Superhydrophobicity, Spreading and Imbibition

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Overview

1. Water Repellency: Concepts

- Naturally occurring surfaces
- Skating and penetrating states: sticky/slippy, deposition/condensation

2. Topography & Wetting: Theory

- Surface free energy derivations: Wenzel/Cassie-Baxter equations
- Complex topography, defects and symmetric/random patterns

3. Superhydrophobicity: Consequences

- Amplification, attenuation and saturation
- Skating-to-penetrating transition and droplet collapse
- Path definition and droplet motion
- Unexpected superhydrophobicity

4. Porosity, Spreading and Imbibition

- Superspreading, superwetting, hemi-wicking and porosity
- Imbibition and MRI

Water Repellency: Concepts

Naturally Occurring Surfaces

Plants and Leaves

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

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

Acknowledgement Video: "Microcosmos"

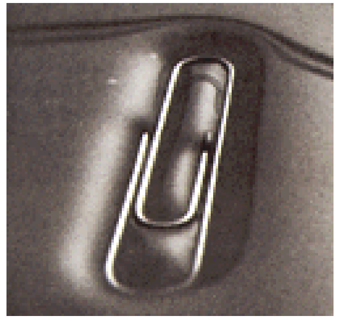
Effects of Surface Tension

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”

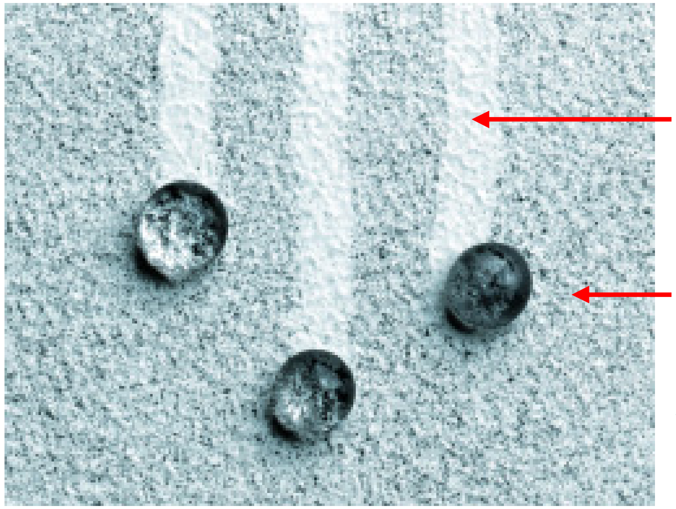
The Sacred Lotus Leaf

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"

Self-poisoning surface

Acknowledgement Neinhuis and Barthlott

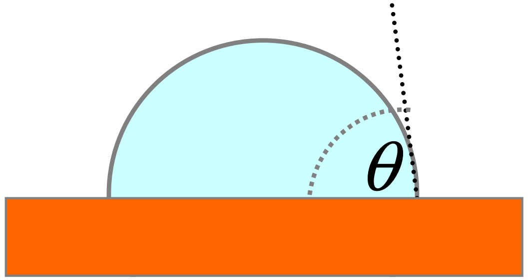
References Neinhuis,C.; Barthlott, W. Ann. Bot., 79 (1997) 667-677; Planta 202 (1997) 1-8.
Onda, T. *et al.*, Langmuir 12 (1996) 2125-2127.

Water Repellency (Hydrophobicity)

Surface Chemistry

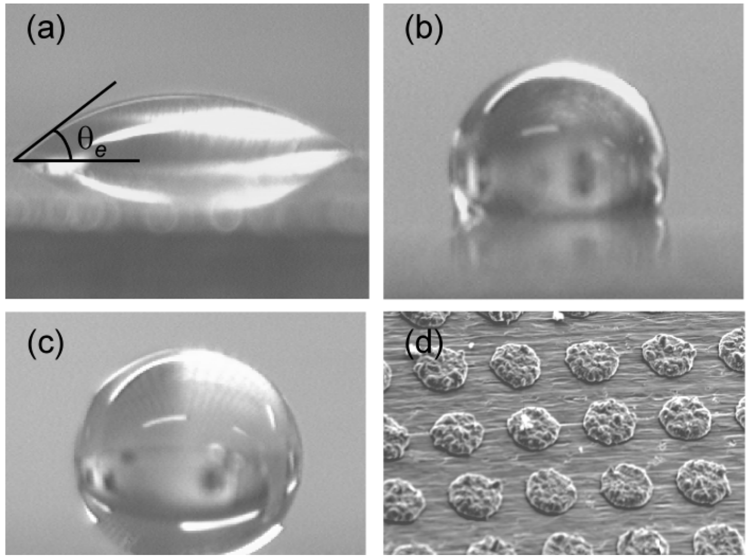
- Terminal group determines whether surface is water hating
- Hydrophobic terminal groups are Fluorine (F) and Methyl (CH_3)

Contact Angles



- Characterize hydrophobicity
- Water-on-Teflon gives ~ 115^o
- 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

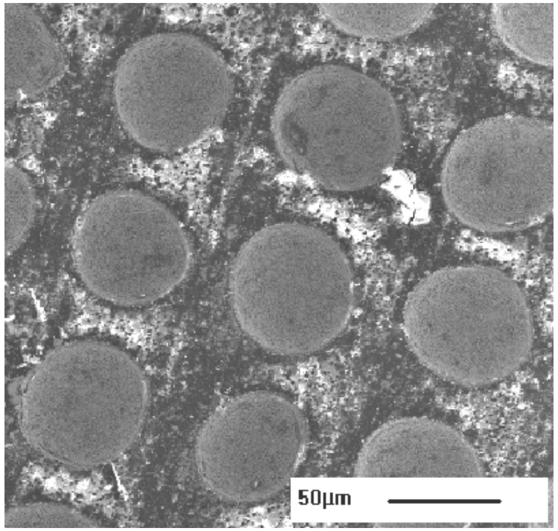
(d) "chocolate-chip-cookie" surface

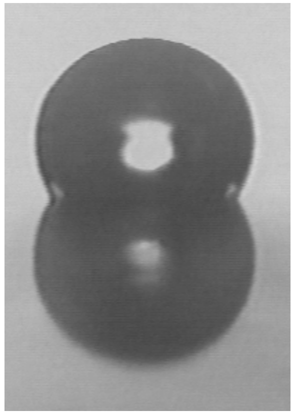
Superhydrophobicity is when θ>150^o
(and contact angle hysteresis is low)

Superhydrophobicity - Man-Made Examples

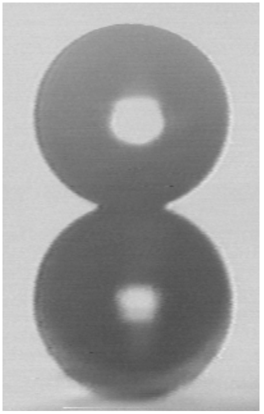
Etched Metal | **Deposited Metal** | **Polymer Microposts**

Etched Metal



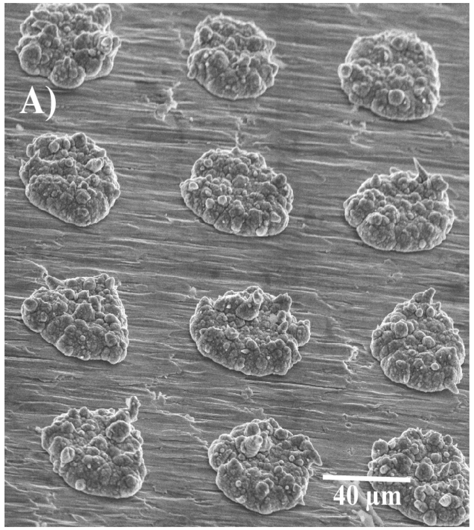


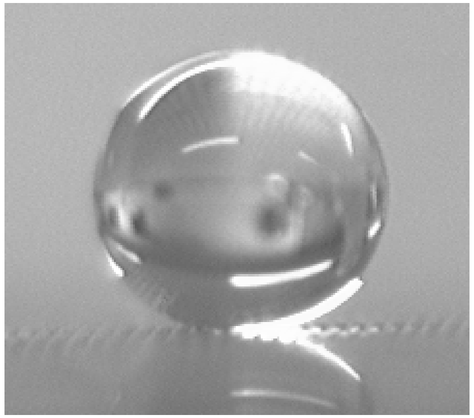
Flat & hydrophobic



Patterned & hydrophobic

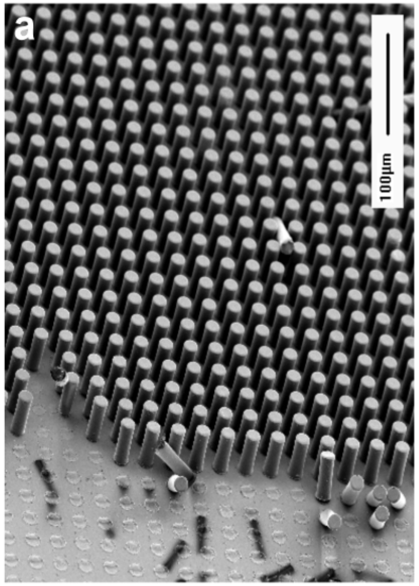
Deposited Metal

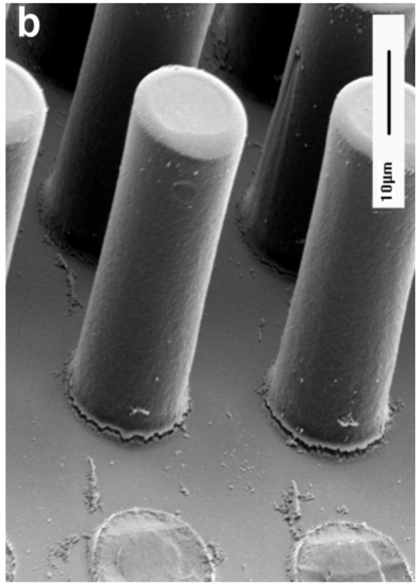


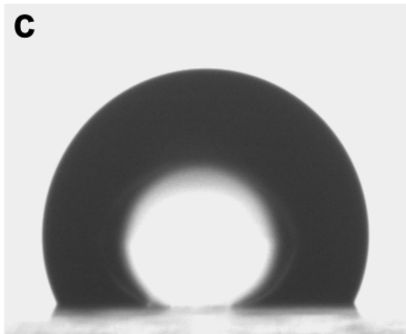


Patterned & hydrophobic

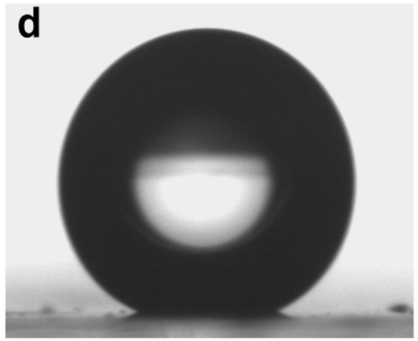
Polymer Microposts







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.

