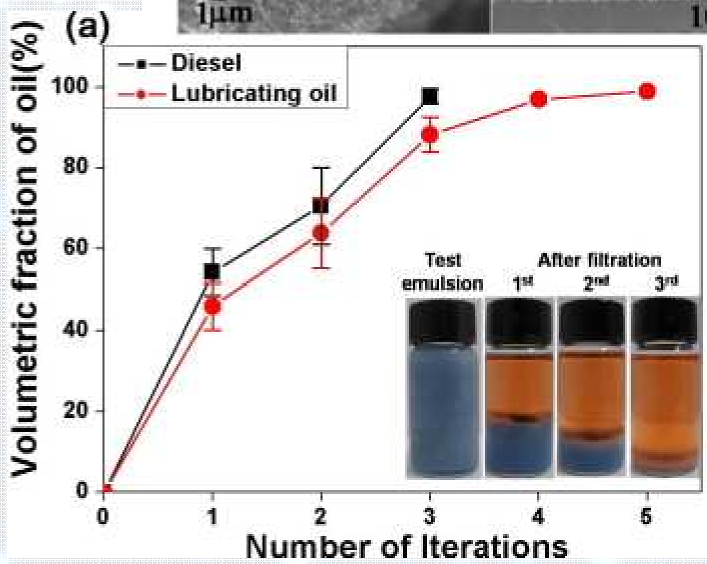
Other Results

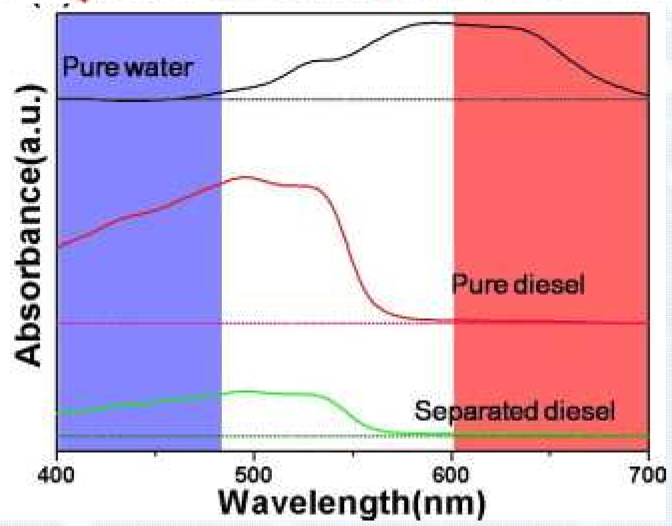


With and without added nanostructure B. Bhushan et al. / Ultramicroscopy 109 (2009) 1029–1034

Phase Breaking of Emulsions





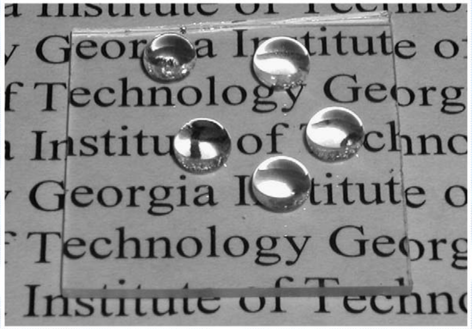


Carbon

Volume 48, Issue 8, July 2010, Pages 2192-2197

Materials Methods for Surface Fabrication

Basic Approach



- Create ordered or disordered surface structures
- Keep solid surface fraction low
- Keep size scale for gaps << 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 << μm
- 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

figure Y. Xiu et al. / Thin Solid Films 517 (2009) 1610–1615

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

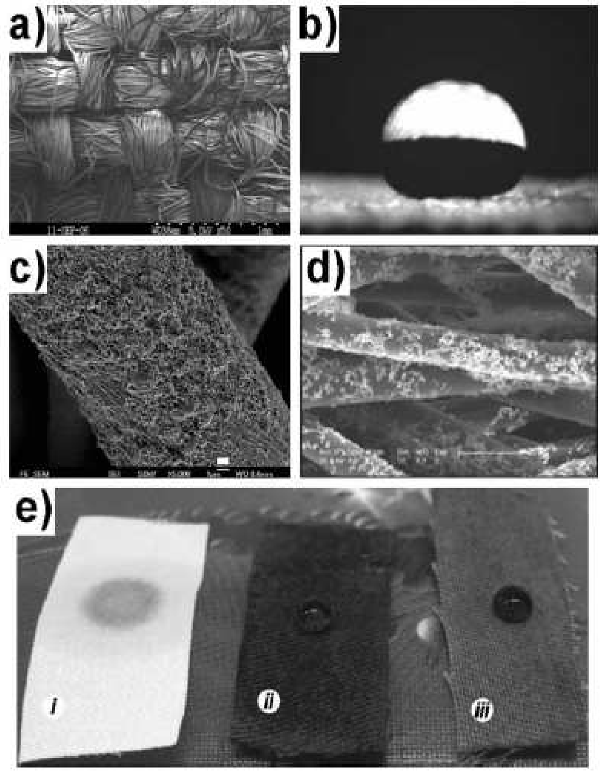


Fig. 3 Woven superhydrophobic surfaces (a) multifilament woven fabric,[15] (b) droplet resting on surface shown in (a), (c) CNT-treated cotton fibre,[16] (d) cloth surface impregnated with gold particles,[17] and (e) water droplets on[16] i) untreated woven cotton sheet, ii) CNT-treated woven cotton 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.

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

Fibers, Textiles and Fabrics

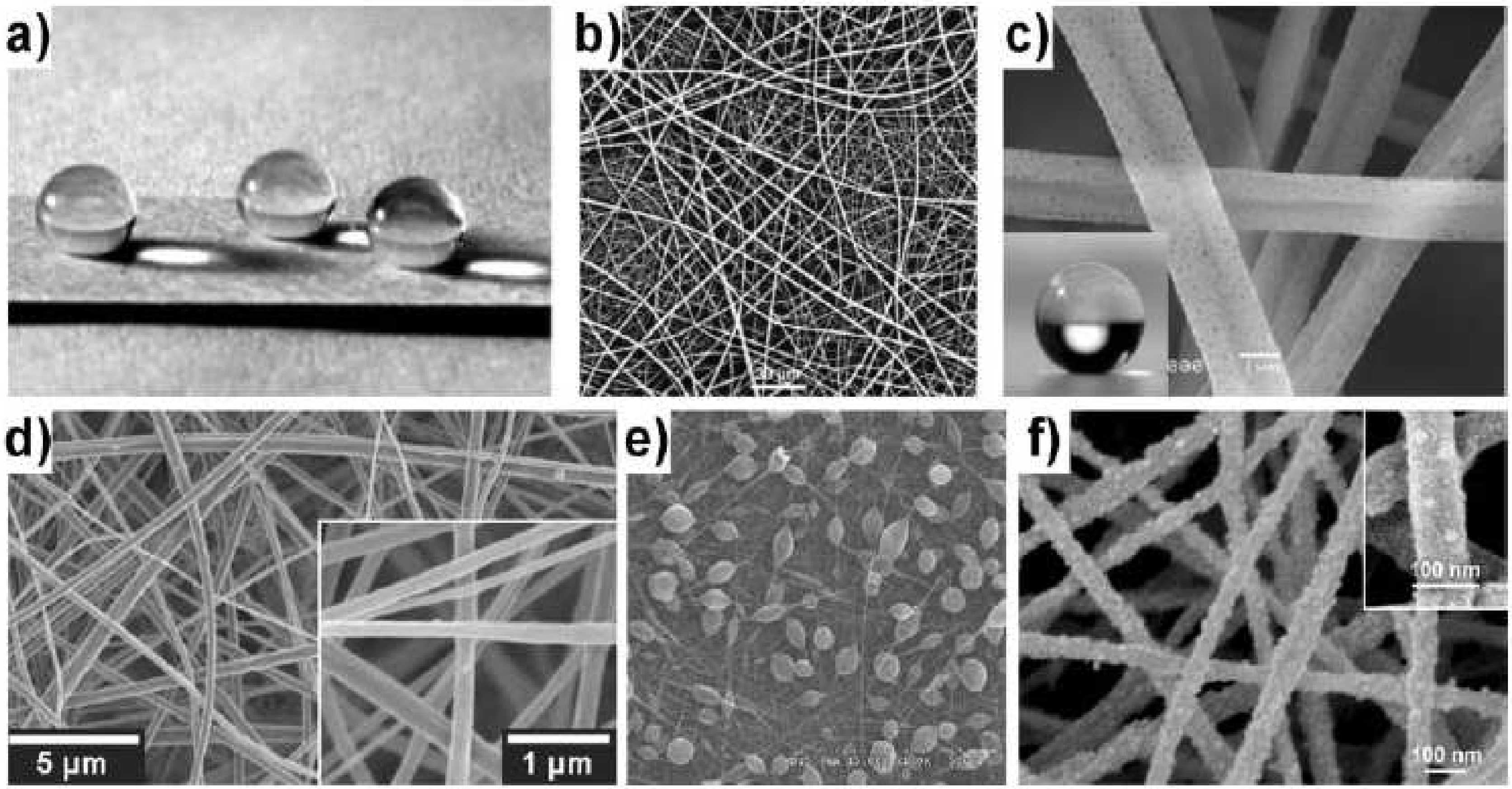


Fig. 4 Superhydrophobic fibre surfaces (a) water droplets on a block copolymer electrospun fibre mat,[23] (b) electrospun fluoropolymer mat,[24] (c) porous electrospun fluorinated fibres,[25] (d) cellulose acetate fibrous membrane,[26] (e) micro-bead connected fibres by elecrospinning.[27] Images reprinted 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

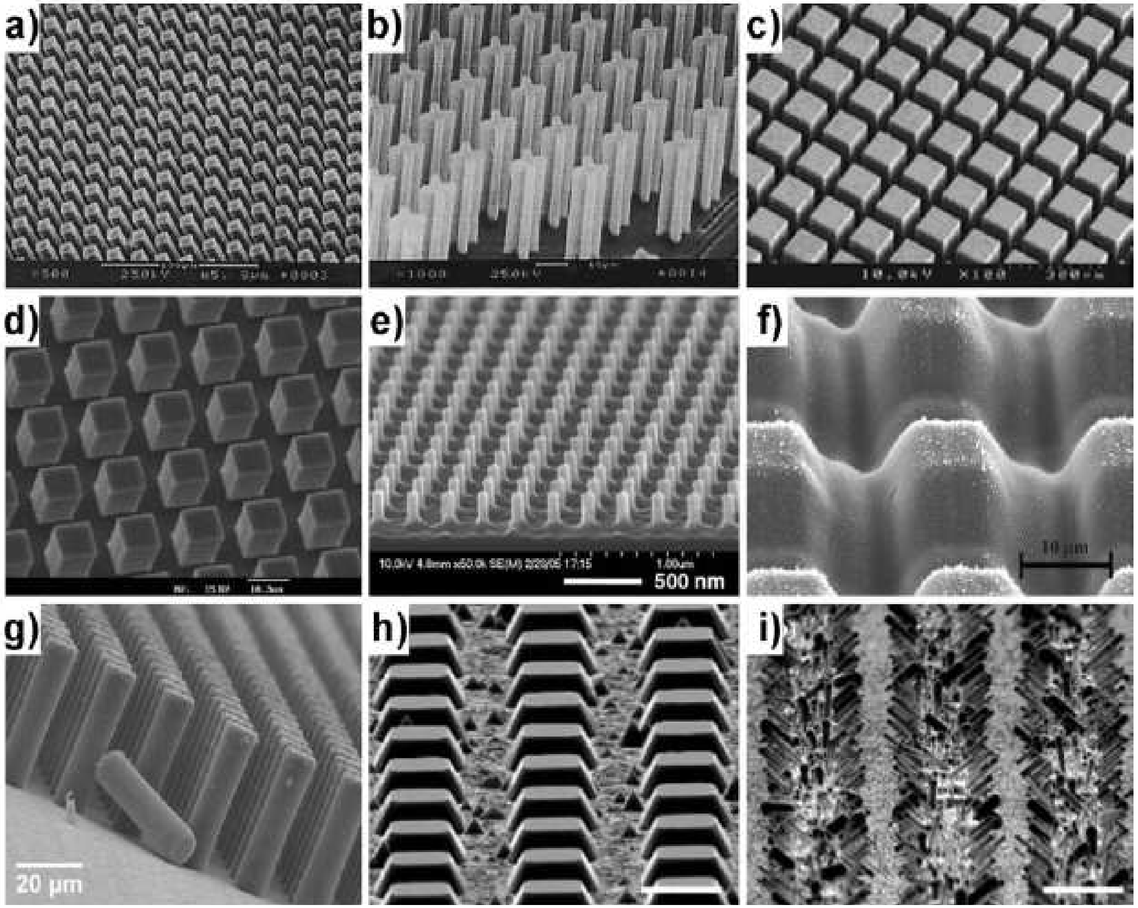


Fig. 9 Lithographic surface modification (a) photolithographic towers and (b) indented square posts,[114] (c) diced silicon wafer,[115] (d) photolithographic towers,[116] (e) silicon nano-towers,[117] (f) laser-modified SU8 surface,[118] (g) SU8 towers,[86] (h) silicon islands and (i) silicon nano-wires 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-100µm
- 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

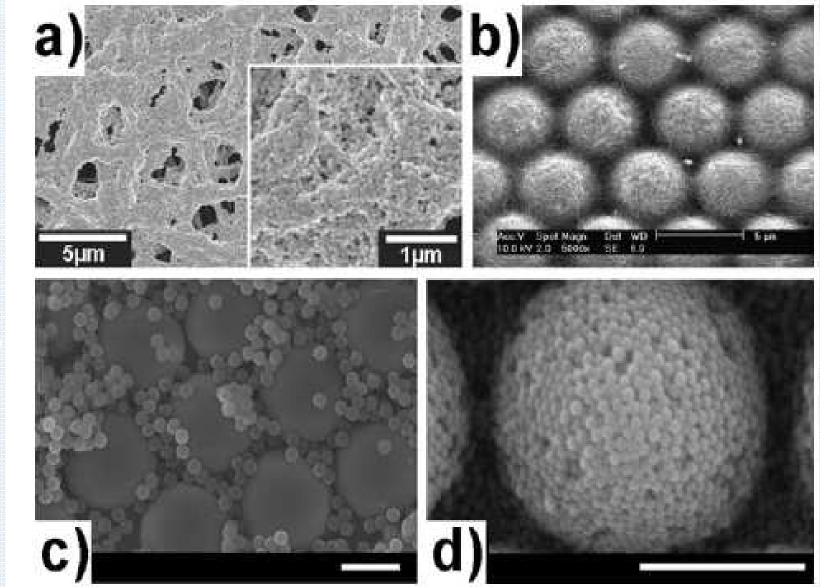


Fig. 10 Particle aggregation (a) layer-by-layer deposition of TiO_2 particles on fibres,[26] (b) CNT-coated polystyrene-sphere array,[128] (c) silica-sphere array with additional smaller sphere aggregates (scale bar = 5 µm) and (d) micron-sphere array produced from 300 nm particles silica nano-spheres (scale bar = 5 µm).[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