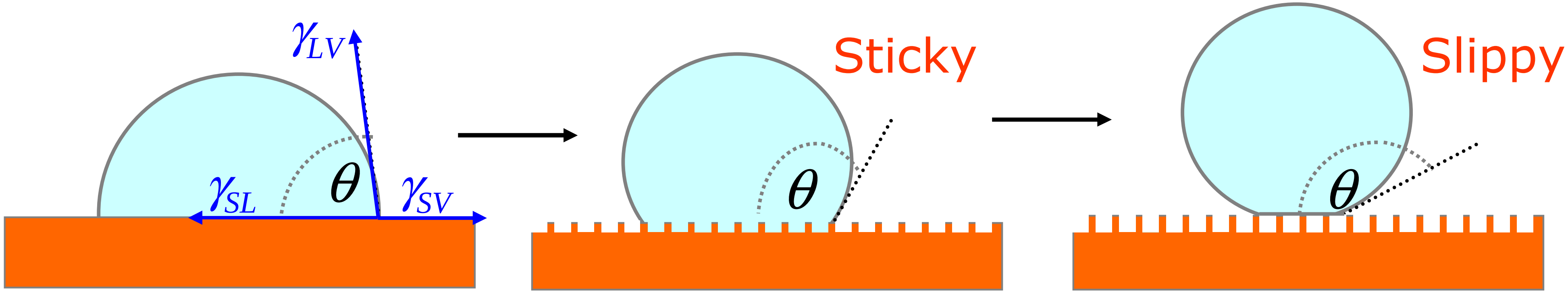
Topography & Wetting: Theory

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

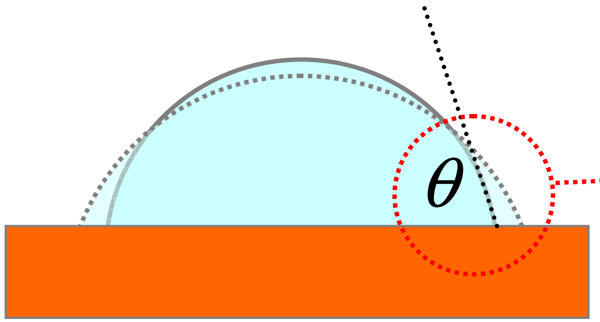
f_s = solid surface fraction

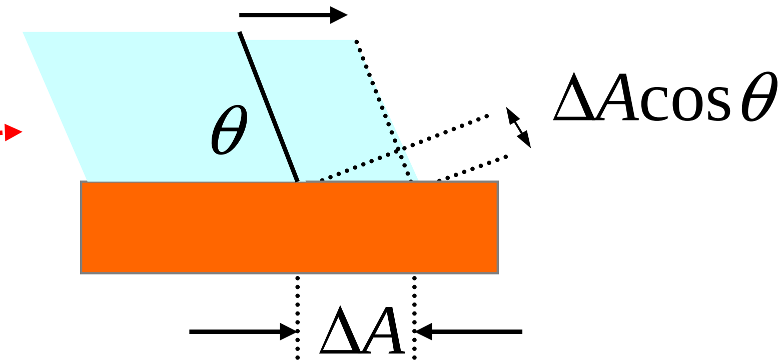
References Cassie, A. B. D.; Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. Wenzel, R. N. Ind. Eng. Chem. 28 (1936) 988-994; J. Phys. Colloid Chem. 53 (1949) 1466-1467.

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

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

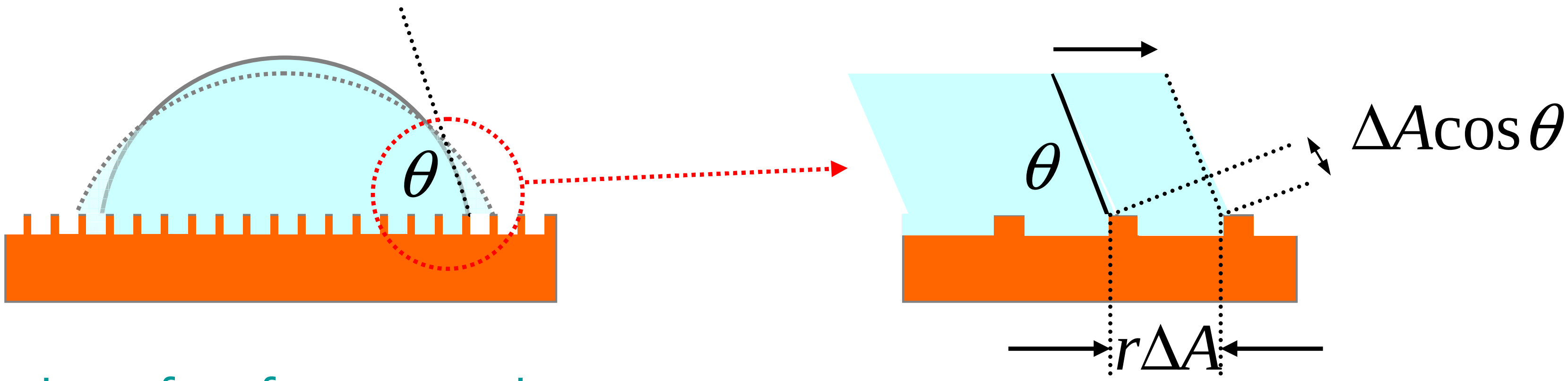
Equilibrium is when $\Delta F(x) = 0$ $\Rightarrow$

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

Young's Law

Same result as from resolving forces at contact line

Topography 1: Wenzel's Equation



Change in surface free energy is

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

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

$$\cos\theta_W(x) = r(x)\cos\theta_e$$

Wenzel Eq

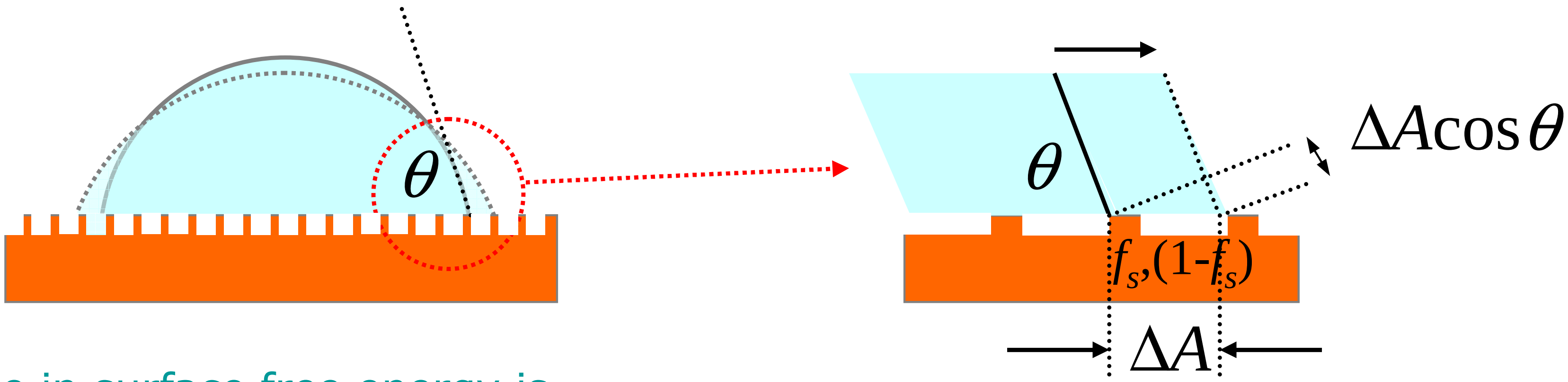
Topography $\Rightarrow$ $r(x)$ = roughness factor

Chemistry $\Rightarrow$ Young's Law θ_e

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

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

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

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

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

Cassie-Baxter Eq

Topography $\Rightarrow$ $f_s\,(x)$= solid surface fraction

Chemistry $\Rightarrow$ Young's Law θ_e

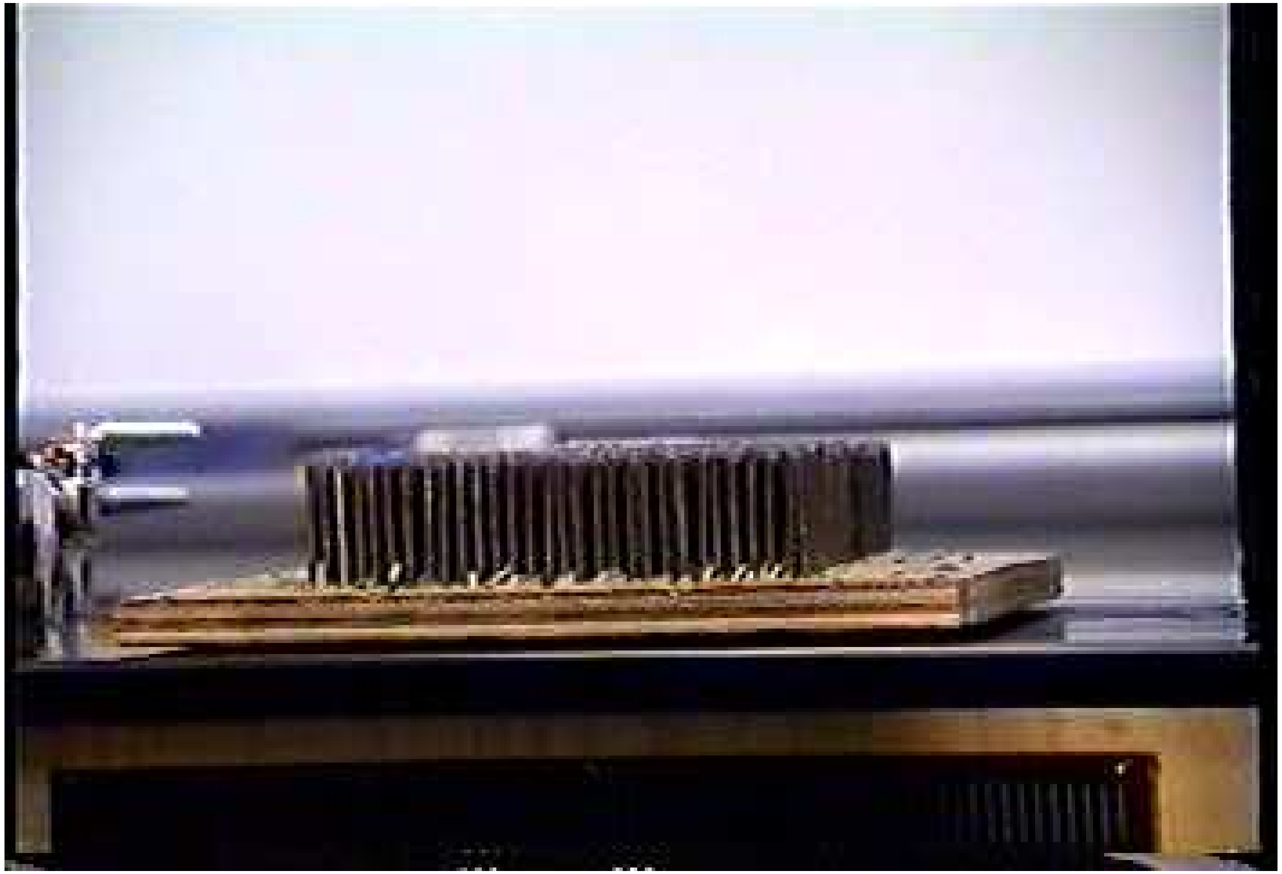
Air gaps $\Rightarrow$ cos(180°) = -1

Simplistic view: Weighted average using $f_1(x)\cos\theta_1(x)$ and $f_1(x)\cos\theta_1(x)$

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

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.

Fakir’s Carpet - “Bed of Nails” Effect



Balloon on a Bed of Nails

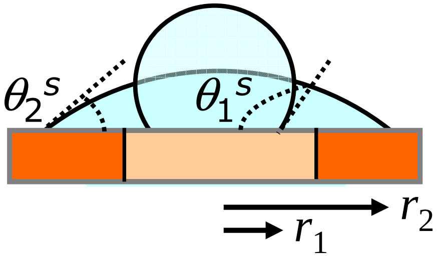
But …. liquid skin interacts with solid surfaces and “nails” do not need to be equally separated. A useful analogy, but it is not an exact view.

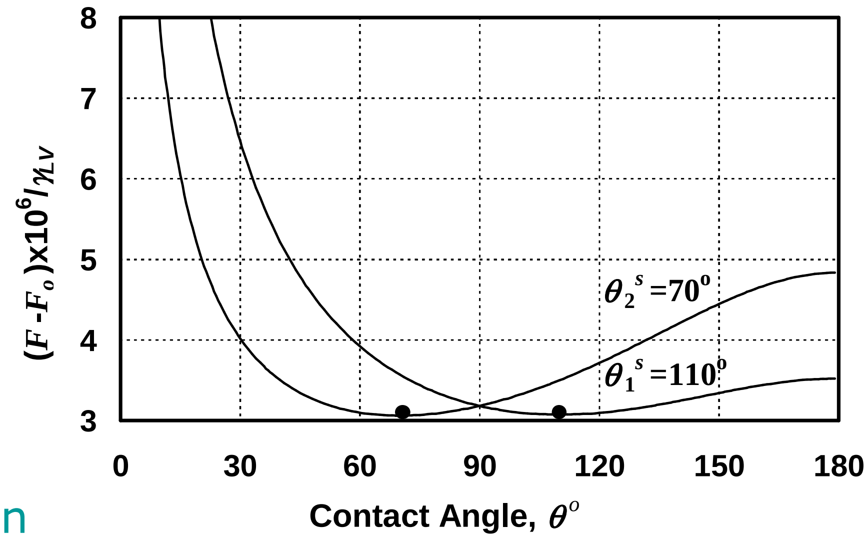
Acknowledgement Wake Forest University

1D Pictures to 2D Cassie-Baxter Surfaces

Isolated Defect Surface

Surface has θ_1^s=110°, θ_2^s =70°

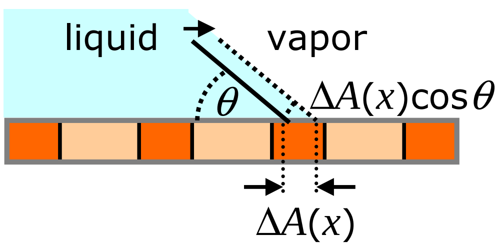


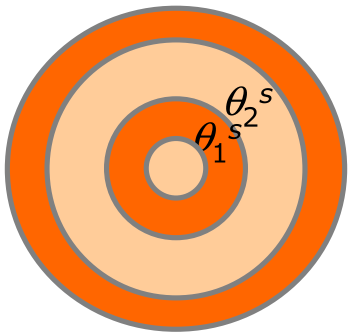


Two droplet configurations exist with min in

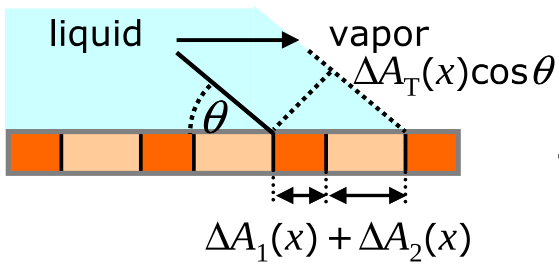
their local surface free energy corresponding to the same droplet volume

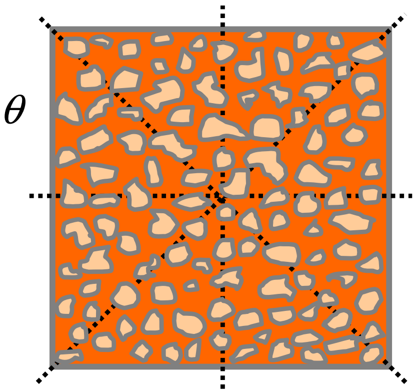
Radial Symmetry





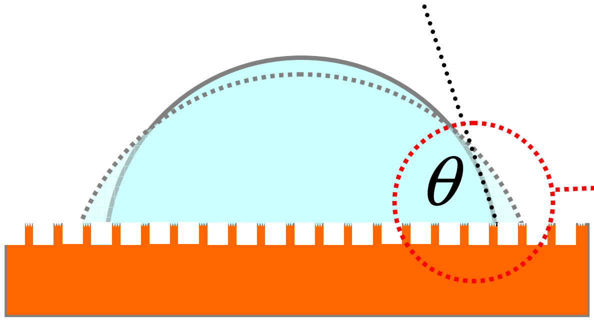
Random Surface

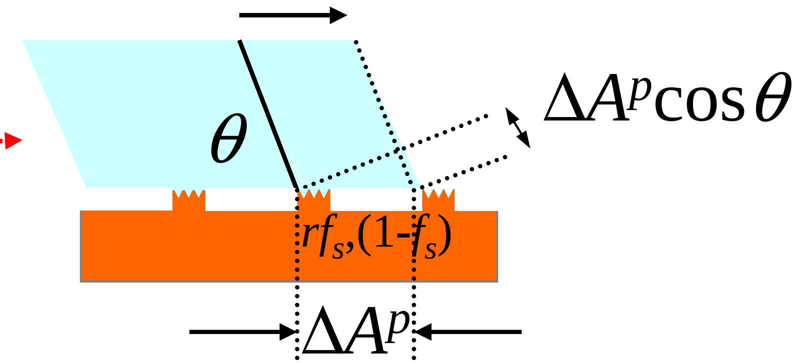




References Gao, L.C.; McCarthy, T.J. Langmuir 23 (2007) 3762-3765.
McHale, G. Langmuir 23 (2007) 8200-8205.

Topography 4: Top-Filled Dual Scale Surfaces





Change in surface free energy is

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

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

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

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

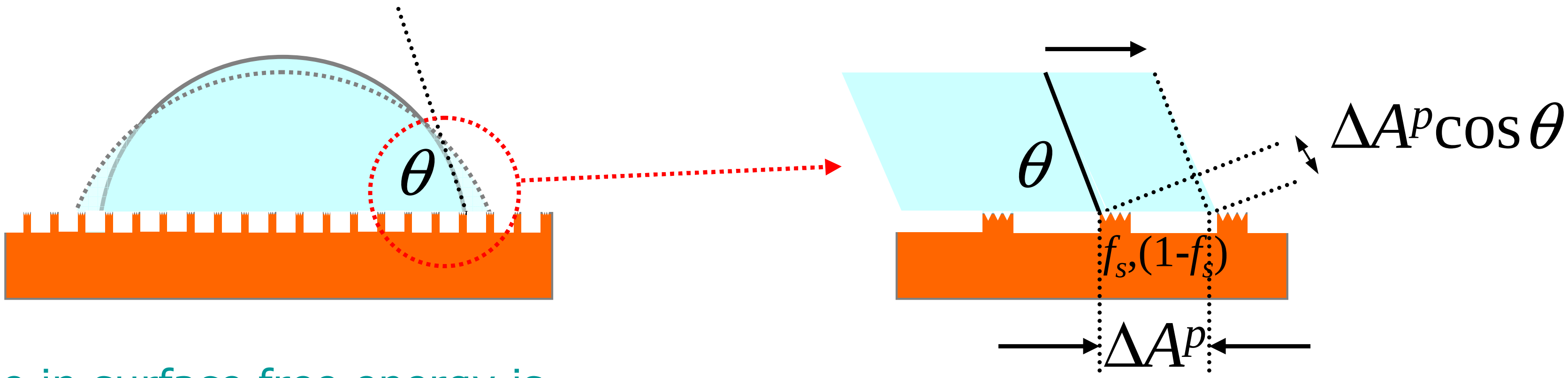
$r = \Delta A_{SL} / \Delta A_{SL}{}^P$ = roughness of "tops" of features

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

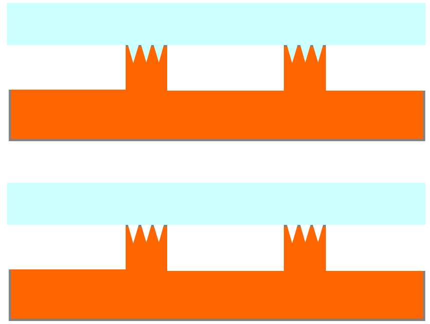
Transformation via Cassie-Baxter and then by Cassie-Baxter again

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

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

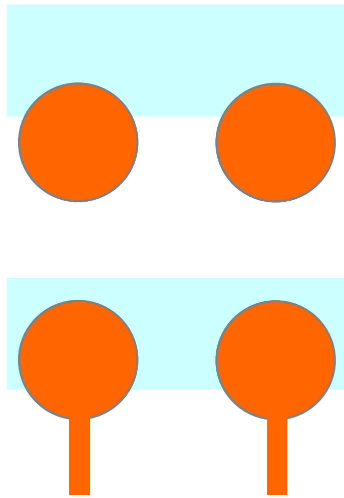
Complex Topography

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

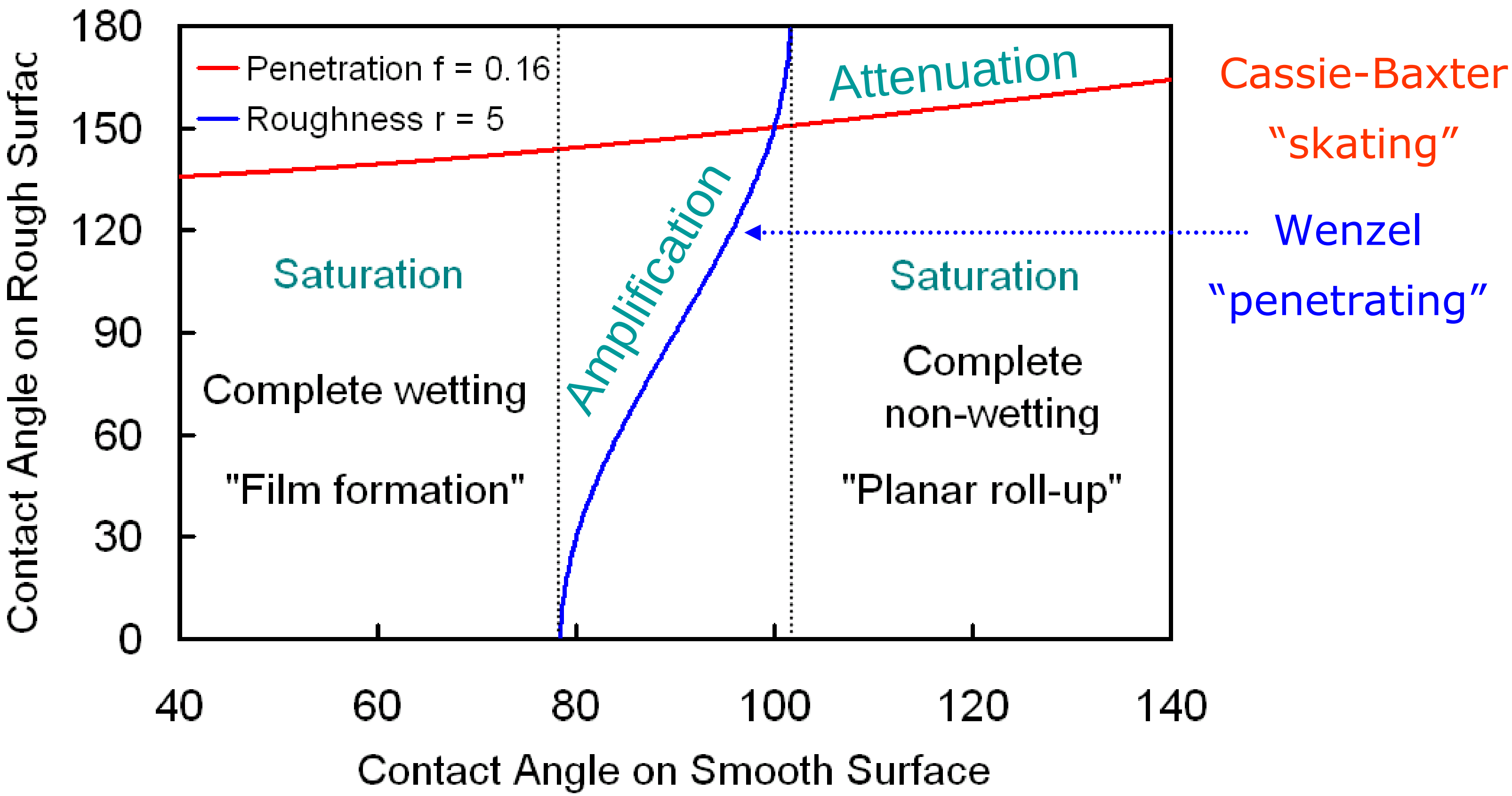
- Roughness, $r(x)$, and solid surface fraction, $f_s(x)$, become dependent on contact line position[4], x
- Can create gradients in superhydrophobicity[5]

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.