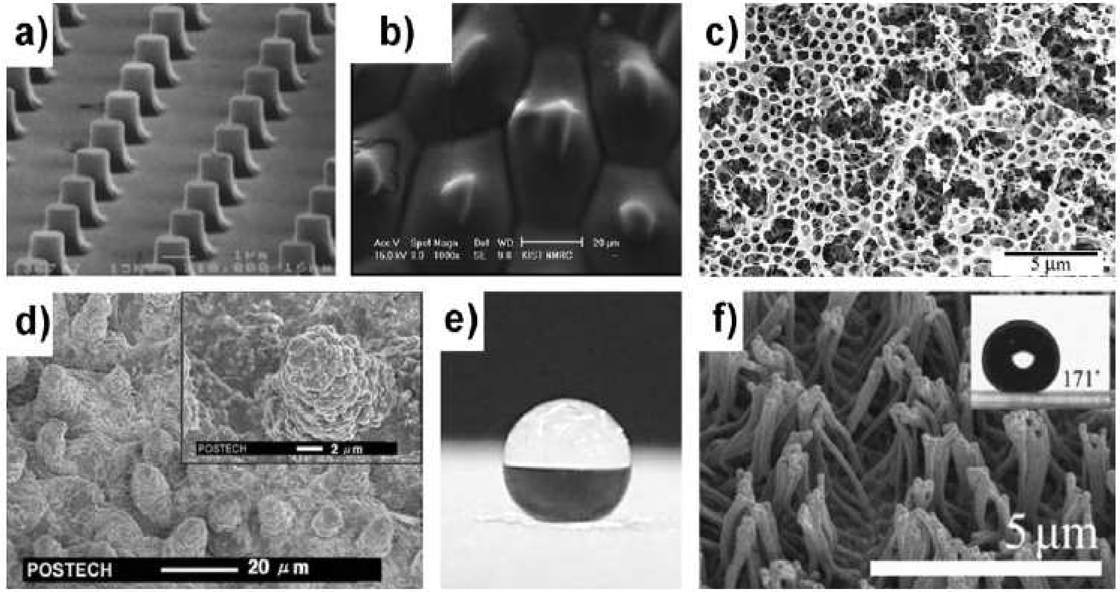


Fig. 11 Replica surfaces produced by templating (a) micro-posts,[143] (b) PMMA replica of *Colocasia*-like leaf surface,[144] (c) a polyvinylidene fluoride inverse opaline structure,[145] (d) photoresist replica of lotus leaf by UV-NIL,[127] (e) water droplet resting on a polymer hot-press transferred 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

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

Phase Separation

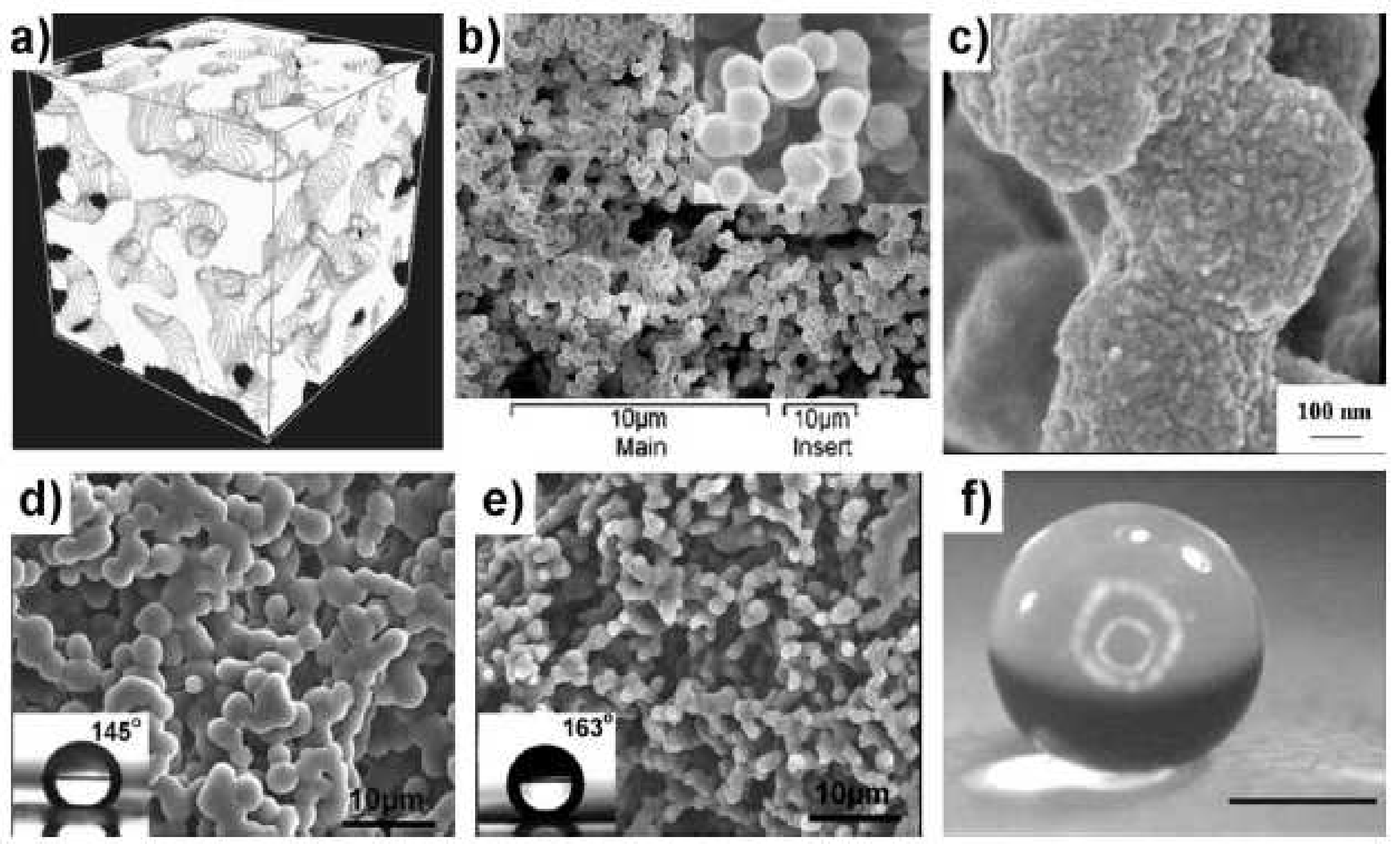


Fig. 5 Examples of phase separation, (a) model of a bicontinuous structure,[39] (b) sol–gel foam produced using acetone as co-solvent,[40] (c) super-hydrophobic PVC film,[41] (d) and (e) phase-separated block copolymer films,[42] (f) water droplet on an organic xerogel (scale bar = 1 mm)[43] Images reprinted 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 allows 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

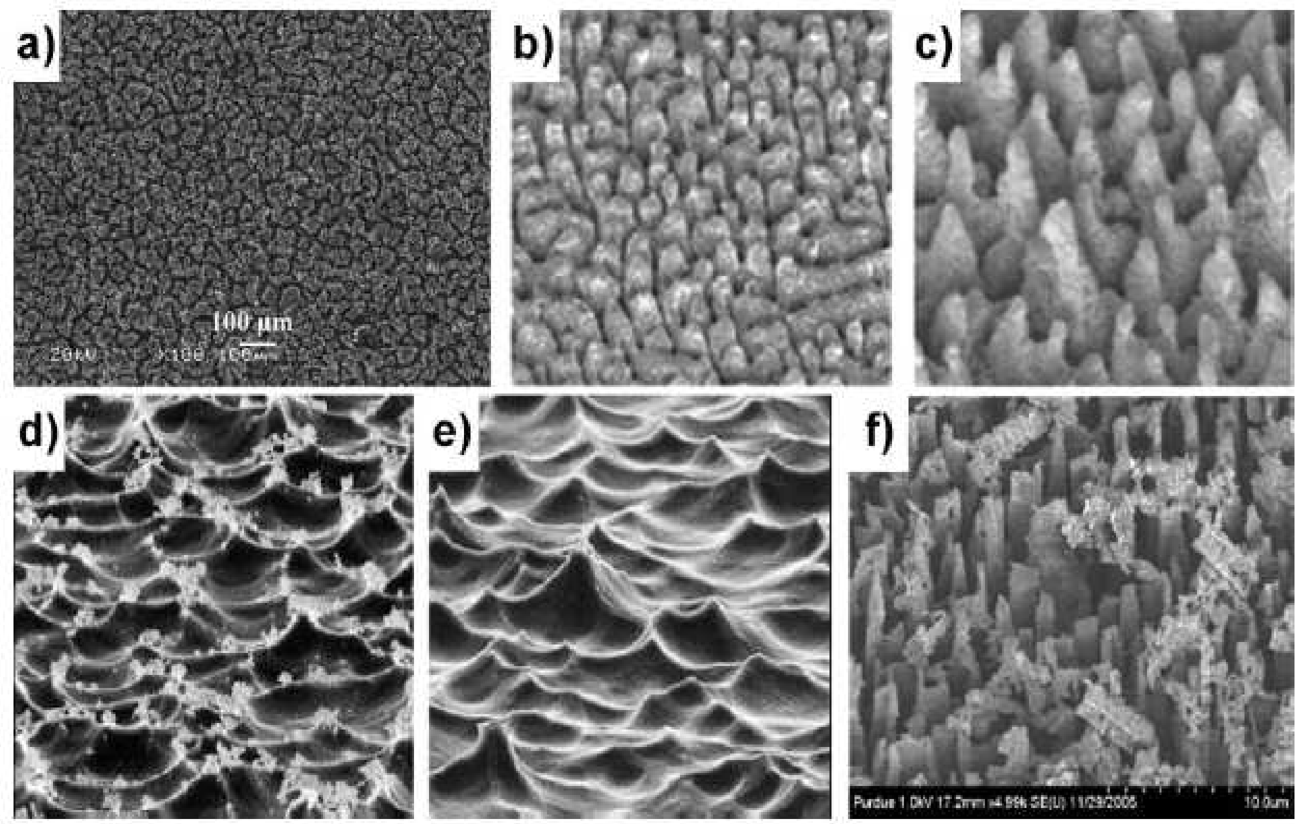


Fig. 7 Etching (a) roughened aluminium alloy,[79] (b) laser-etched silicon surface in SF_6 3.2 kJ m^{-2} and (c) using 5 kJ m^{-2},[80] (d) silicon wafer/photoresist layer over-etched by an inductively-coupled SF_6 plasma before cleaning,[81] and (e) after ultrasonication to remove residual photoresist, 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 separted 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 SnO_2 nano-rod surfaces and photocatalytic metal oxides (e.g. TiO_2) – 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. SnO_2, 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

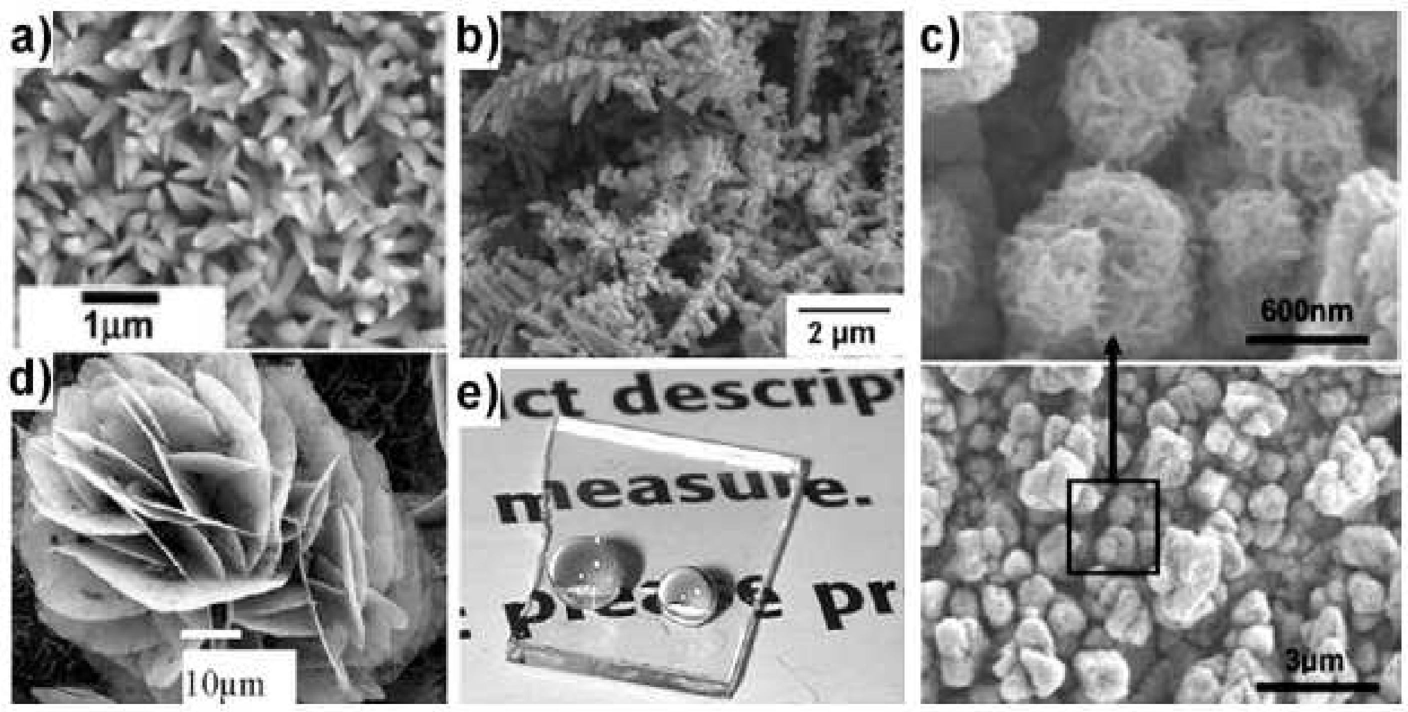


Fig. 6 Rough surfaces by crystal growth (a) cobalt hydroxide crystalline nano-pins (brucite-type) with diameter of 6.5 nm,[53] (b) silver aggregates deposited on a silicon wafer,[54] (c) CuS-coated copper oxide; enlargement shows nanostructure,[55] (d) flower-like tin oxide structure,[56] and (e) transparent 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

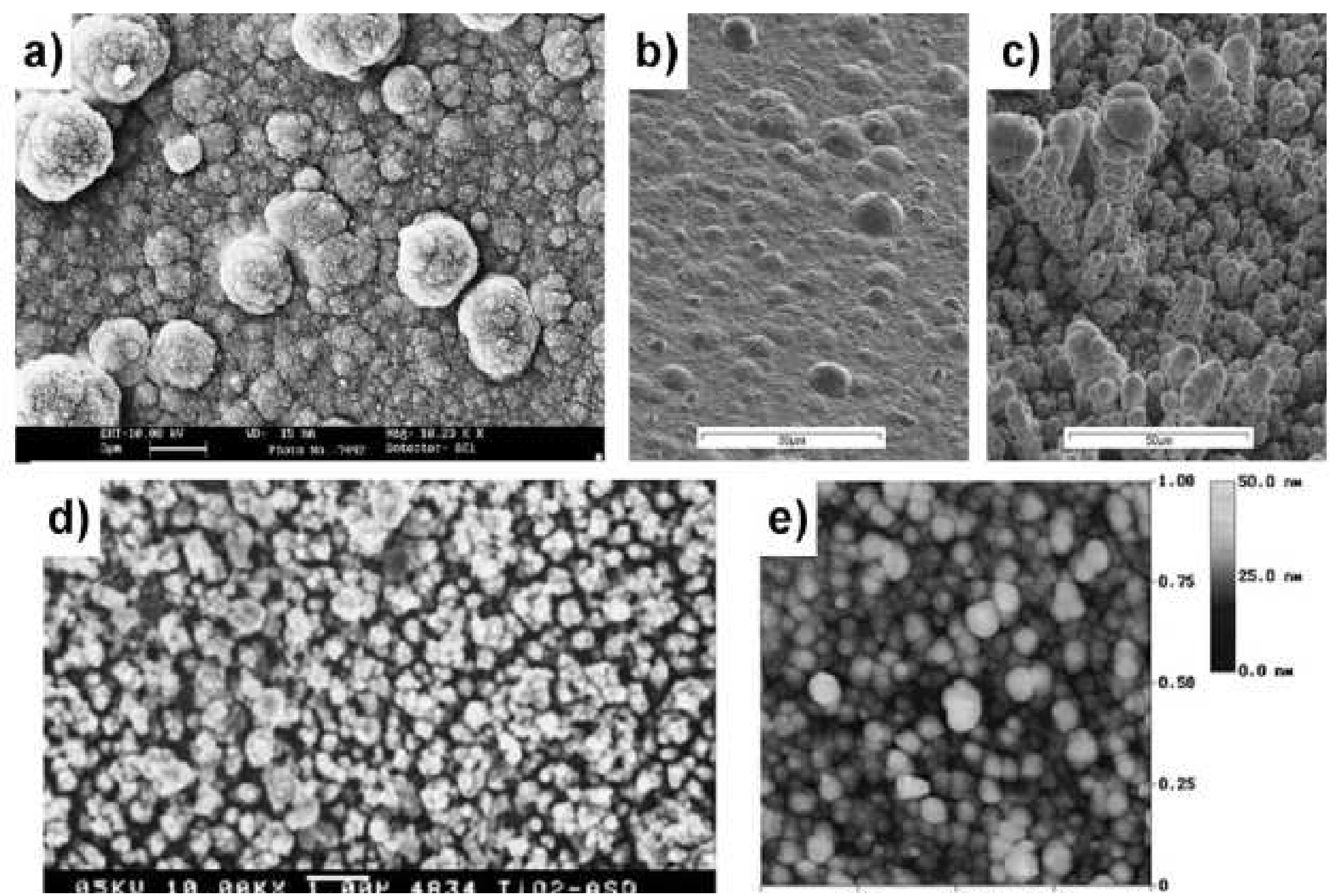


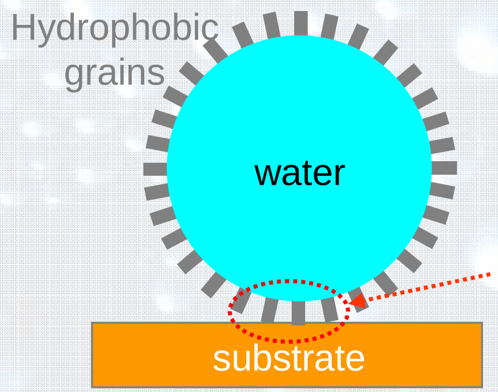
Fig. 8 Diffusion-limited growth on surfaces (a) plasma-deposited Teflon structures,[96] (b) electrochemically deposited copper at 100 mA cm^{-2}, and (c) 200 Ma cm^{-2},[8] (d) an electrodeposited amorphous TiO_2 thin film,[97] and (e) HMDS plasma-deposited polymer.[98] Images reprinted with permission 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.

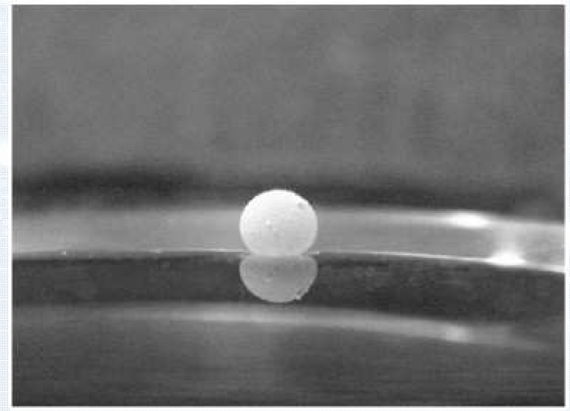
Beyond Simple Superhydrophobicity

Gas Exchange, Directional Wetting, Bioadhesion, Ice, Superwetting, Superspreading, Hemi-wicking, Porosity, Interfacial slip, Surfactants

Liquid Marbles



Similar to pillars, but solid conformable to liquid

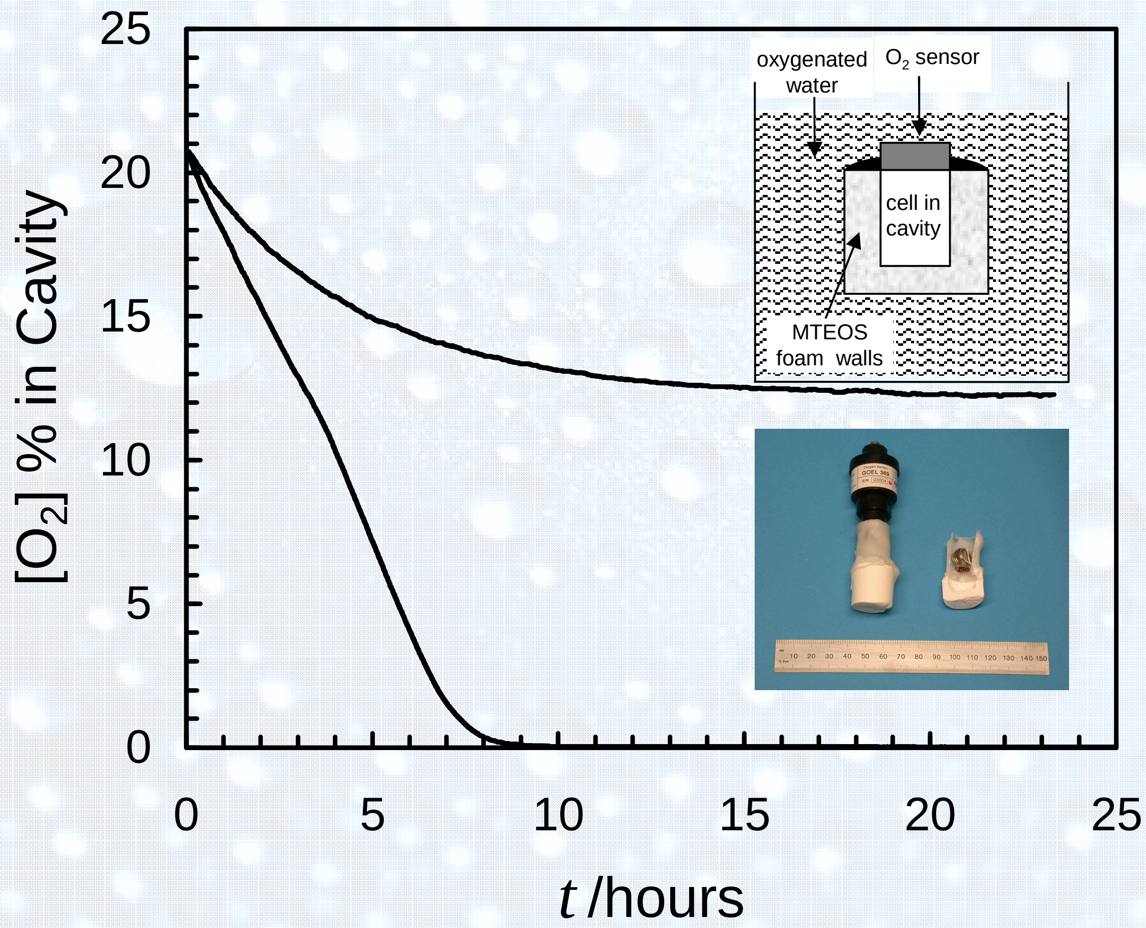


Water floating on water

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

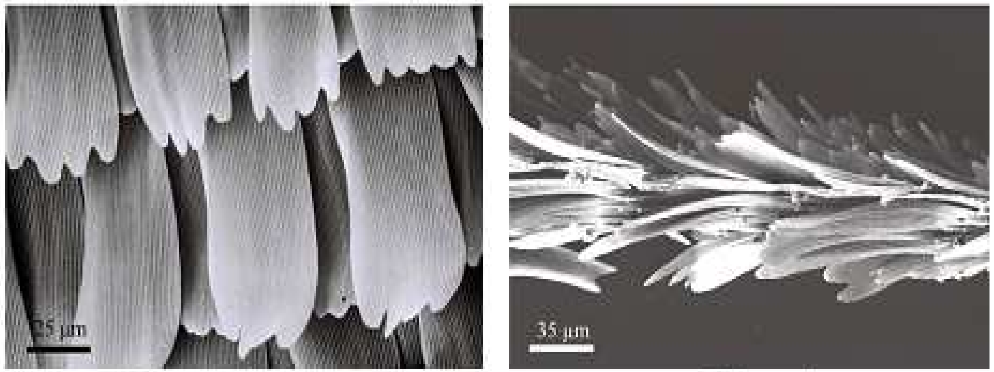
Superhydrophobicity: Plastron Respiration

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.; Prakashc, M.; Adv. Insect Physiol. 34 (2008) 117-192.

Butterfly Wings

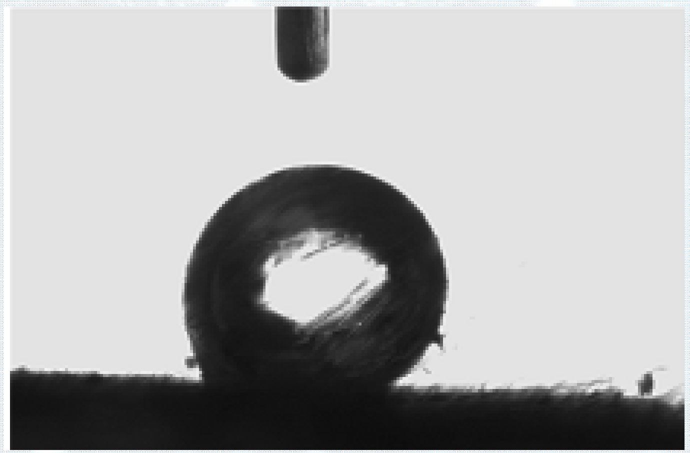


(a) Flat arranging (b) Transection

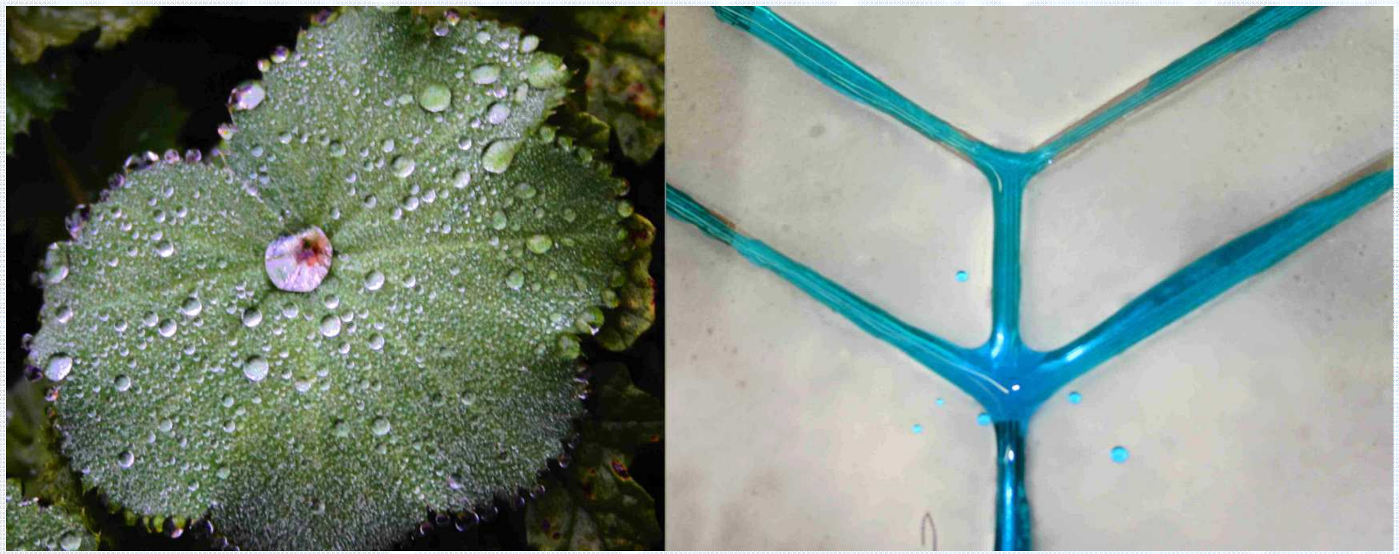
Fig. 2 SEM images of the butterfly (*Pontia daplidice*) wing surface.