Superhydrophobicity

Consequences

Theory: Amplification, Attenuation, Saturation



<u>Roughness/Topography</u>

θ_e^s > threshold ⇒ enhances repellence

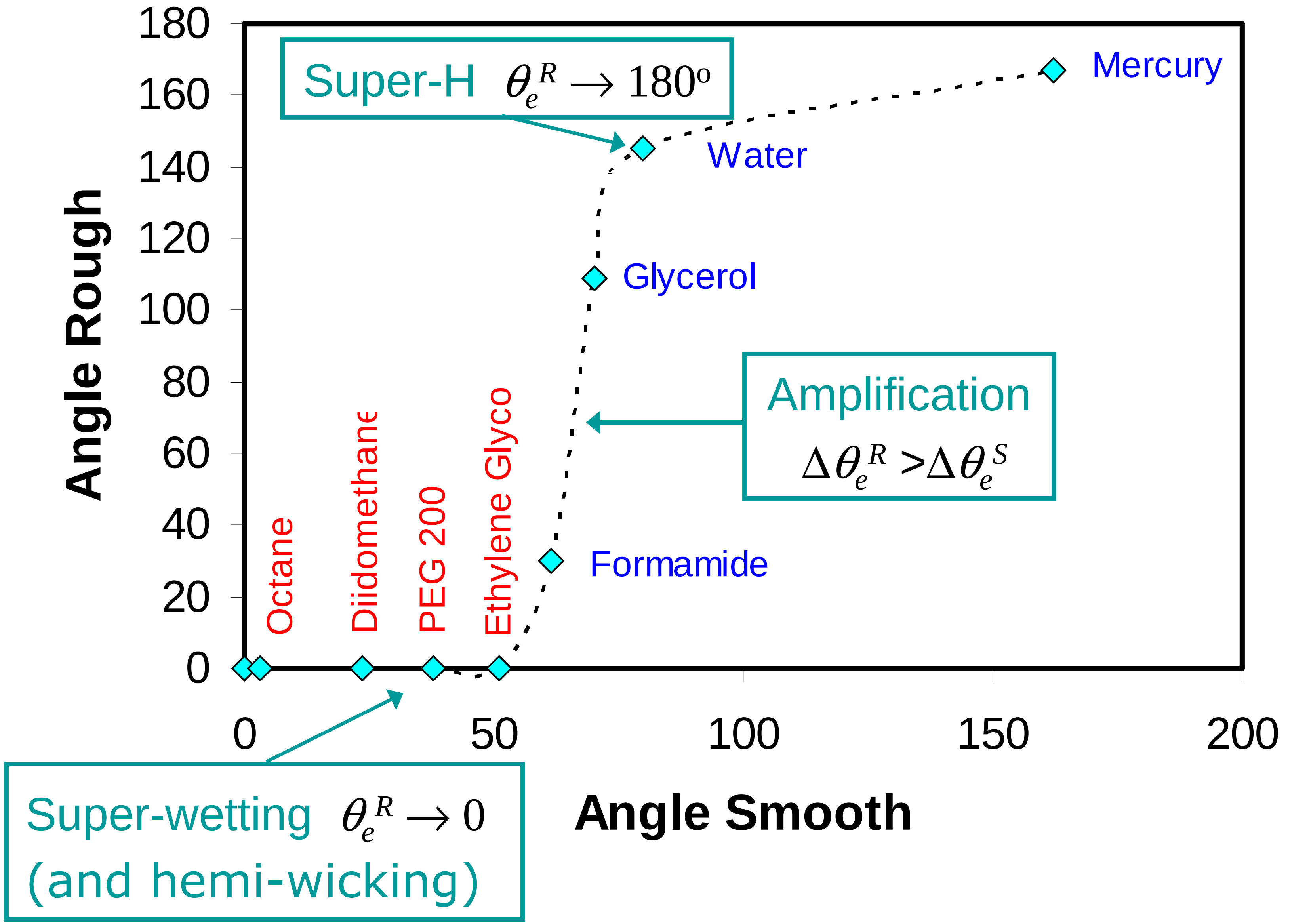
θ_e^s < threshold ⇒ enhances film formation

<u>Superhydrophobic</u>

"Skating case" ⇒ most existing examples

Pressure ⇒ transition to penetrating

Liquids on a Superhydrophobic Surface



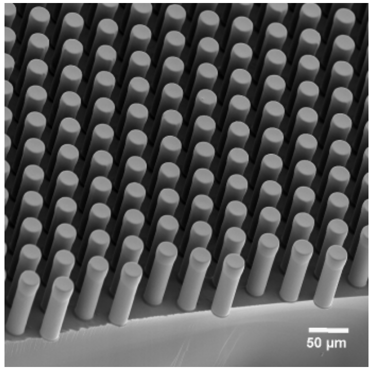
References McHale, G. *et al.*, Analyst 129 (2004) 284-287; Langmuir 20 (2004) 10146-10149.

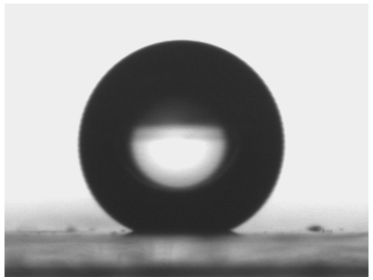
Skating-to-Penetrating Transition

Micro-Structured Surface

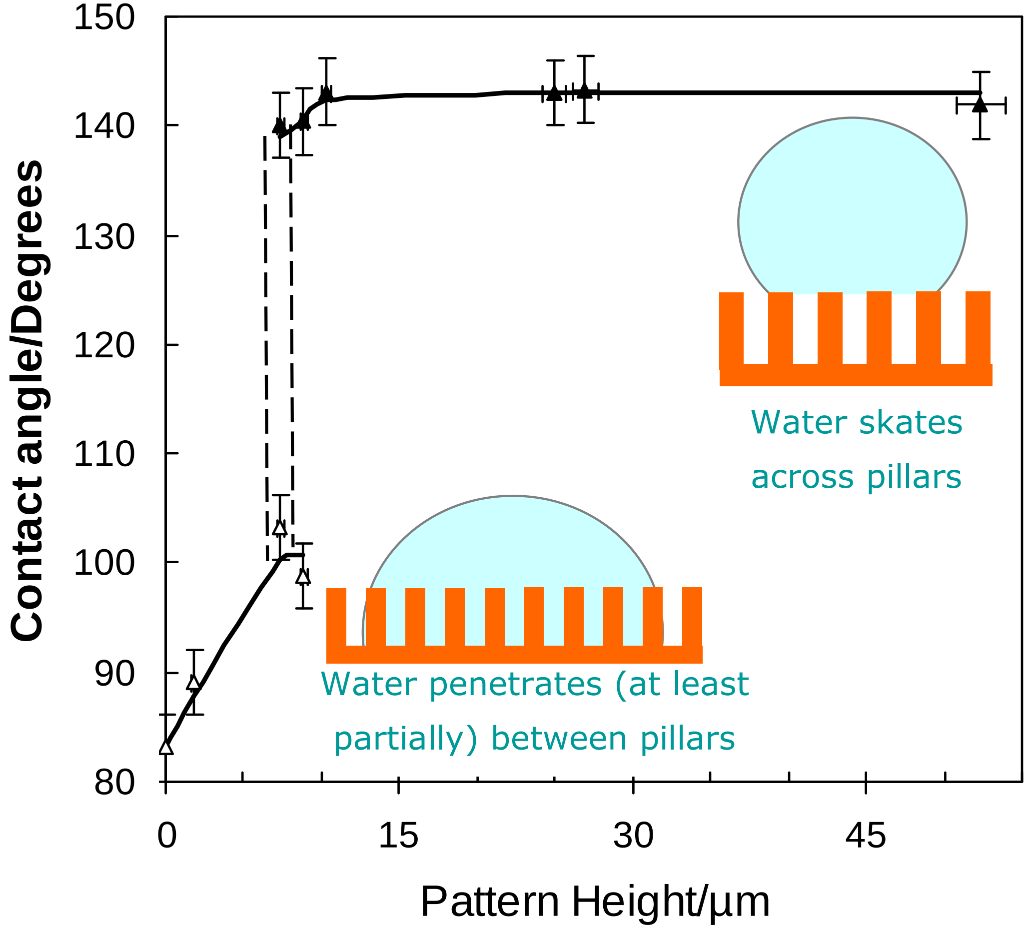
SU-8 pillars[1] 15 μm

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*).

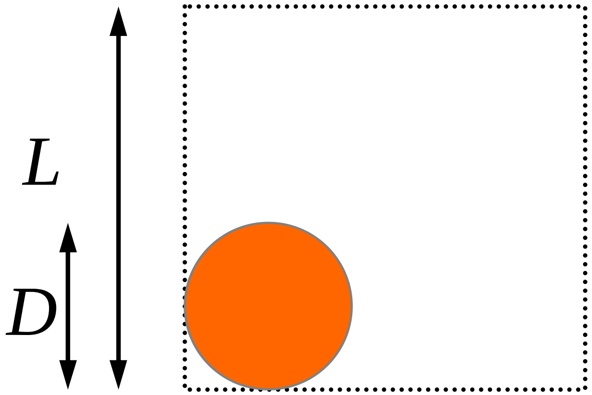
References Shirtcliffe, N.J. *et al.*, J. Micromech. Microeng. 14 (2004) 1384-1389. Bico, J. *et al.*, Coll. Surf. A206 (2002) 41-46. Quéré, D. Physica A313 (2002) 32-46; Ishino, C.; Okumura, K.; Quéré, D. Europhys. Lett. 68 (2004) 419-425.