Butterflies show directional wetting, drops move preferentially away from the body

An artificial version uses inclined nanopillars



Simpler Case

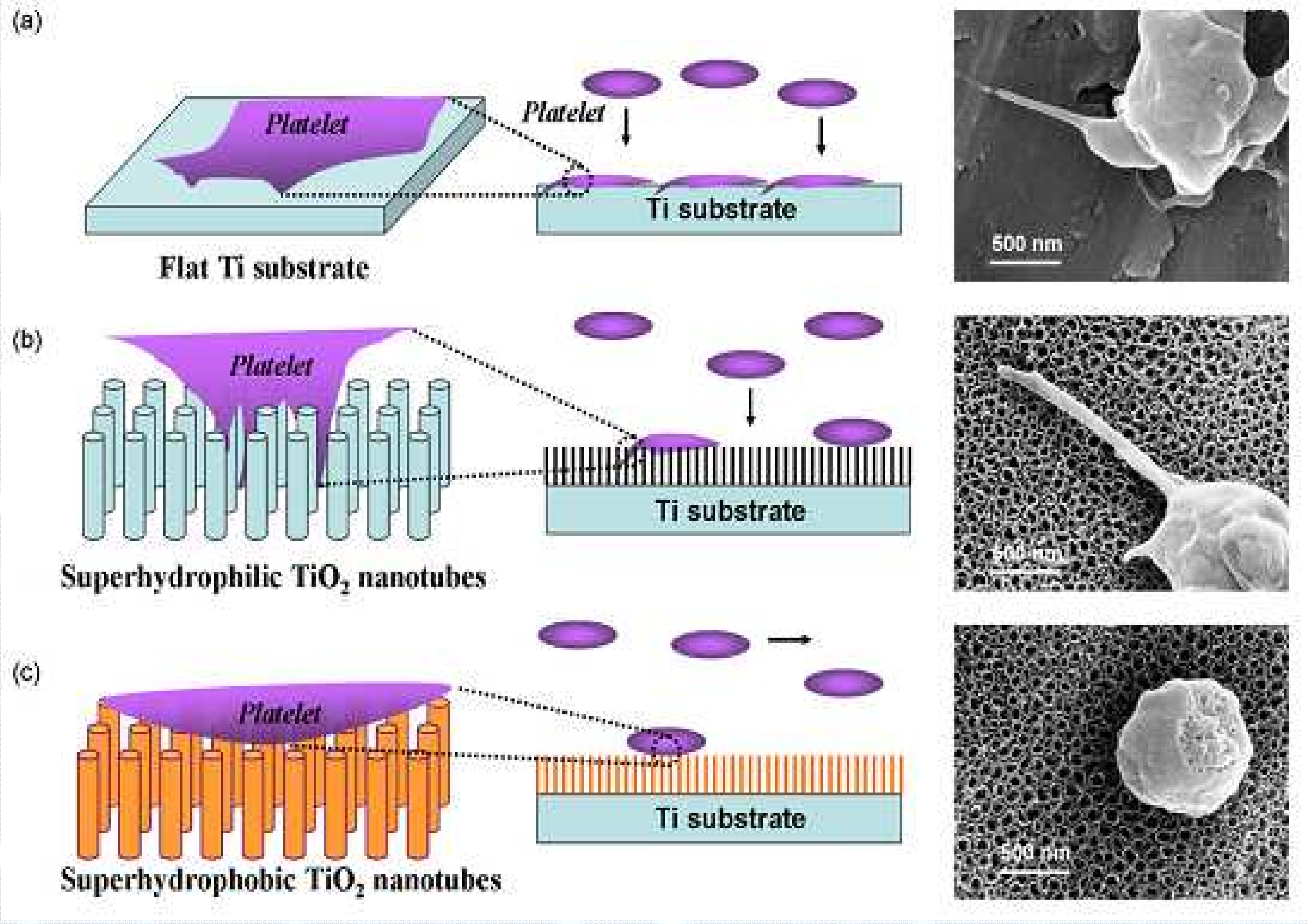


Learning from superhydrophobic plants: The use of hydrophilic areas on superhydrophobic surfaces for droplet control

N. J. Shirtcliffe*, G. McHale, and M. I. Newton

(DOI: 10.1021/la901557d)

Biological Interfaces



Y. Yang et al. / Colloids and Surfaces B: Biointerfaces 79 (2010) 309–313

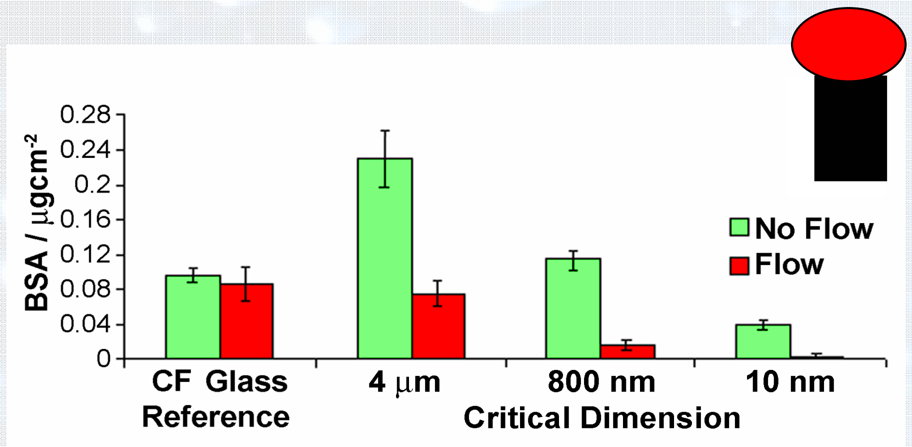
Biofouling and Superhydrophobic Channels

Superhydrophobic Surfaces Used

1. Glass slides
2. Sputter coated 200 nm Cu on 5 nm Ti on slides
3. Large grained (4 μm particles, 20 μm pores) superhydrophobic sol-gel on slides
4. Small grained (800 nm particles, 4 μm pores) superhydrophobic sol-gel on slides
5. CuO nanoneedles (10 nm) on Cu sheet

Proteins on Superhydrophobic Surfaces

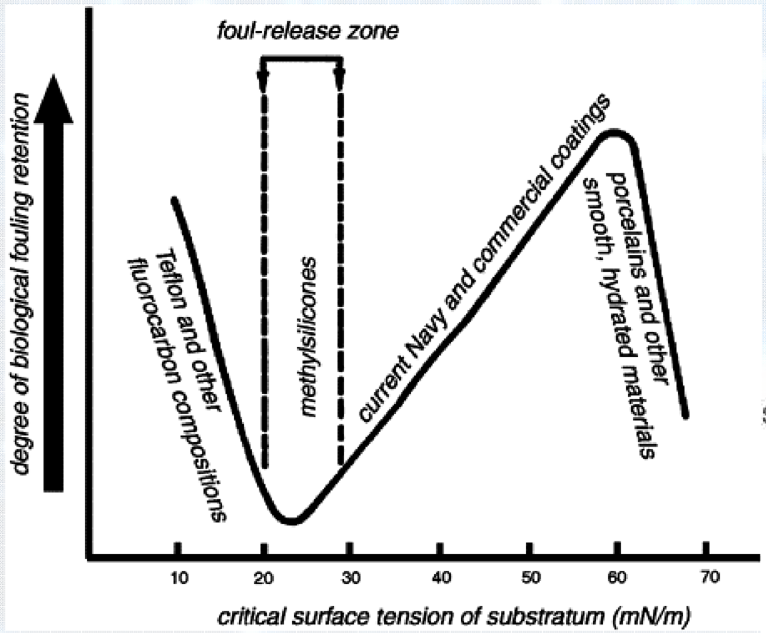
1. Substrates incubated in BSA protein (15 nm in size) in phosphate buffer
2. Flow cell 1500μm x 650μm x 65mm using buffer solution
3. Fluorimetric assay to quantify protein removal

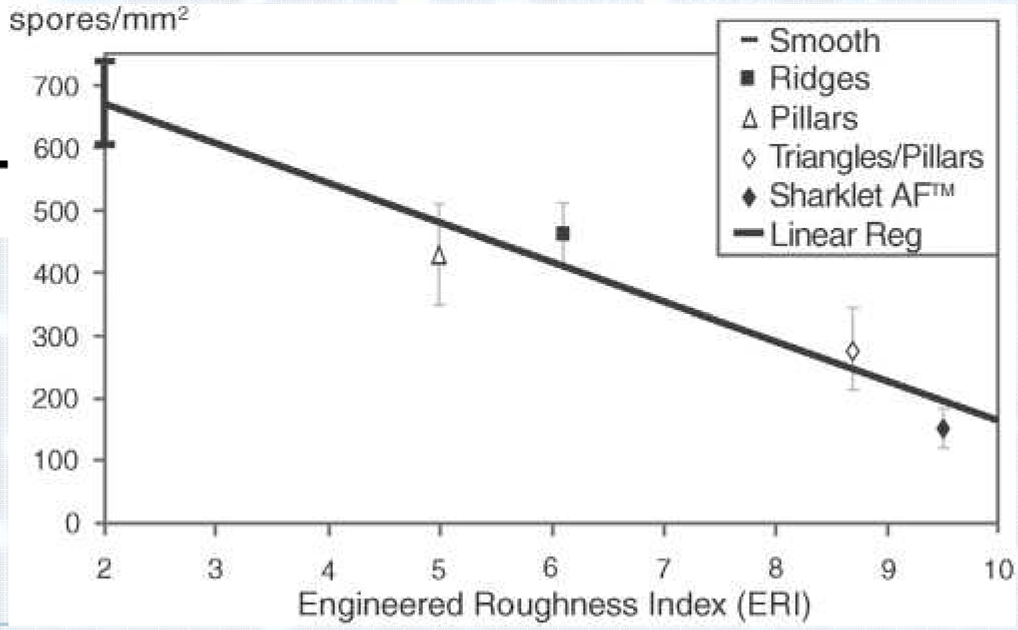


Fluorinated nanoscale superhydrophobic surfaces showed almost complete removal of protein under shear flow

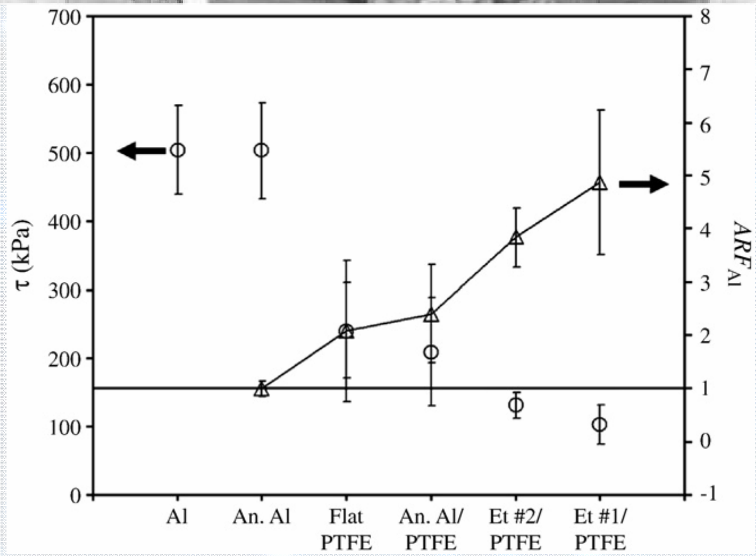
Reference Koc, Y.; de Mello, A.J., McHale, G.; Newton, M.I.; Roach, P.; Shirtcliffe, N.J. Lab on a Chip 81 (2008) 582-586.

Bioadhesion



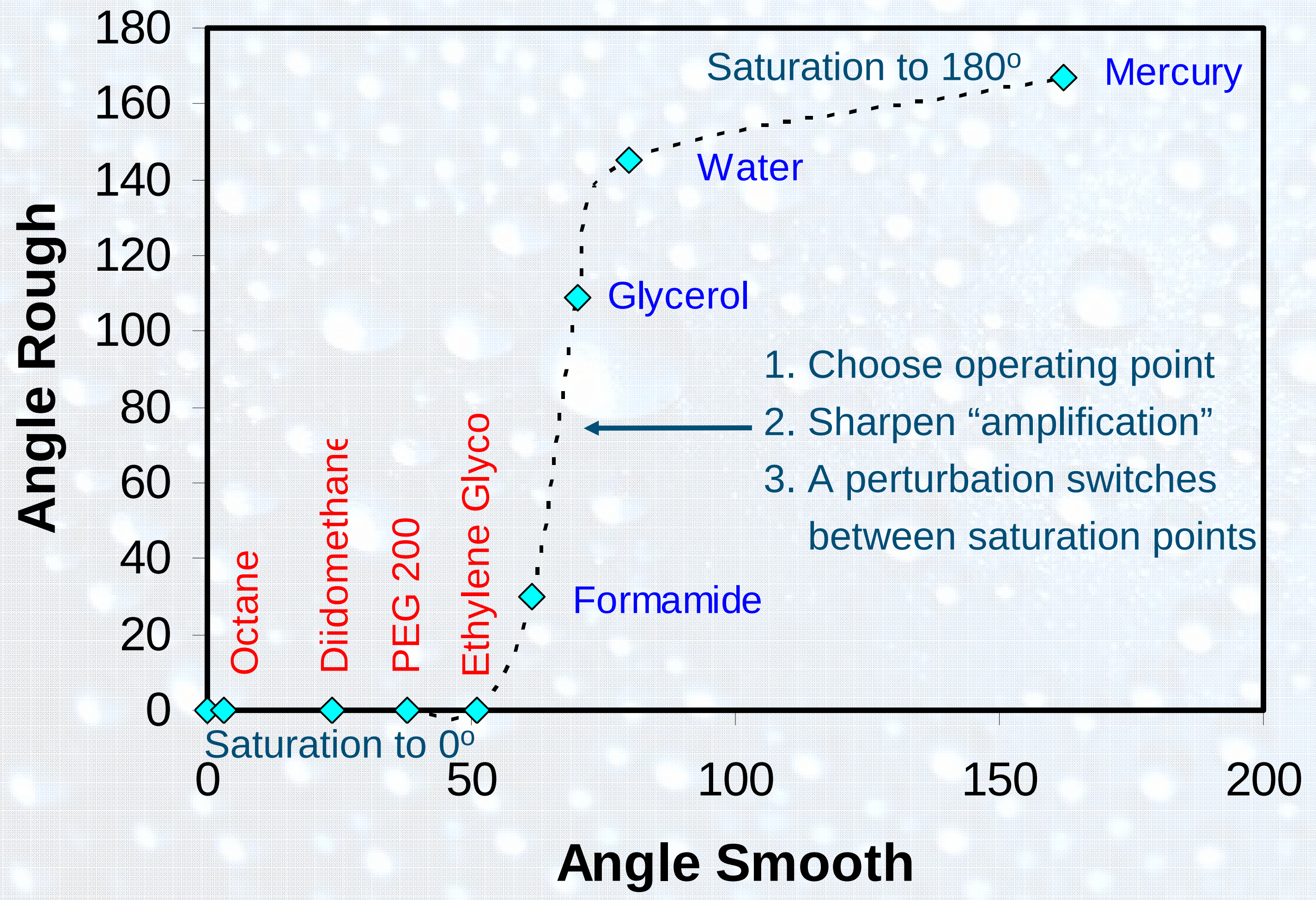


Ice



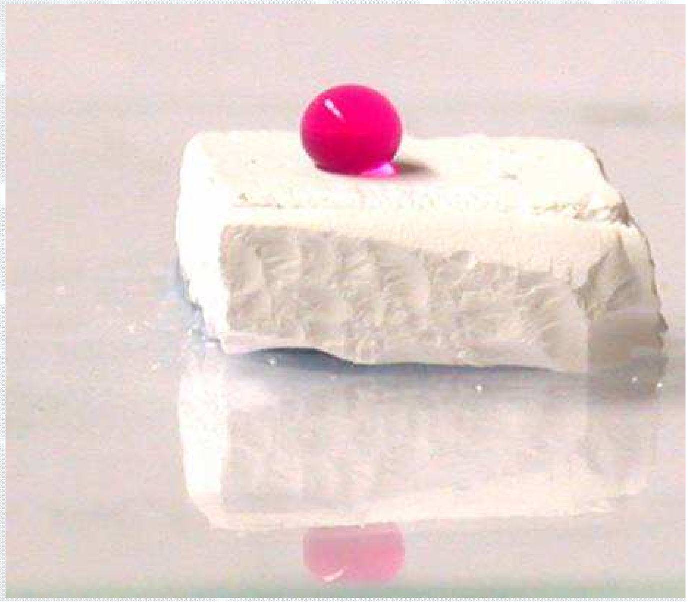
Ice adhesion can be reduced, although deposition is not prevented the frequency of shedding can be increased and the mass decreased, useful on bridges/rigs/ships

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



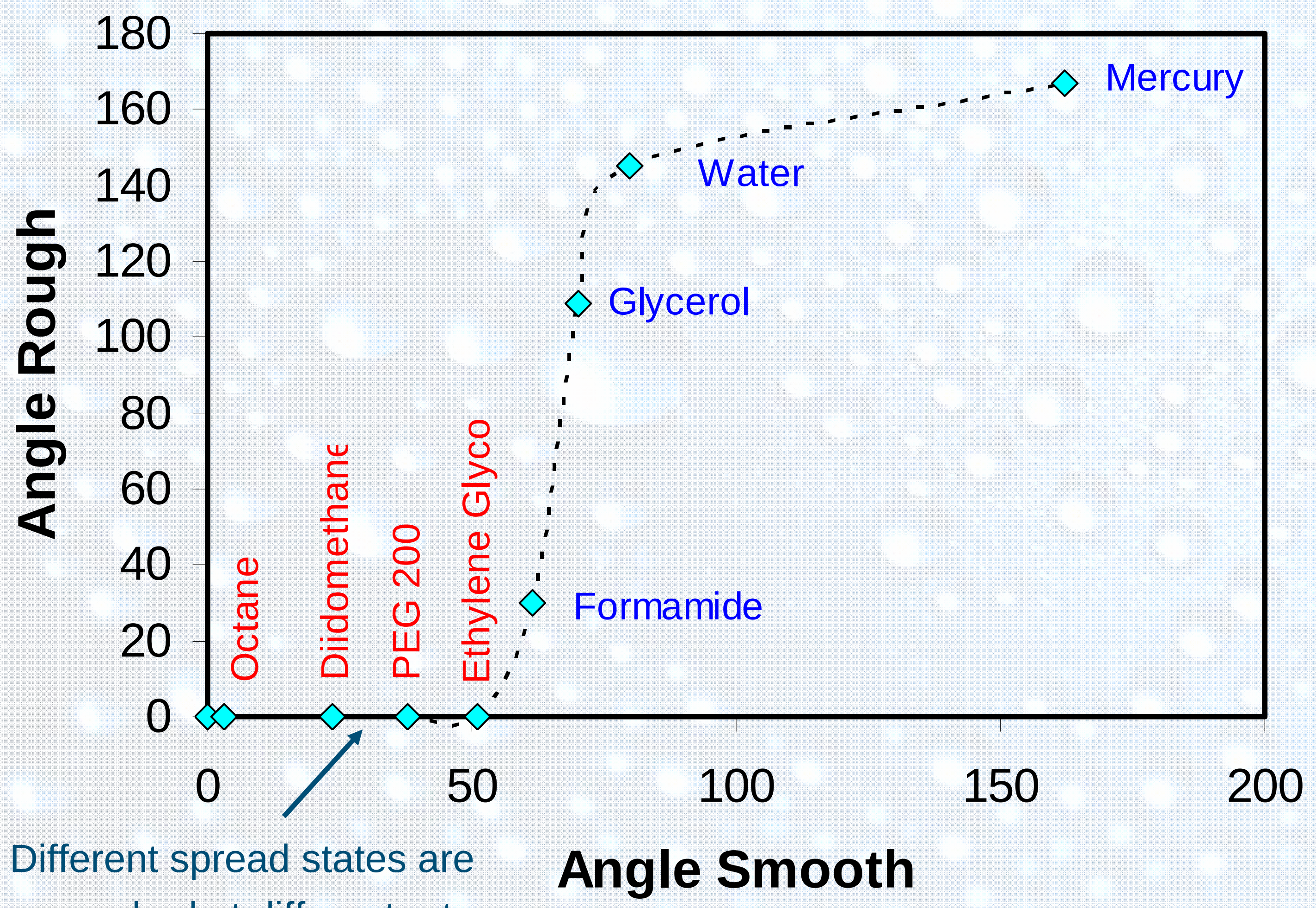
Foam heated (and cooled) prior to droplet deposition

<u>Mechanisms for Switching</u>

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

Reference Shirtcliffe, N.J. *et al.*, Chem. Comm. (25) (2005) 3135-3137
(Nature News "*Quick change for super sponge*" On-line 20/7/05)

Super-spreading



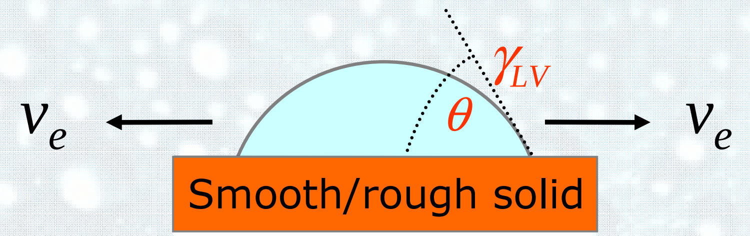
Different spread states are approached at different rates

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 equlibrium

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



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

$$\Rightarrow v_E \propto \theta\,\gamma_{LV}((r\text{-}1)+((\theta^2 - r\theta_e^{s2})/2)$$

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

Superspreading of PDMS on Pillars

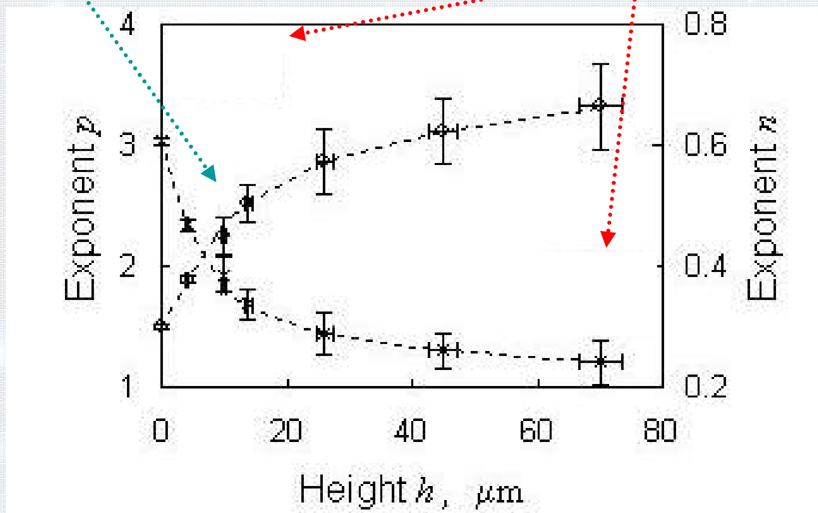
Tanner's Law exponents *p* and *n*

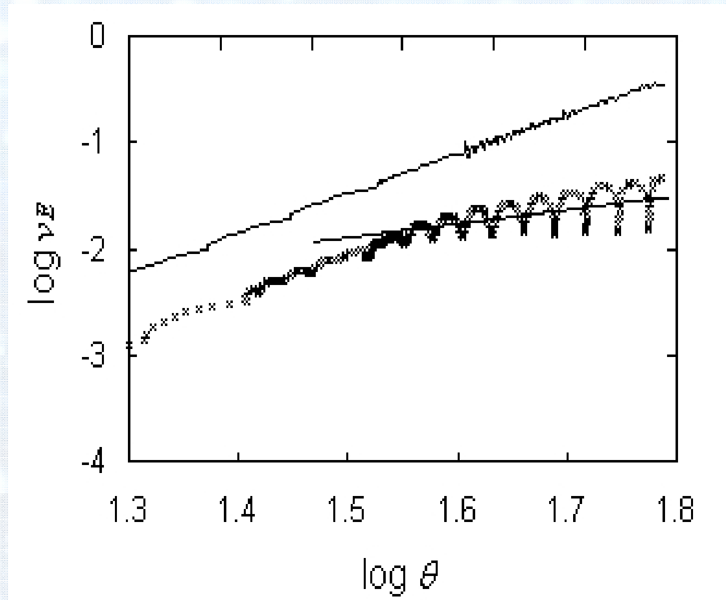
(cubic to linear transition)

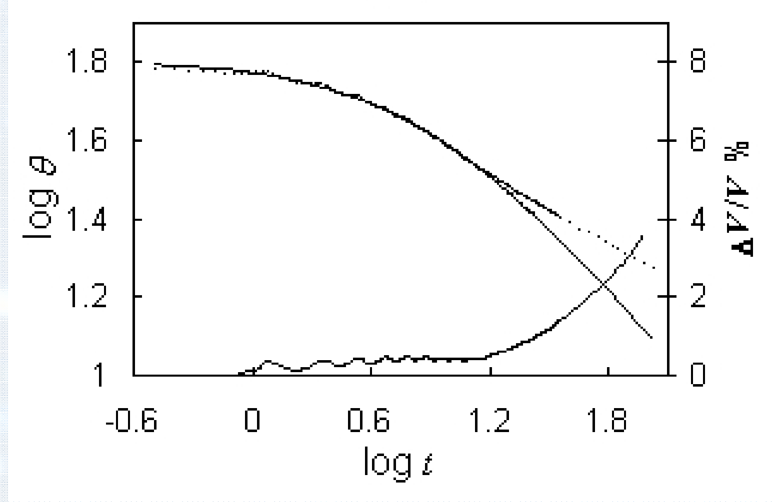
$$v_E \propto v^* \theta^p \qquad \theta \propto \left(\frac{V^{1/3}}{v^*} \right)^n \frac{1}{(t+t_o)^n}$$

Effect of substrate on PDMS

Effect of substrate on water

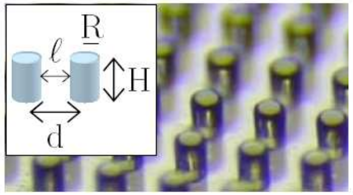


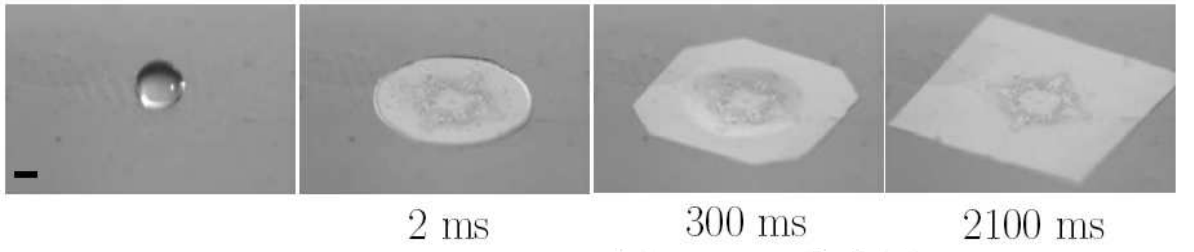


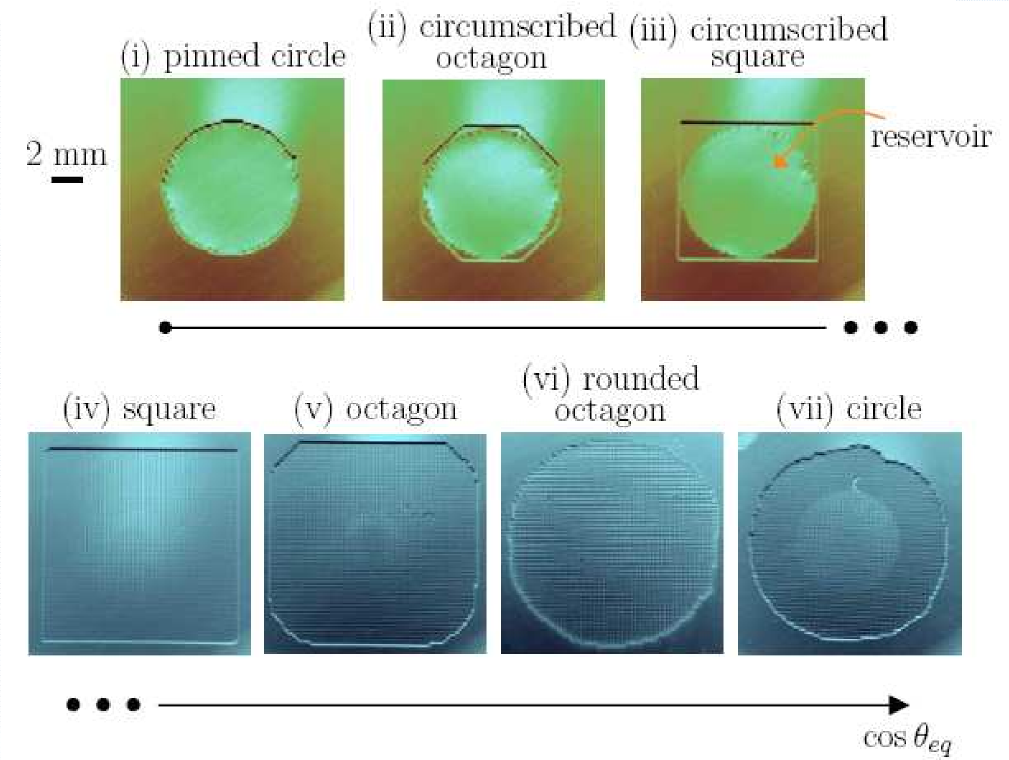


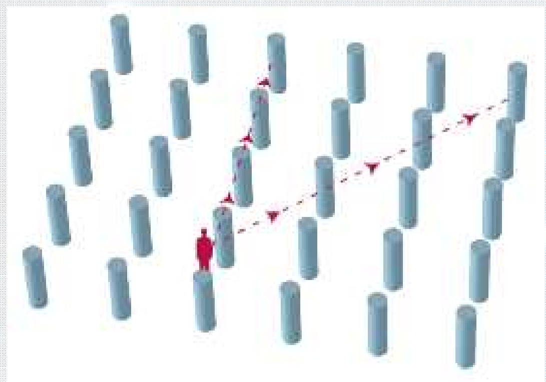
Reference McHale, G. *et al*., Phys. Rev. Lett. 93 (2004) art. 036102.

Topography Induced Wetting: Hemi-Wicking







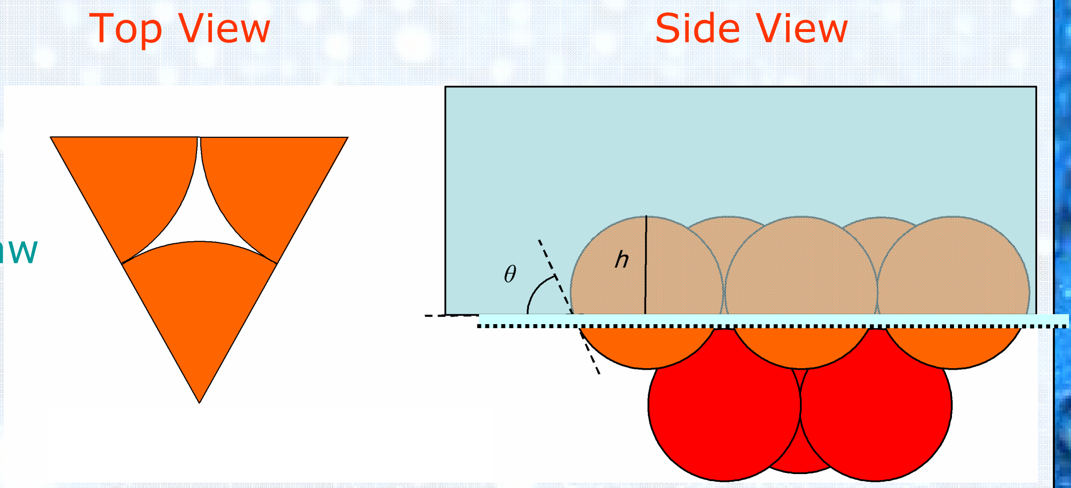


References Bico, J. *et al*., Coll. Surf. A206 (2002) 41-46. Quéré, D. Physica A313 (2002) 32-46. Courbin *et al*, Nature Materials. 6 (2007) 661-664; McHale, 6 (2007) 627-638.