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 $\theta_{CB}=152^o$

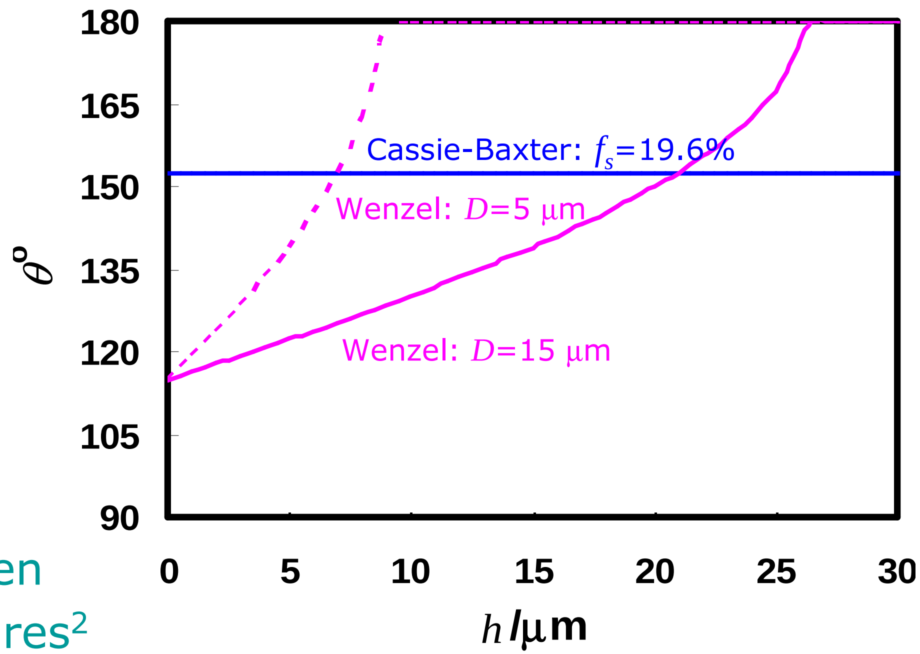
For penetrating transition:

$D=15$ 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]

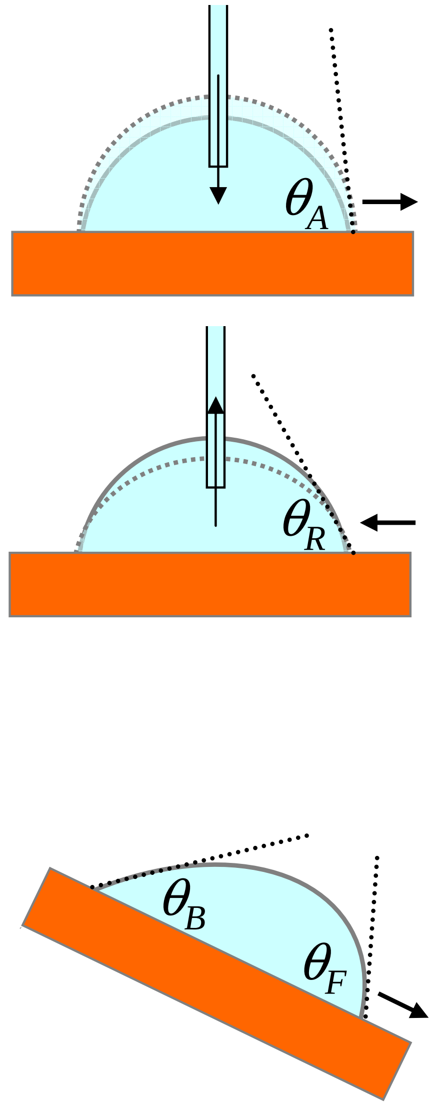


References [1]Bico, J. *et al.*, Coll. Surf. A 206 (2002) 41-46. De Gennes, P.G.; Brochard-Wyard, F.; Quéré, D. "Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves" Springer-Verlag (2003). [2] Wier, K.A.; McCarthy, T.J. Langmuir 22 (2006) 2433-2436.

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]

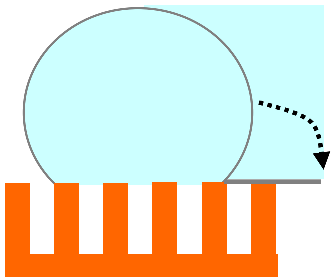
Assumes contact area changes are dominant effect and amplify an intrinsic hysteresis of the surface

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



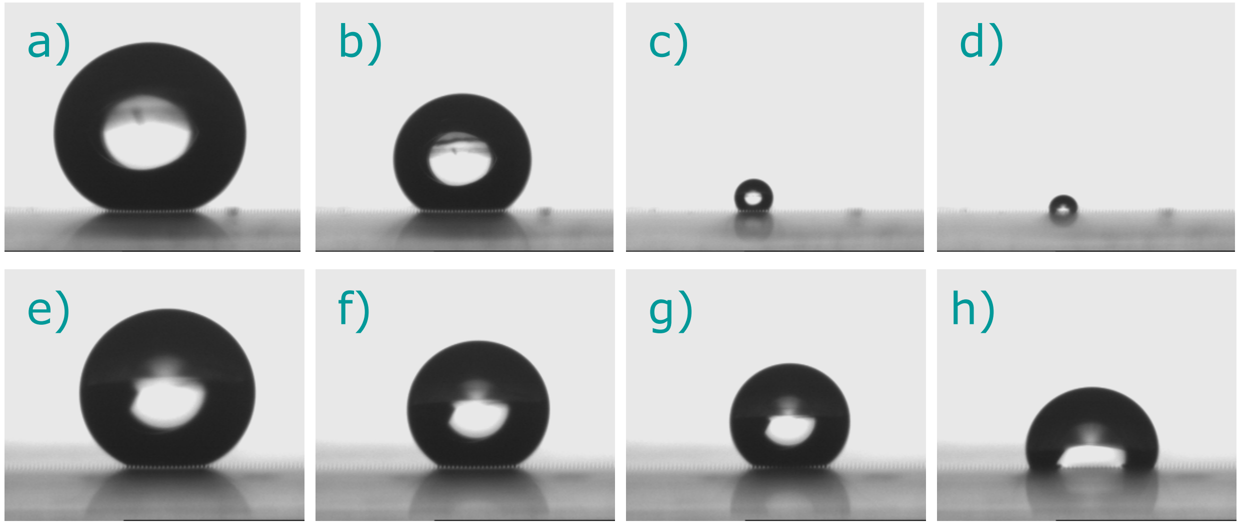
References [1]Quéré, D.; Lafuma, A.; Bico, J. Nanotechnology 14 (2003) 1109-1112. [2] Öner, D.; McCarthy, T.J. Langmuir 16 (2000) 7777-7782; 22 (2006) 6234-6237. [3]McHale, G. *et al.*, Langmuir 20 (2004) 10146-10149. [4]Kusumaatmaja, H.; Yeomans, J.M. Langmuir 23 (2007)

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

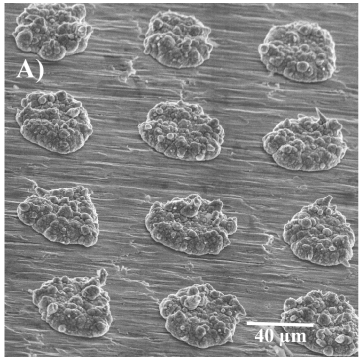
Yeomans[2] suggests three processes during evaporation:

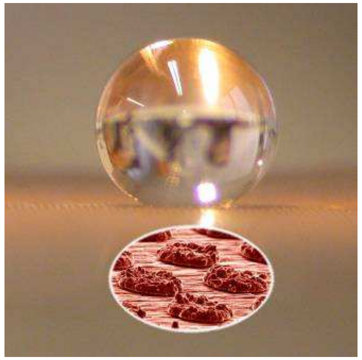
1. the contact line retreats inwards across the surface
2. the free energy barrier to collapse vanishes and the drop moves smoothly down the posts (long posts)
3. the drop touches the base of the surface patterning and immediately collapses (short posts) – critical curvature of droplet $\propto b^2/h$,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

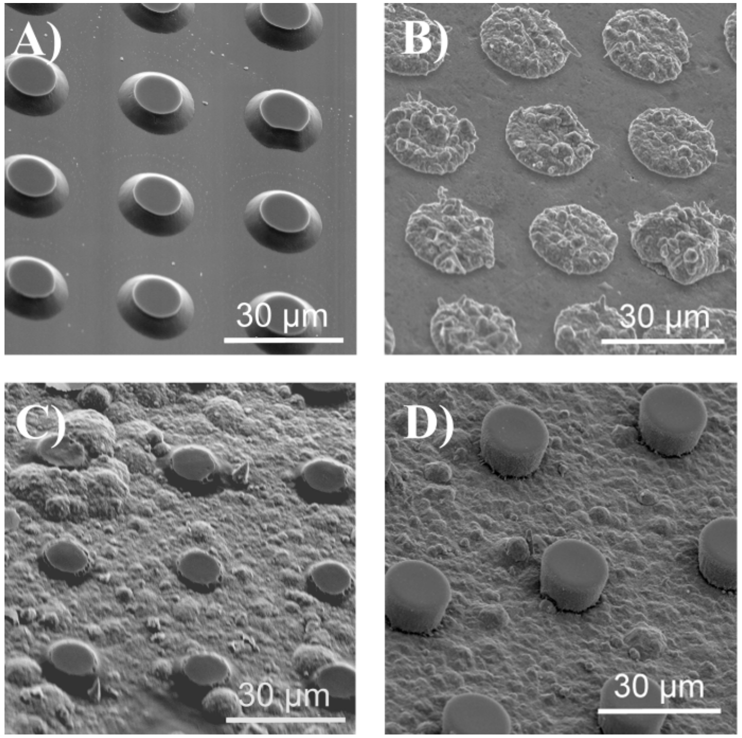
3D simulation suggests the drop can depin from all but the peripheral posts, so that its base resembles an inverted bowl.

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.,

Double Length Scale Systems

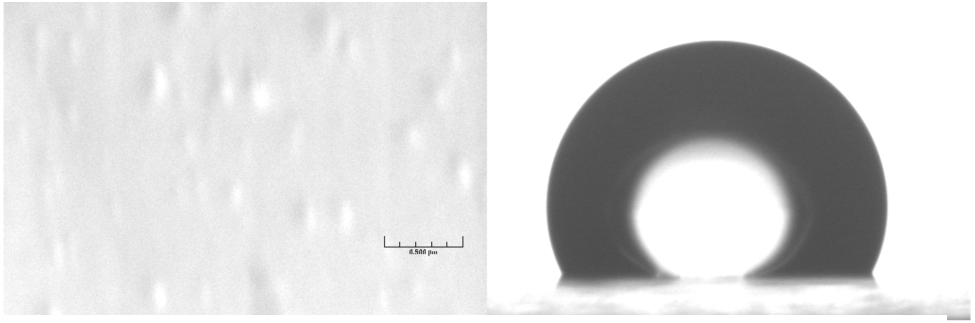




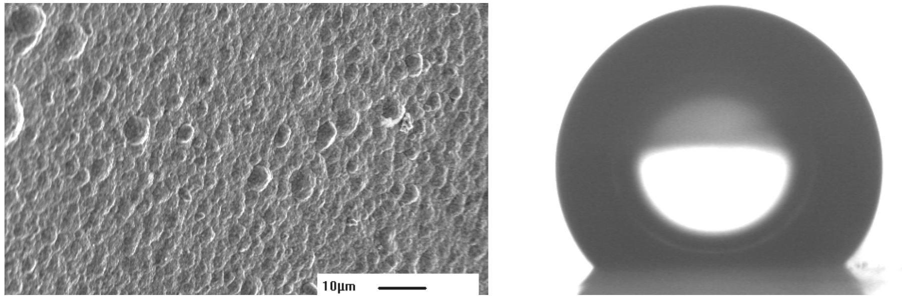


Two length scales is extremely effective

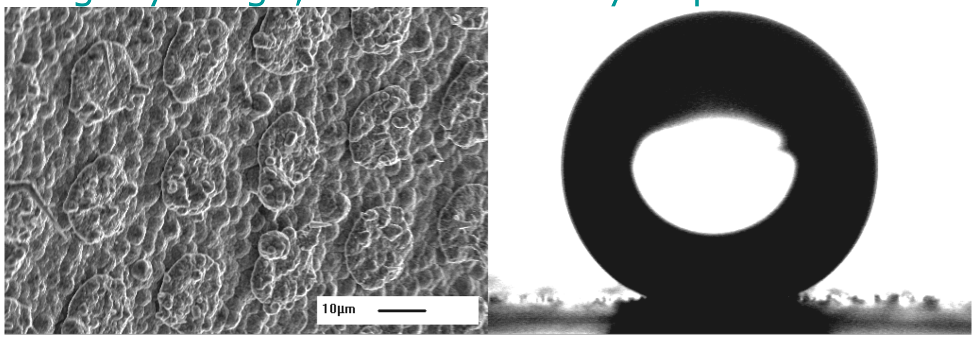
Smooth and hydrophobised: 115°



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.