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



Results for Close Packing

1. Change in surface free energy with penetration depth, h, into first layer of particles

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

2. Equilibrium exists provided liquid does not touch top particle of second layer
   1. If liquid touches second layer at depth, h_c, then complete infiltration is induced

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

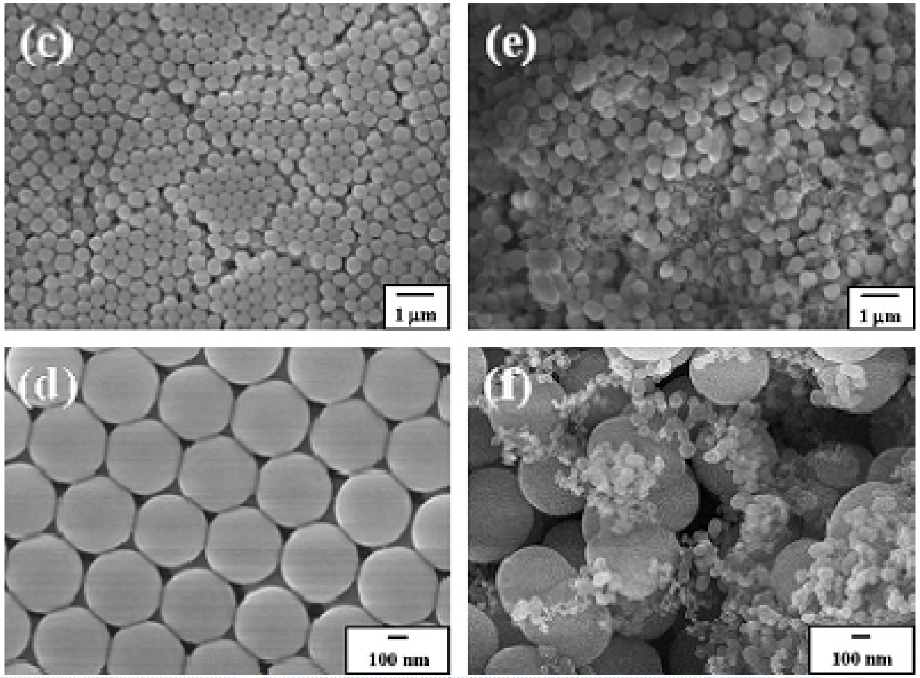
   2. Critical contact angle, θ_c, when h_c reached[1,2]

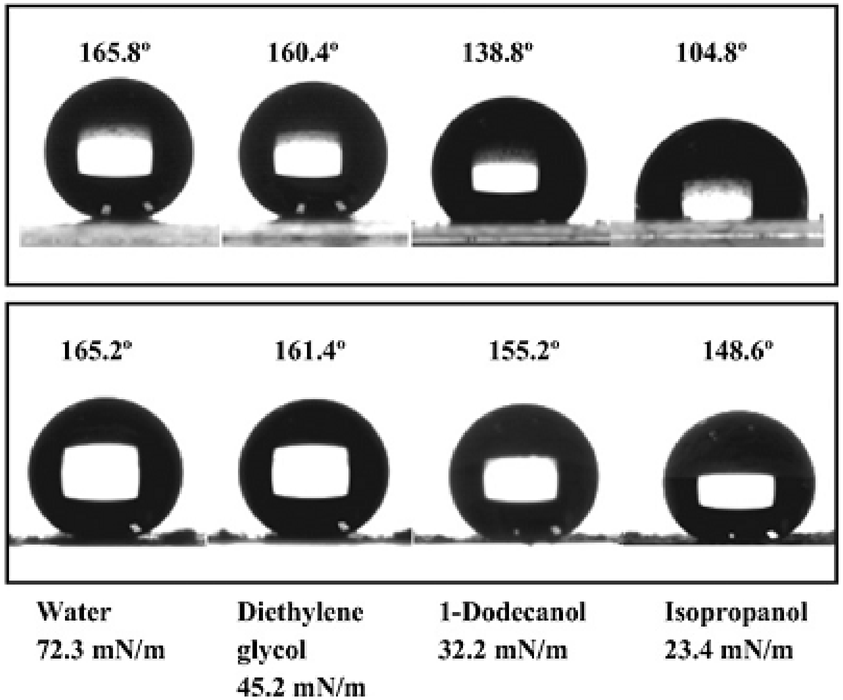
$\theta_c = 50.73^o$

Creating superhydrophobic surfaces with curved features allows liquids to be supported even when $\theta_e < 90^o$ – so-called re-entrant surface features[3]

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

Small Scale



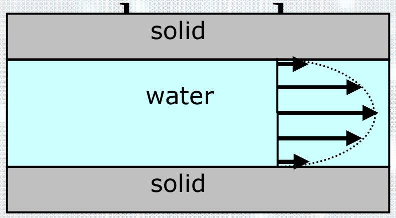


This is silica nanospheres with fluorocarbon coating showing the same effect

C.-T. Hsieh et al. / Materials Chemistry and Physics 121 (2010) 14–21

Flow in Pipes with Superhydrophobic Walls

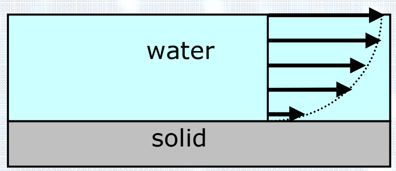
Closed-



Two walls cause frictional drag

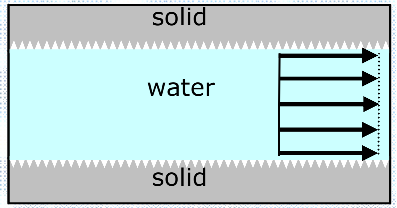
Open-channel

Low frictional drag to air



High frictional drag to solid

Super-channel



Walls appear as cushions of air

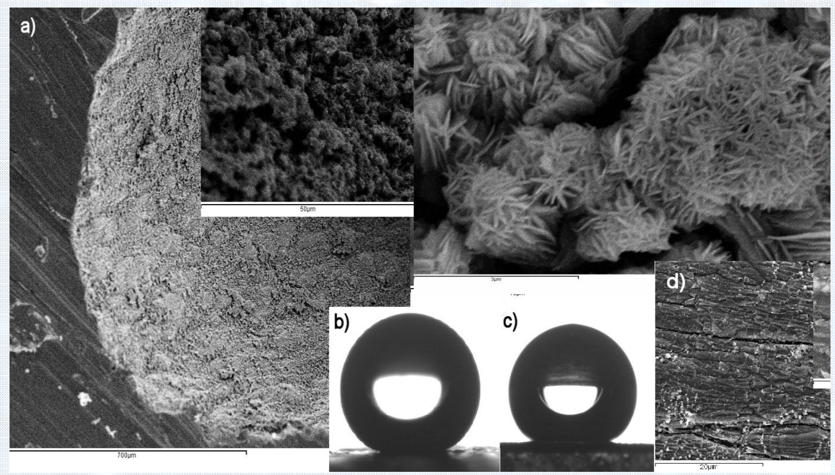
Concept

Experiment

Forced flow through small-bore Cu tubes

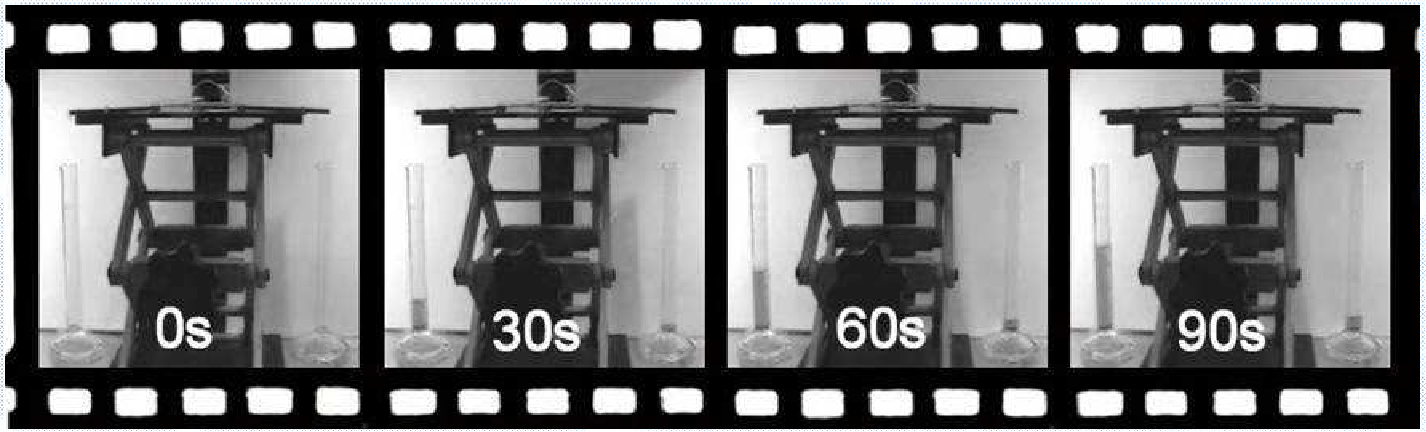
Electron microscope images of hydrophobic nano-ribbon (1μm x 100nm x 6nm) decorated internal copper surfaces of tubes (0.876 mm radii).

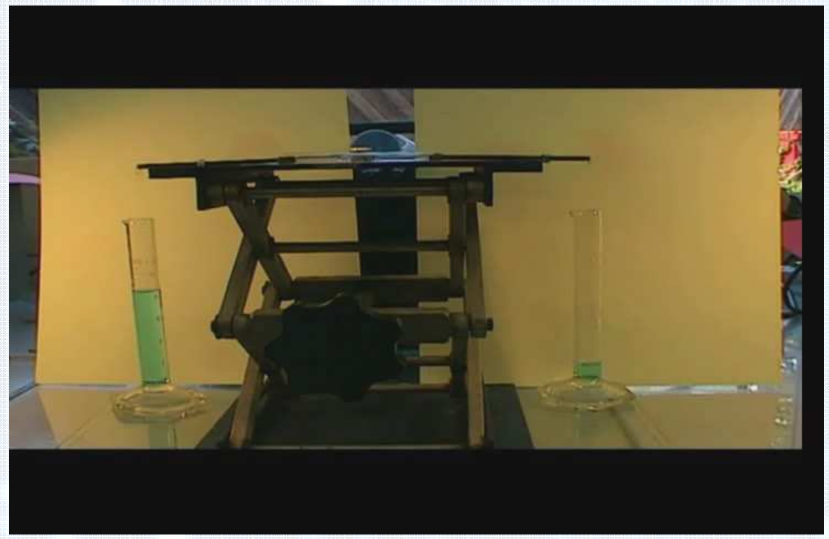
Side-profile optical images of droplets of b) water, and c) glycerol on surface shown in a) the original surface is shown in d)



Reference Shirtcliffe, N.J.; McHale, G.; Newton, M.I.; Zhang, Y. ACS Appl. Maters. Interf. 1 (2009) 1316-1323.

Visualization Results – Extracted Frames





Reference Shirtcliffe, N.J.; McHale, G.; Newton, M.I.; Zhang, Y. ACS Appl. Maters. Interf. 1 (2009) 1316-1323.

Interaction of Surfactants with Superhydrophobicity

Fig. 6. Bulk sol–gel foams after immersion in a water: SDS mixture with red dye added. Samples from left (1) sample heated to 300 °C, no SDS; (2) sample heated to 300 °C, 0.08 M SDS; (3) sample unheated, 0.08 M SDS; (4) sample heated to 400 °C, 0.08 M SDS.

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

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

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

NOTTINGHAM TRENT UNIVERSITY

Appendices

Additional References

Book

"Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves", de Gennes, P.G.; Brochard-Wyard, F.; Quéré, D. Springer-Verlag New York (2003) ISBN 0387005927

Reviews

"Progess in superhydrophobic surface development", Roach, P.; Shirtcliffe, N.J.; Newton, M.I. Soft Matter 4 (2008) 224-240

"Design and creation of superwetting/antiwetting surfaces", Feng, X.J.; Jiang, L. Adv. Maters. 18 (2006) 3063-3078

"Superhydrophobic surfaces", Ma, M.L.; Hill, R.M. Curr. Opin. Coll. Interf. Sci. 11 (2006) 193-202

"Bioinspired surfaces with special wettability", Sun, T.L.; Feng, L.; Gao, X.F.; Jiang, L. Accts. Chem. Res. 38 (2005) 644-652

"On water repellency", Callies, M,; Quéré, D.; Soft Matter 1 (2005) 55-61

"Non-sticking drops", Quéré, D. Rep. Prog. Phys. 68 (2005) 2495-2532

Other

"Self-cleaning surfaces - virtual realities", Blossey, R. Nature Maters 2 (2003) 301-306.

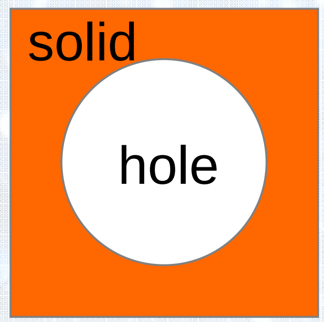
"Transformation of a simple plastic into a superhydrophobic surface", Erbil, H.Y.; Demirel A.L.; *et al.* Science 299 (2003) 1377-1380.

Cylindrical Model for Capillary Infiltration

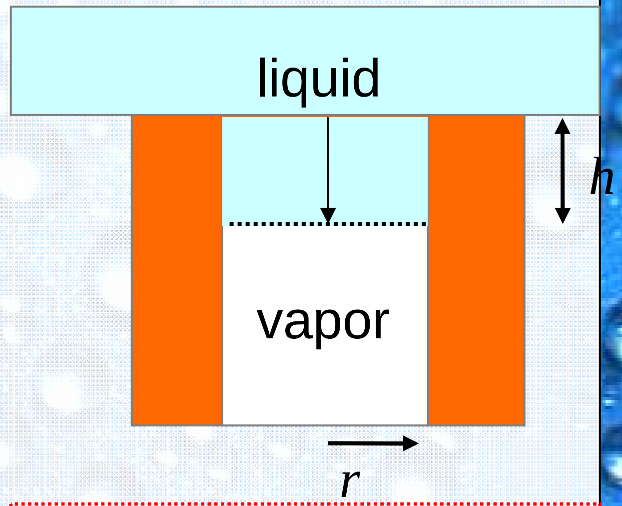
<u>Assumptions</u>

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

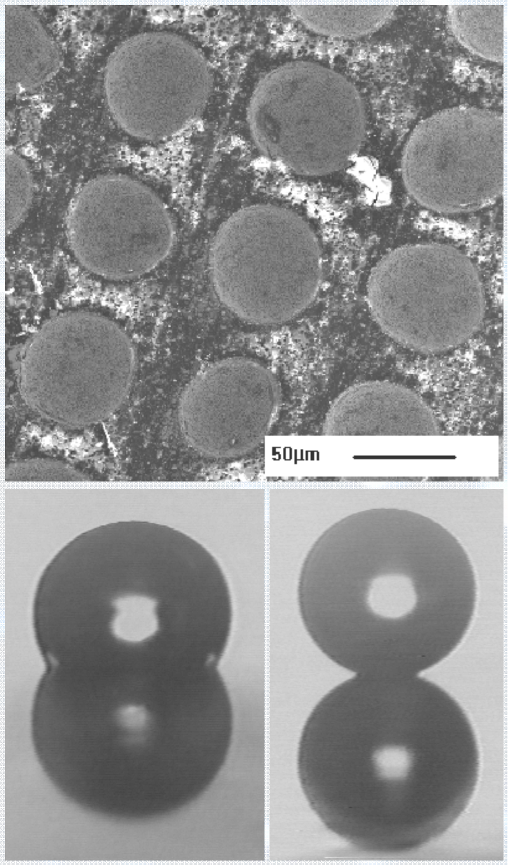
$$\Delta F = (\gamma_{SL} - \gamma_{SV}) 2\pi r \Delta h \quad \underset{\text{Young's Law}}{\Rightarrow} \quad \Delta F = -\gamma_{LV} \cos\theta_e 2\pi r \Delta h$$

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

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

Superhydrophobicity - Man-Made Examples

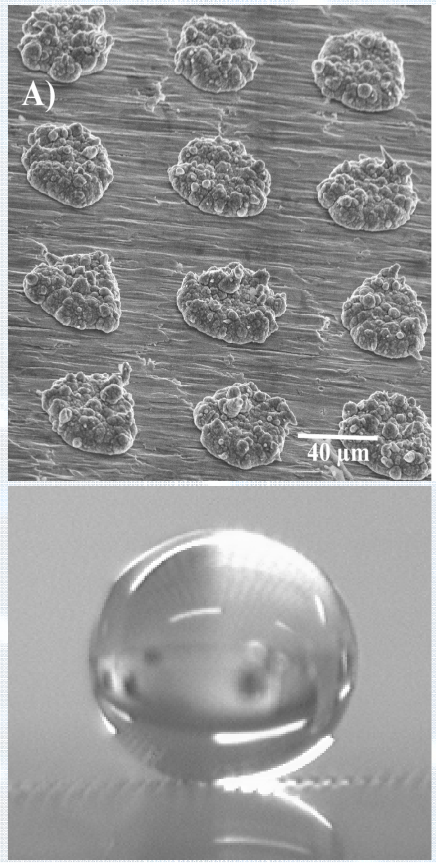
Etched Metal



Flat & hydrophobic

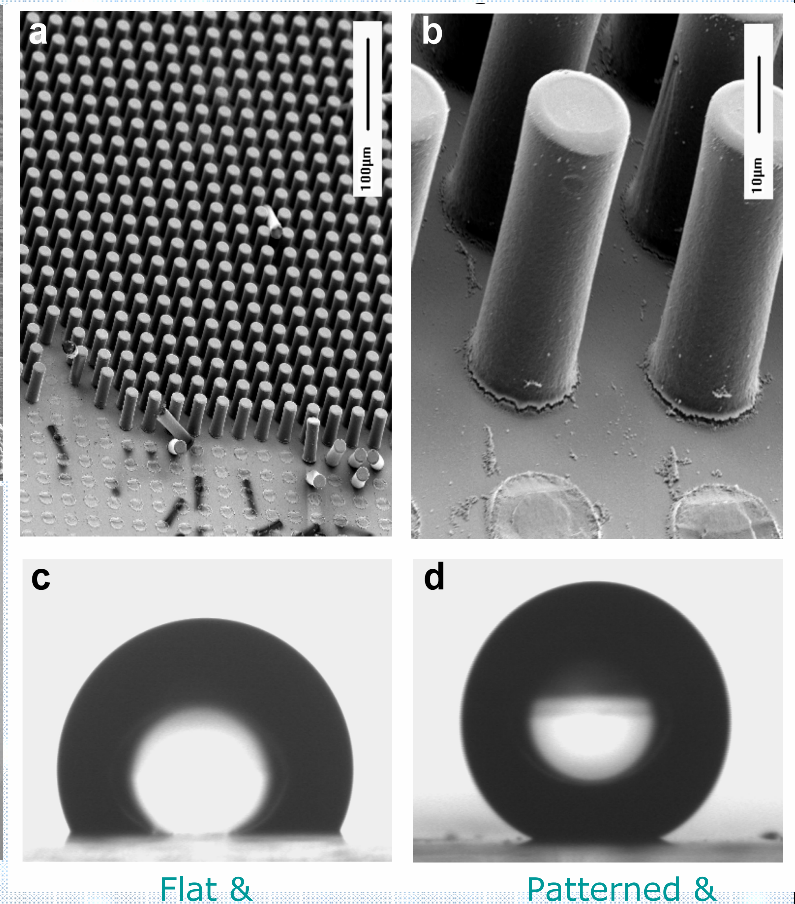
Patterned & hydrophobic

Deposited Metal



Patterned & hydrophobic

Polymer Microposts



Flat & hydrophobic

Patterned & hydrophobic

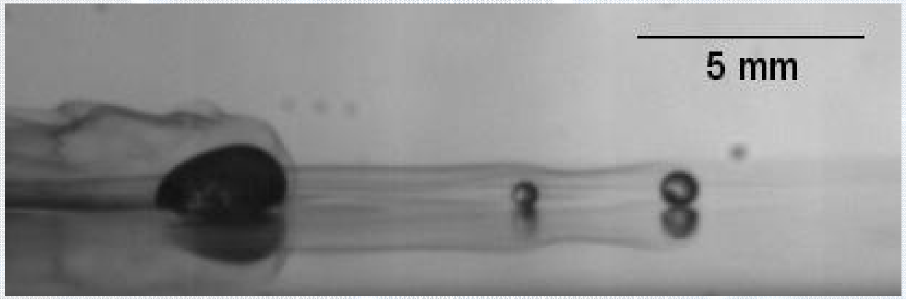
References Shirtcliffe, N.J. *et al.*, Langmuir 21 (2005) 937-943; Adv. Maters. 16 (2004) 1929-1932; J. Micromech. Microeng. 14 (2004) 1384-1389.

Leidenfrost Effect

Perfect Superhydrophobicity?

- Cassie-Baxter with solid fraction $f_s=0$
- Droplet floats on a layer of vapor: $\cos\theta_{CB}=0 \times \cos\theta_e-(1-0) \Rightarrow \theta_{CB}=180^o$
- Droplet of water deposited onto a hot surface (~200 °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

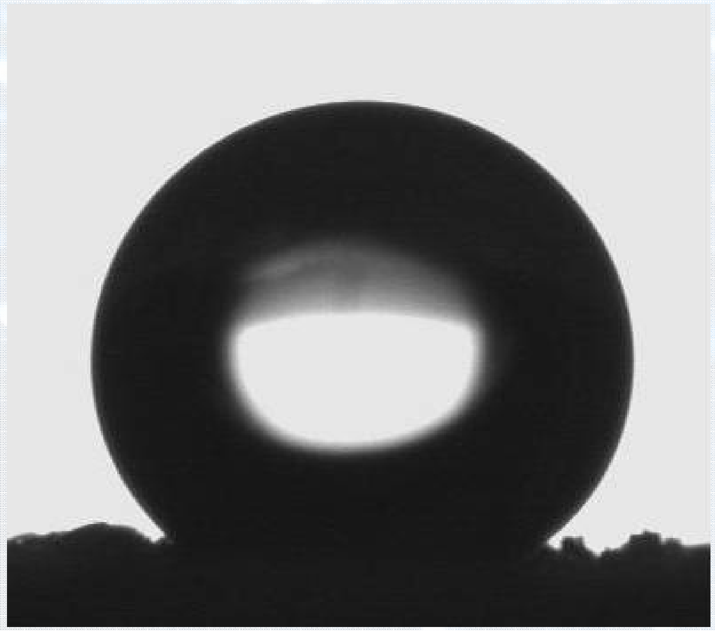
Leidenfrost Puddle

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

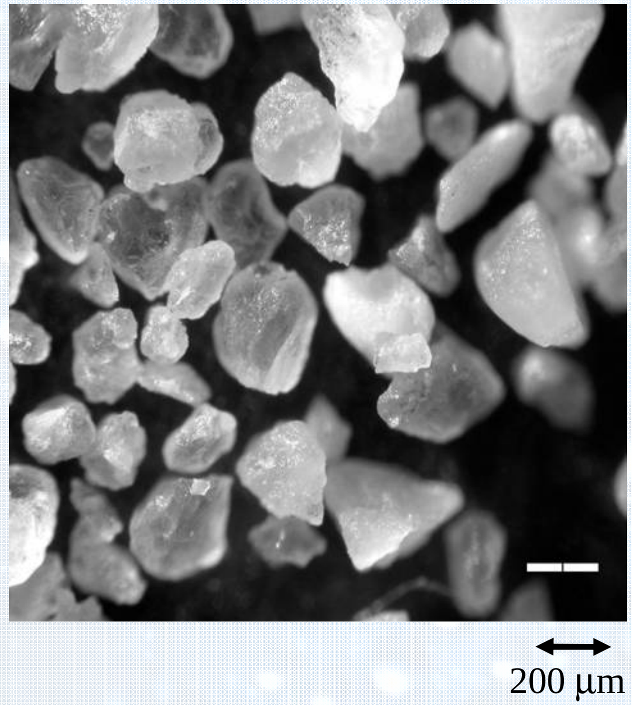
Reference Biance, A.L.; Clanet, C.; Quéré, D. Phys. Fluids. 15 (2003) 1632-1637.
http://www.pmmh.espci.fr/fr/gouttes/recherche/

Super Water-Repellent Sand/Soil

Sand with 139º



Shape and Packing

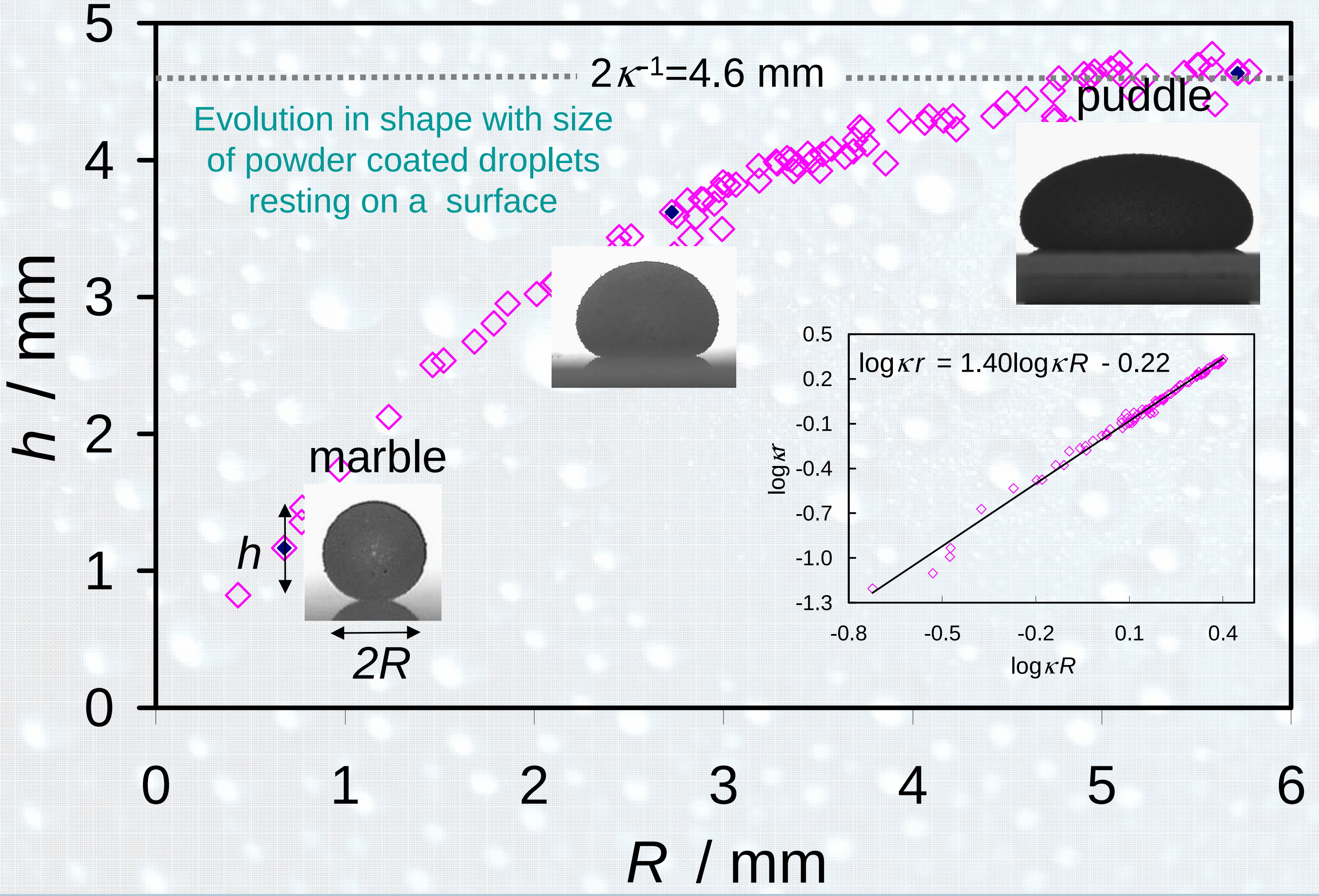


Comments

1. Effect occurs naturally, but can also be reproduced in the lab
2. Water droplet doesn't penetrate, it just evaporates
3. Need to use ethanol rich mixture to get droplet to infiltrate (MED test)

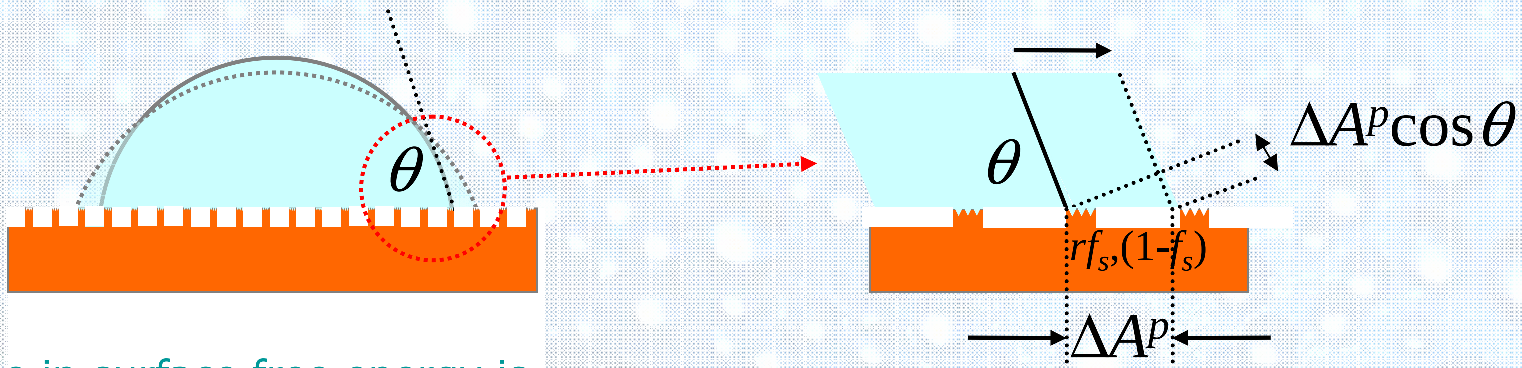
References McHale, G. *et al.*, Eur. J. Soil Sci. 56 (2005) 445-452; Hydrol. Proc. 21 (2007) 2229-2238.