Path Definition & Self-Actuated Motion

Gradients in Contact Angle

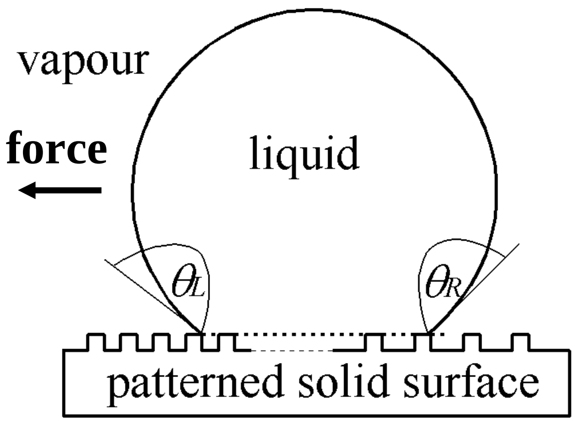
Make contact angle depend on position and surface chemistry $\theta(\underline{x}, \theta_e^s)$

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 $\theta(r) = 110^o \rightarrow 160^o$

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*.

Superhydrophobicity

Unexpected superhydrophobicity?

Leidenfrost Effect

Perfect Superhydrophobicity?

Cassie-Baxter with solid fraction f_s=0

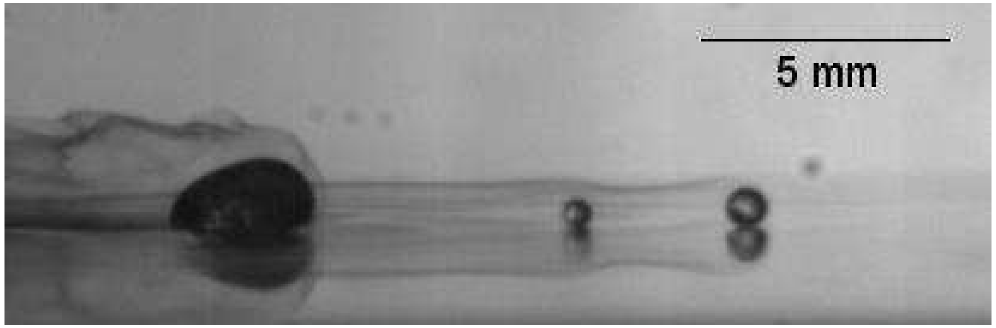
Droplet floats on a layer of vapor: $\cos\theta_{CB}=0 \times \cos\theta_e-(1-0) \Rightarrow \theta_{CB}=180^o$

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

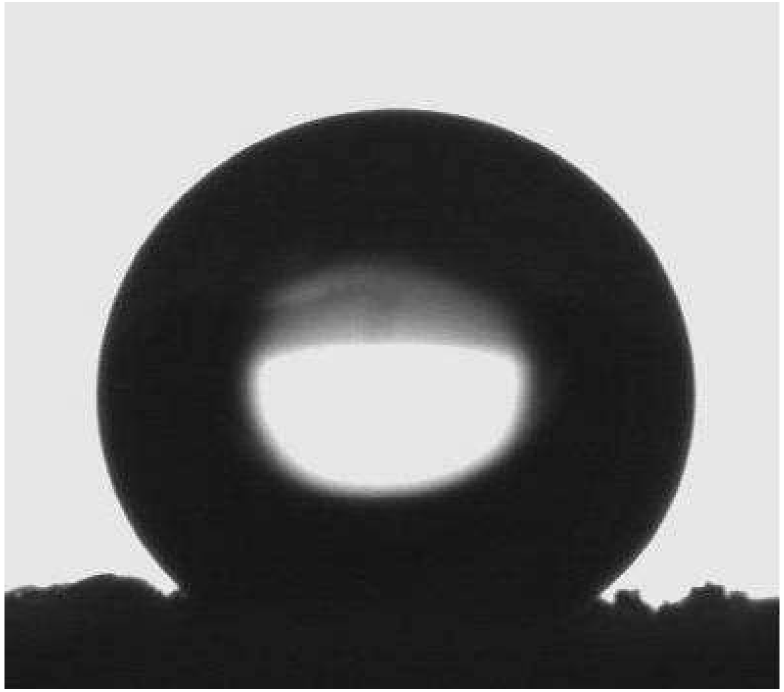
Leidenfrost Puddle

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

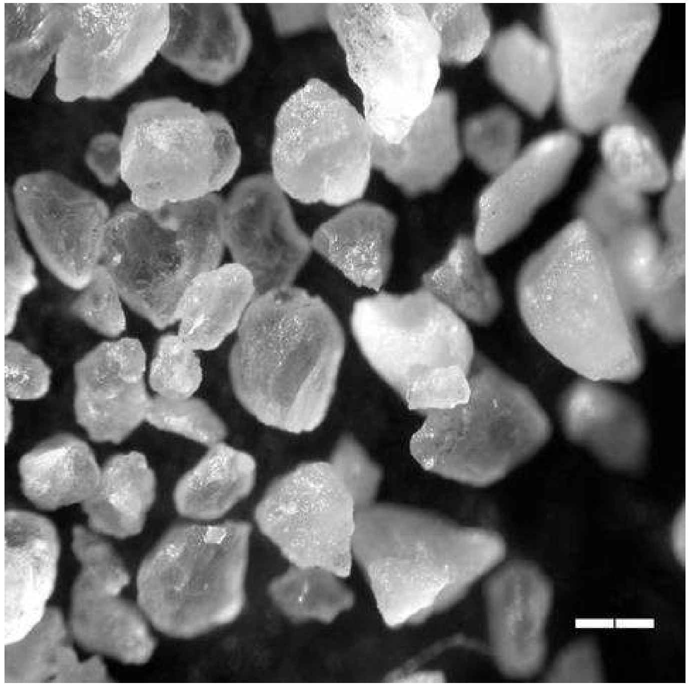
Reference Biance, A.L.; Clanet, C.; Quéré, D. Phys. Fluids. 15 (2003) 1632-1637.
http://www.pmmh.espci.fr/fr/gouttes/recherche/

Super Water-Repellent Sand/Soil

Sand with 139°



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)

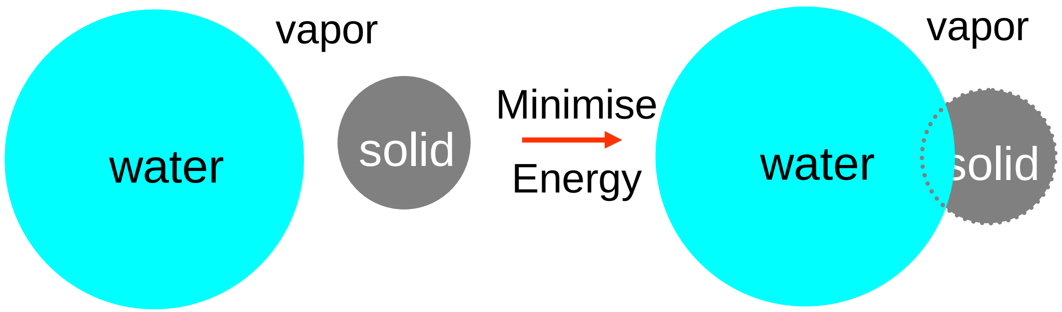
References McHale, G. *et al.*, Eur. J. Soil Sci. 56 (2005) 445-452; Hydrol. Proc. 21 (2007) 2229-2238.

Liquid Marbles

Loose Surfaces

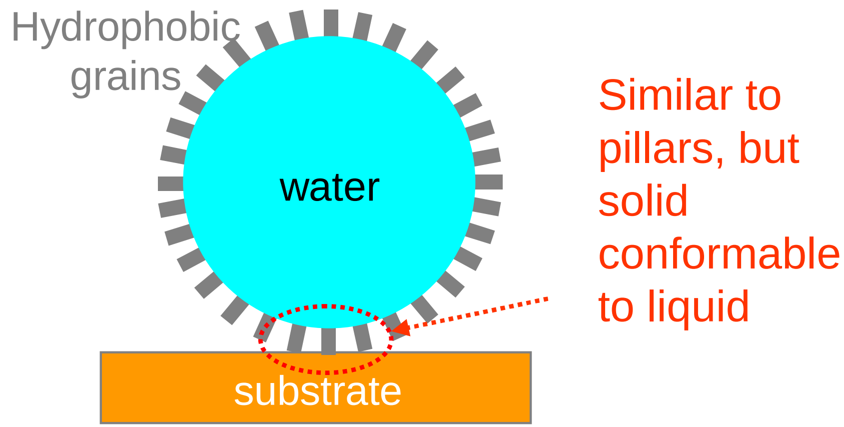
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

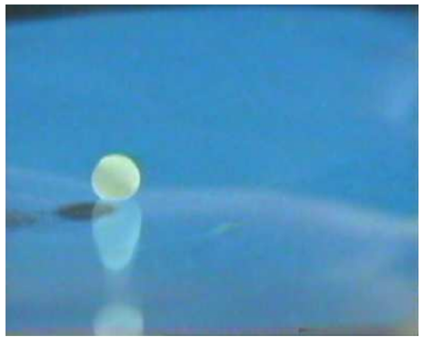
Hydrophobic Grains and Water



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

Energy is always reduced on grain attachment





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. Gao, L.C.; McCarthy, T.J. Langmuir 23 (2007) 10445-10447.

Superhydrophobicity: Plastron Respiration

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

Underwater Breathing:

BBC Radio 4 Broadcast

Edward Cussler, Professor of Chemical Engineering (University of Minnesota)

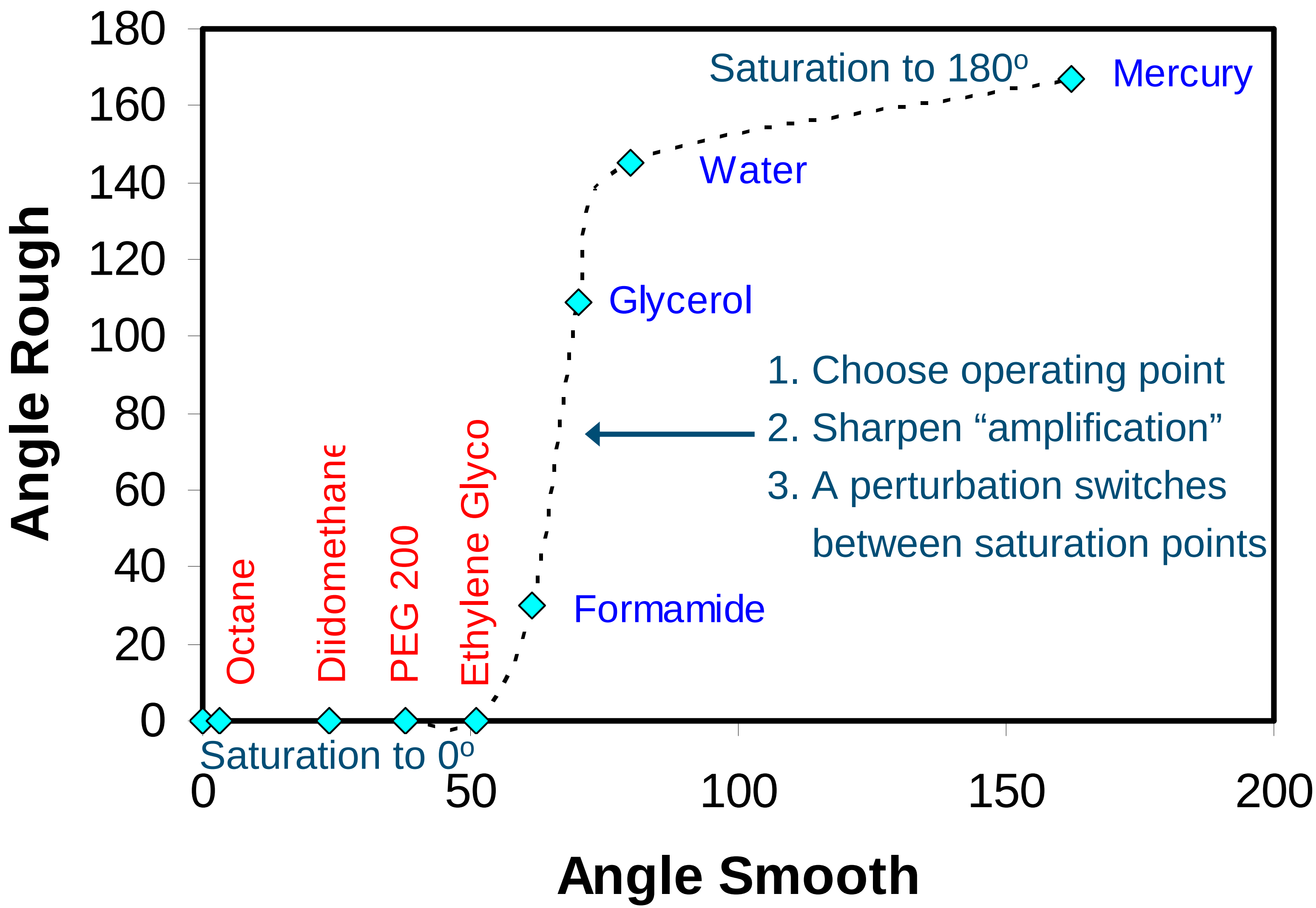
Speaking 9th February 2006

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.

Porosity, Spreading and Imbibition

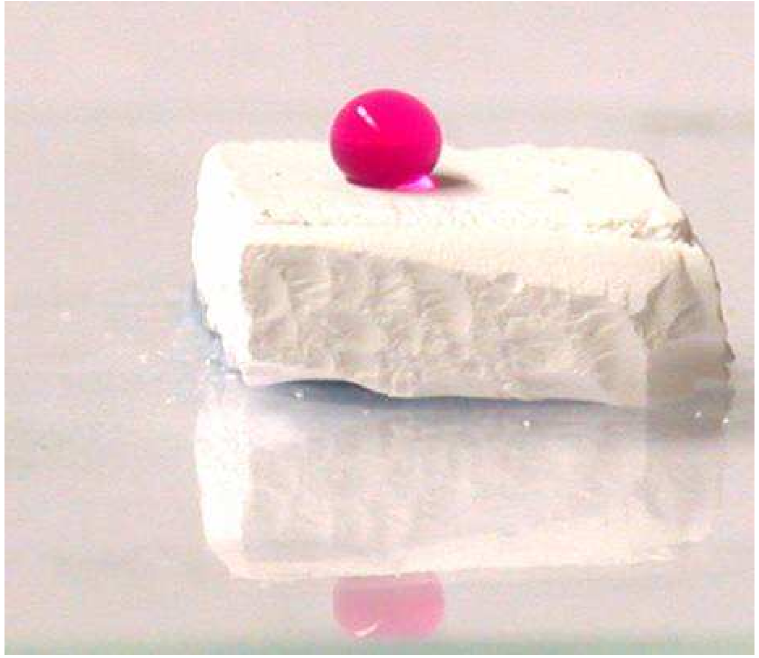
Superwetting, Superspreading, Hemi-wicking and Porosity

Digital Switching



References 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

Mechanisms for Switching

- 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)

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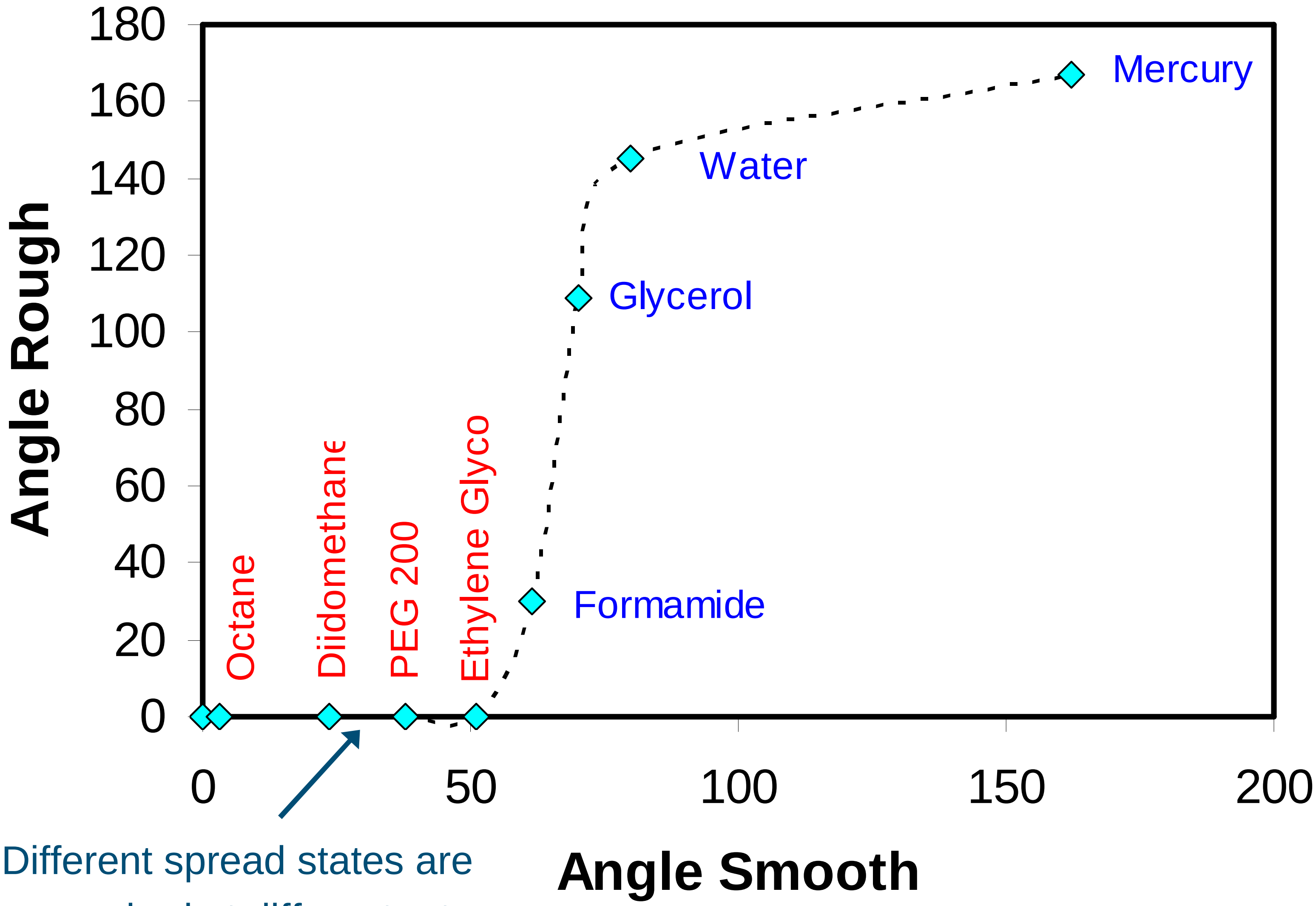
Super-spreading



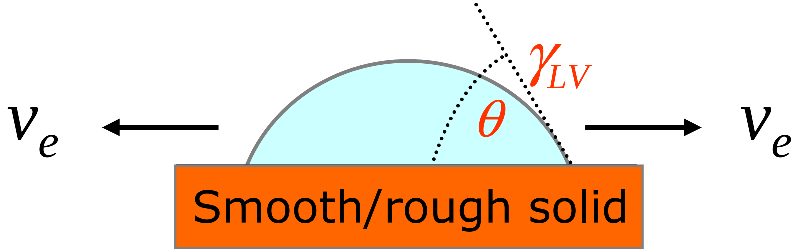
Different spread states are approached at different rates

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

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

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

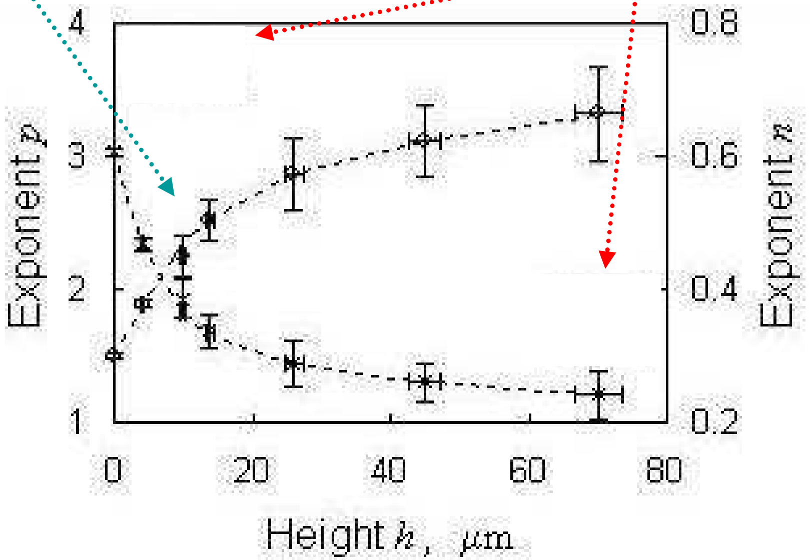
Tanner's Law exponents *p* and *n*

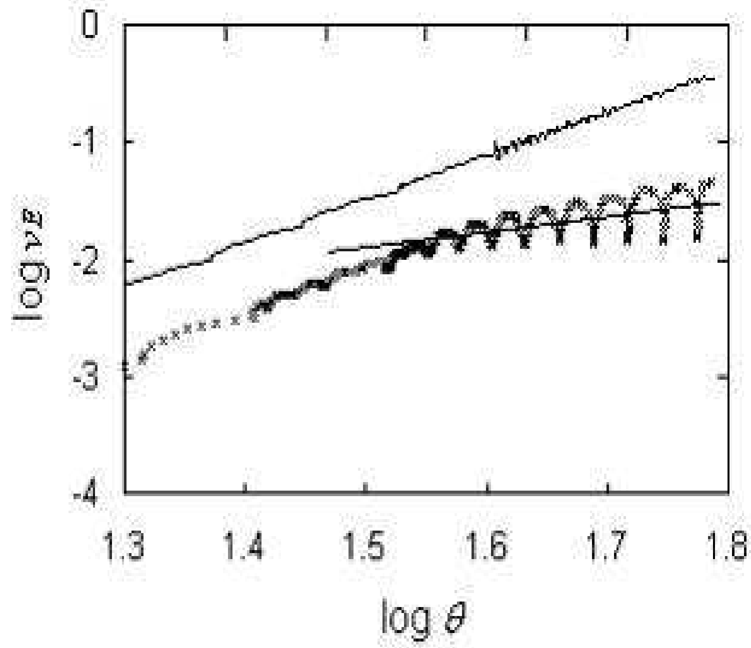
(cubic to linear transition)