Liquid Marble Size Data (Lycopodium)



References Aussillous P, Quéré D. Proc. Roy. Soc. A462 (2006) 973-999; Nature 411 (2001) 924-927. 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

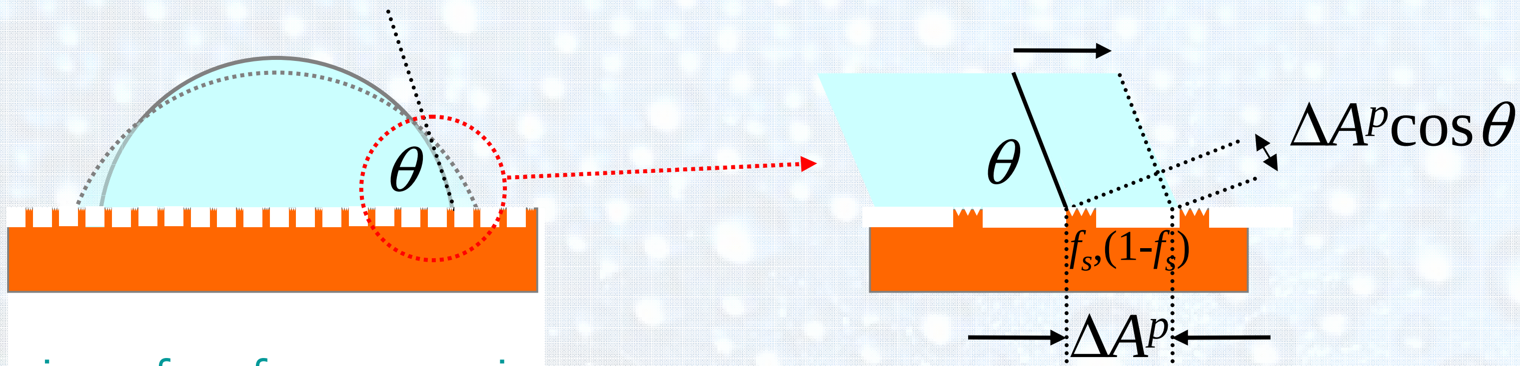
$r = \Delta A_{SL}/\Delta A_{SL}{}^P$ = roughness of "tops" of features

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

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

References Shirtcliffe, N.J. *et al.*, Adv. Maters. 16 (2004) 1929-1932; Bachmann, J.; McHale, G. submitted to EJSS (2008).

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

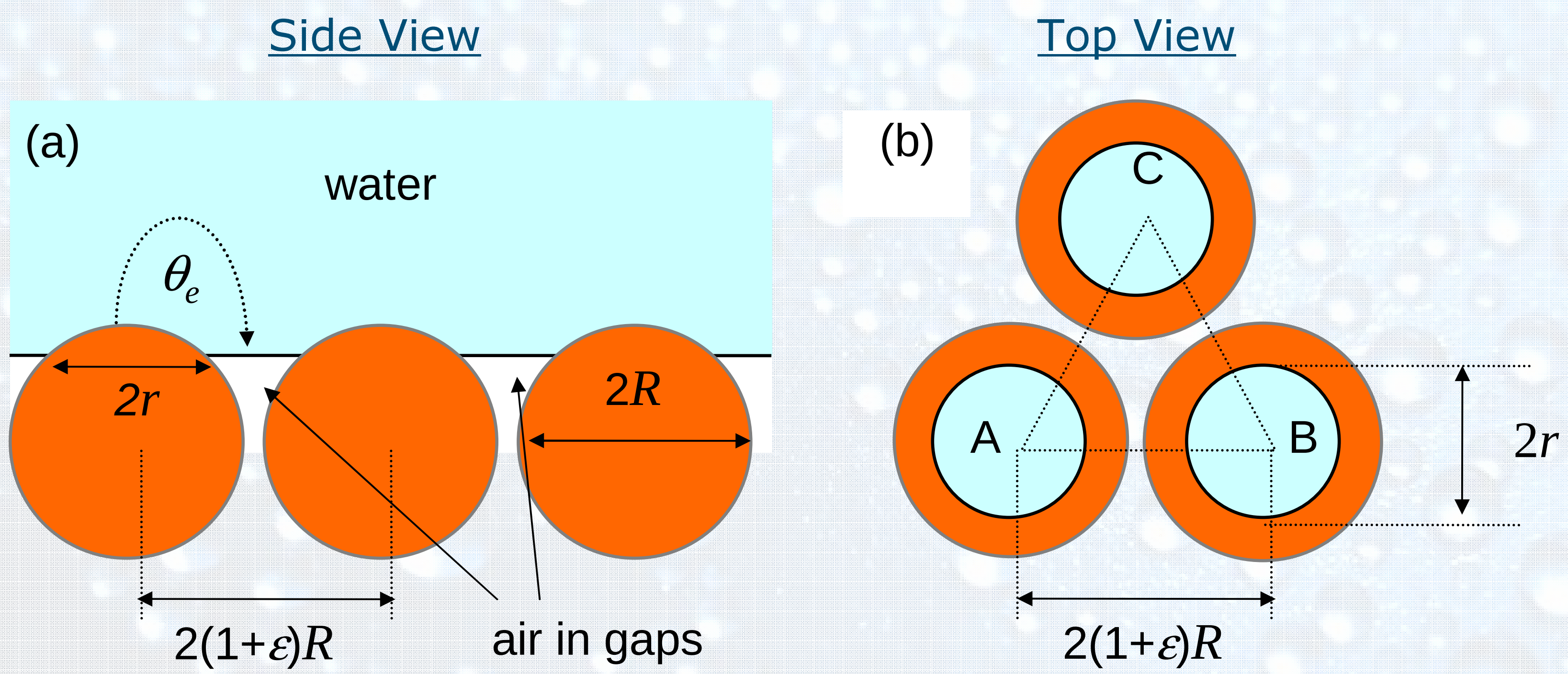
f_s^{large} = solid surface fraction for large scale structure

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

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

References Shirtcliffe, N.J. *et al.*, Adv. Maters. 16 (2004) 1929-1932; Bachmann, J.; McHale, G. submitted to EJSS (2008).

Model of Bead Pack/Soil



Assumptions

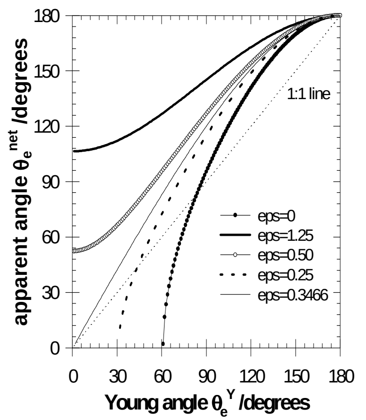
1. Uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges air gaps horizontally between spheres
3. Capillary (surface tension) dominated size regime of gaps<<κ^{-1}=2.73 mm

References McHale, G. *et al.*, Eur. J. Soil. Sci. 56 (2005) 445-452. Bachmann, J.; McHale, G. submitted to EJSS (2008).

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

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

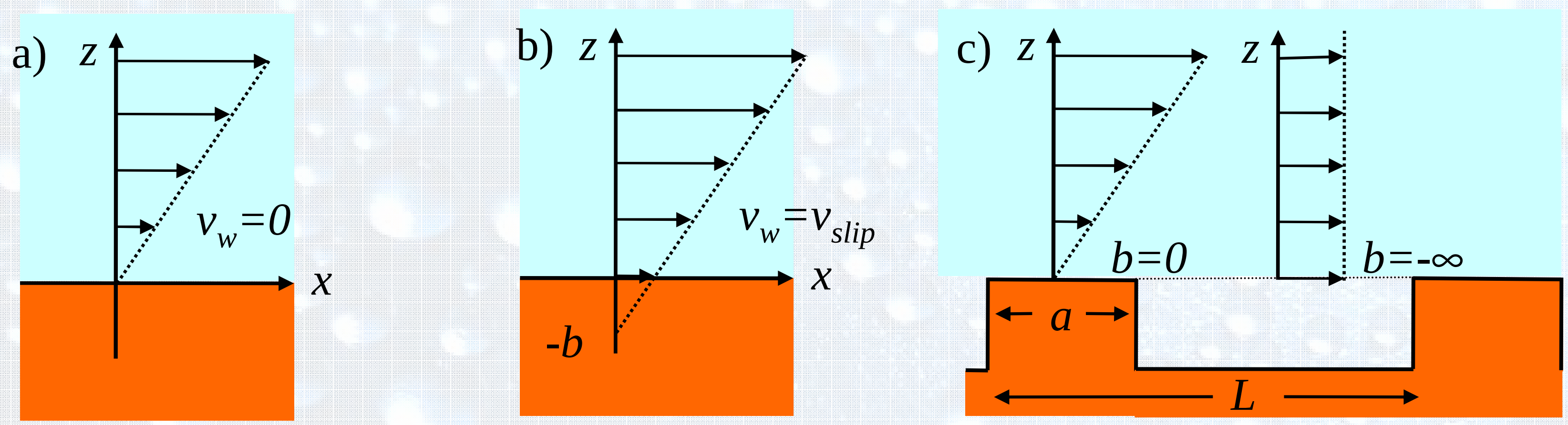
$$\cos\theta_e^{net} = f_S r_s \cos\theta_e - (1 - f_S)$$

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

References McHale, G. *et al.*, Eur. J. Soil. Sci. 56 (2005) 445-452. Bachmann, J.; McHale, G. submitted to EJSS (2008).

Slip by Simple Newtonian Liquids

No Slip | Slip | Mixed



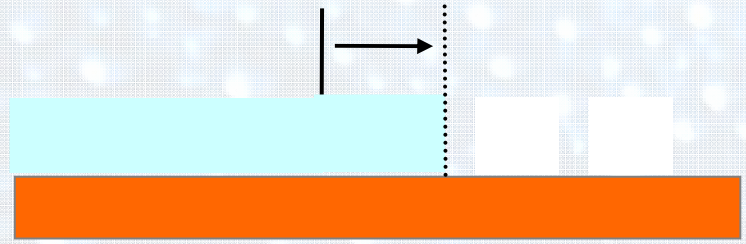
Experimental Evidence – Steady Flow

1. Theory[1,2] supported by simulations suggests $b=L\ f(\varphi_s)/2\pi$
2. Micro-PIV experiments detailing flow profiles[3] (h=1-7 μm ⇒ b=0.28L)
3. Cone-and-plate rheometer experiments[4] – drag reduction > 10%
4. Hydrofoil in a water tunnel experiments[5] – drag reduction of 10%

References [1]Philip, Z. Angew. Math. Phys. 23 (1972). [2]Lauga & Stone, J. Fluid Mech. 489 (2004). [3]Joseph *et al.*, Phys. Rev. Lett. 97 (2006). [4]Choi & Kim, Phys. Rev. Lett. 96 (2006). [5]Gogte *et al.*, Phys. Fluids 17 (2005). See also: Roach, P. *et al.*, Langmuir 23 (2007) 9823-9830. McHale, G.; Newton, M.I. J. Appl. Phys. 95 (2004) 373-380.

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

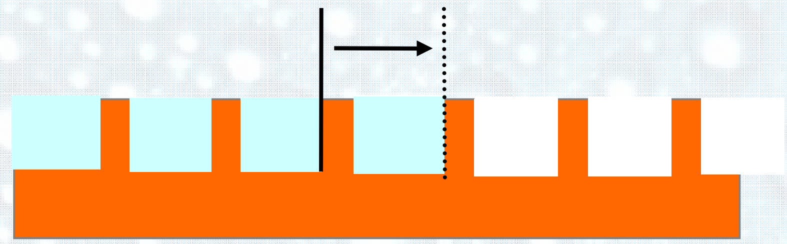
Spreading is when $\Delta F < 0 \quad \Rightarrow$

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

i.e. critical angle is

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

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 $\Delta F < 0 \quad \Rightarrow$

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

i.e. critical angle is between 0^o and 90^o

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

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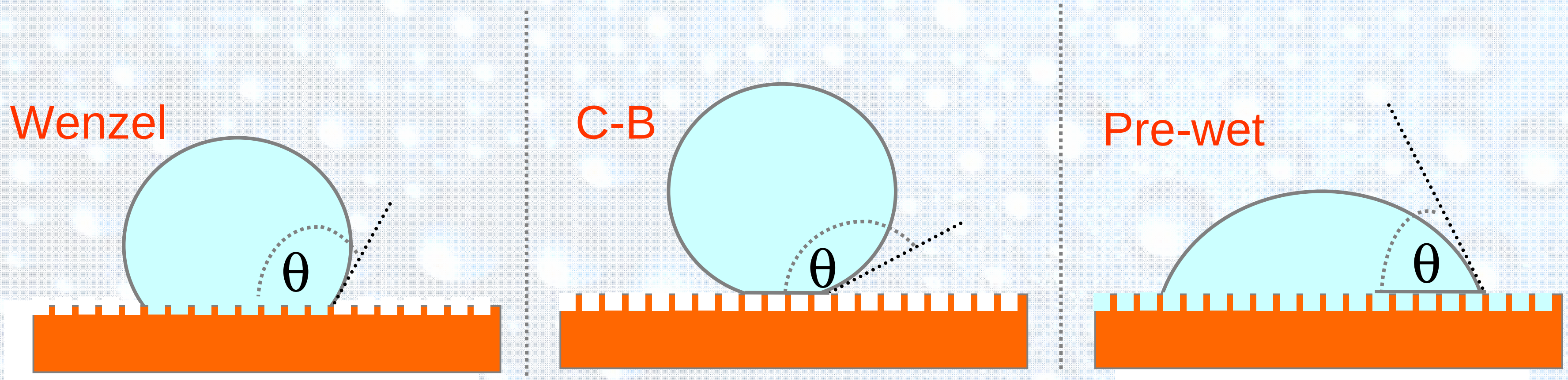
Pre-existing Wetness



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

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

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

sign has been switched to +ve from -ve

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