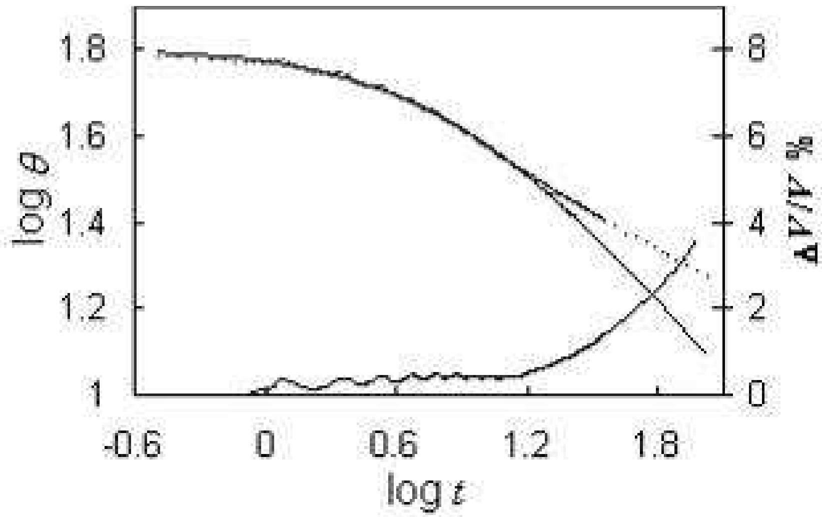
$$v_E \propto v^* \theta^p \qquad \theta \propto \left(\frac{V^{1/3}}{v^*}\right)^n \frac{1}{(t+t_o)^n}$$

Effect of substrate on PDMS

Effect of substrate on water







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

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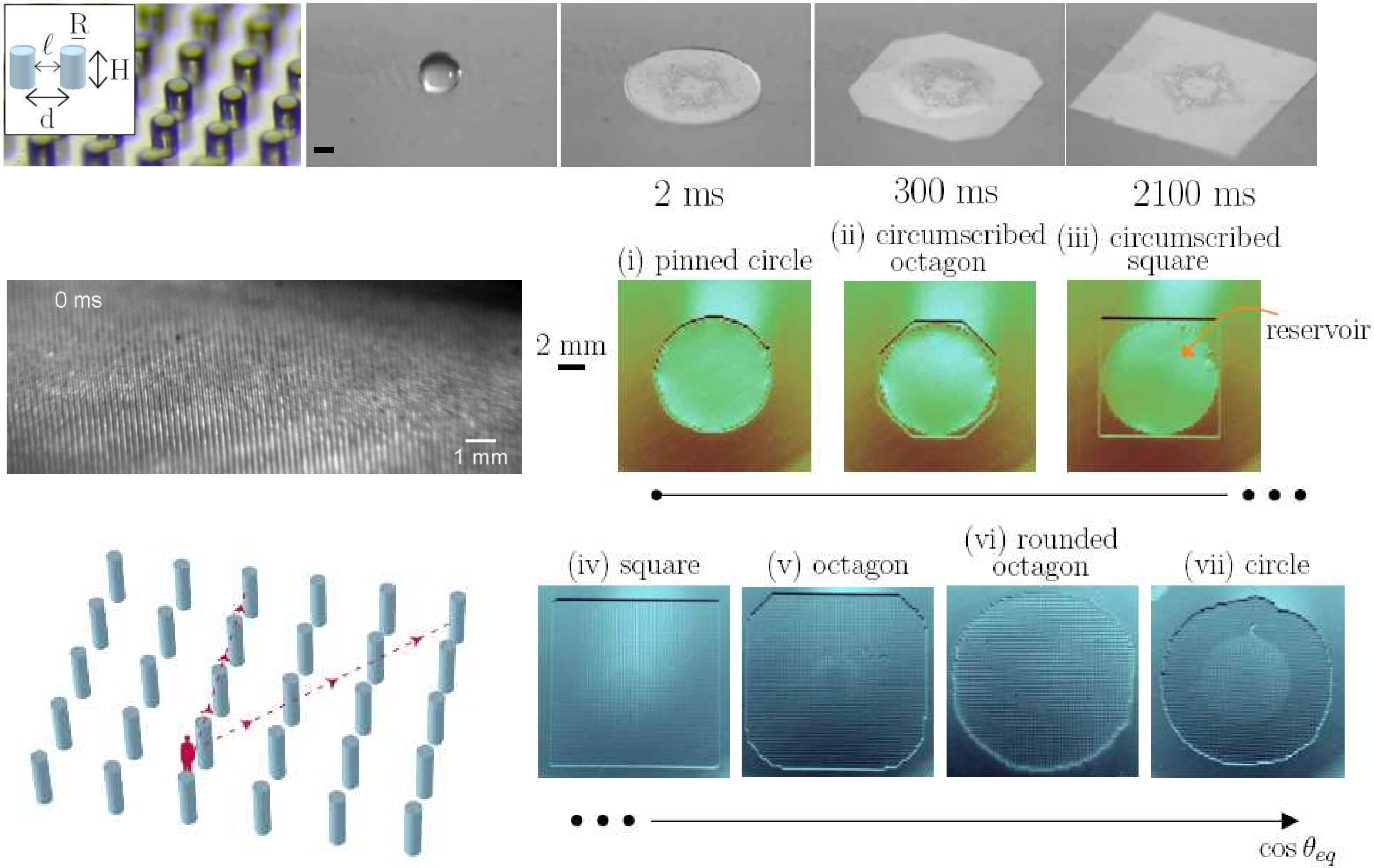
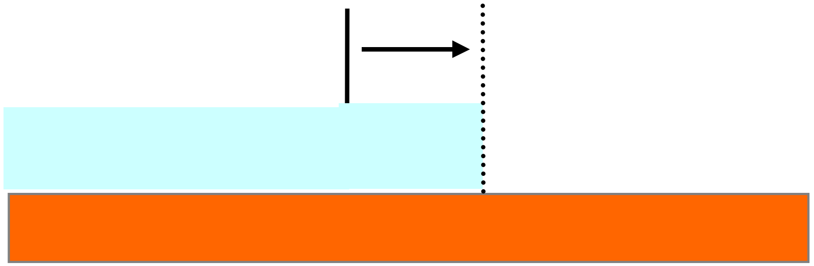
Topography Induced Wetting: Hemi-Wicking



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.

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

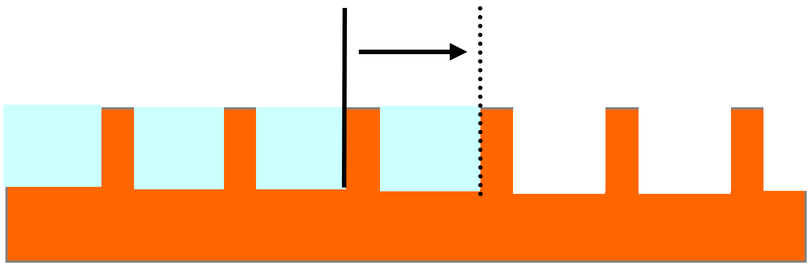
Spreading is when $\Delta F < 0 \quad \Rightarrow$

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

i.e. critical angle is

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

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 $\Delta F < 0 \quad \Rightarrow$

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

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

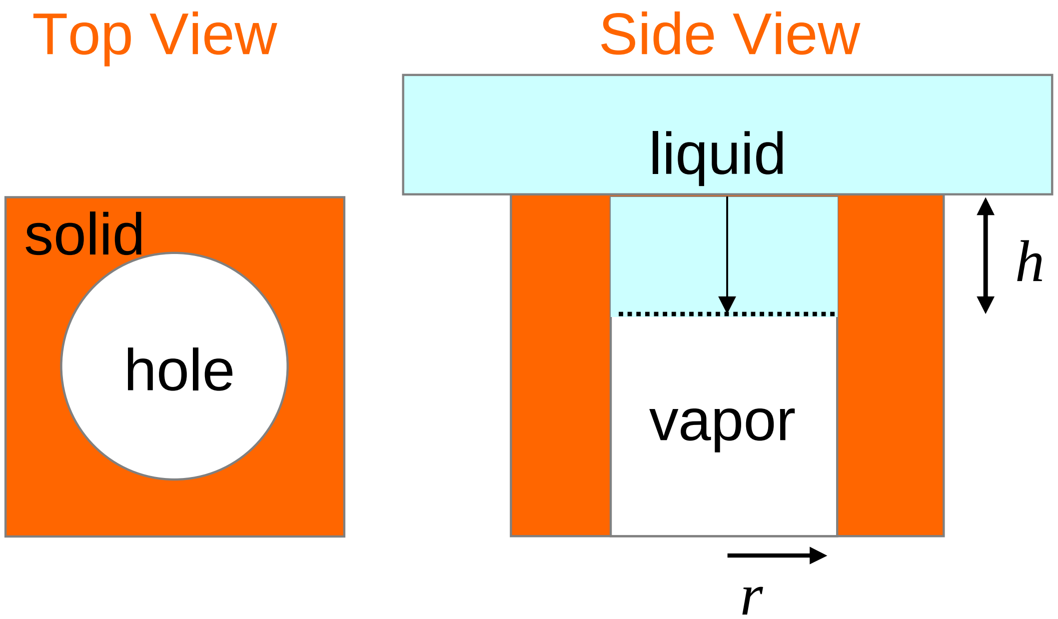
(usual porous media is equivalent to $r \to \infty$)

References Bico, J. *et al.*, Coll. Surf. A206 (2002) 41-46. Quéré, D. Physica A313 (2002) 32-46.

Cylindrical Model for Capillary Infiltration

Assumptions

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



Change in surface free energy = solid-liquid energy per unit area × gain of wall area minus solid-vapor energy per unit area × loss of wall area

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

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

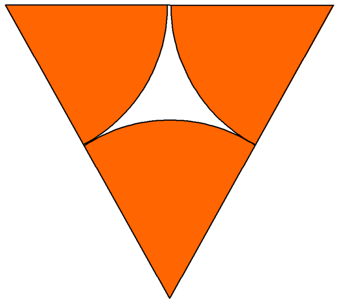
Same result for wetting down sides of posts on a superhydrophobic surface

Transition from Wetting to Porosity

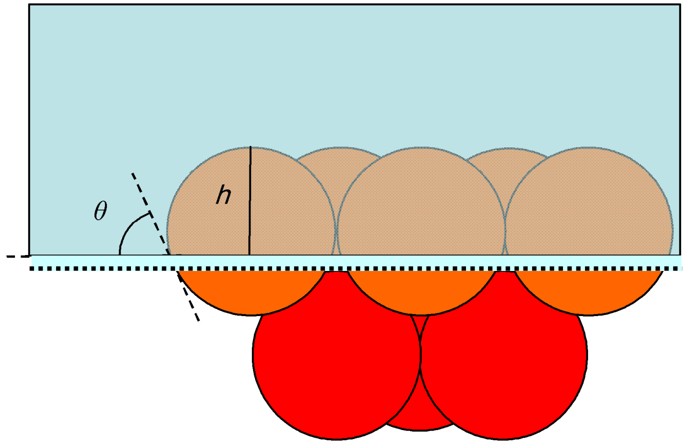
Assumptions

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 <u>provided</u> 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]

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

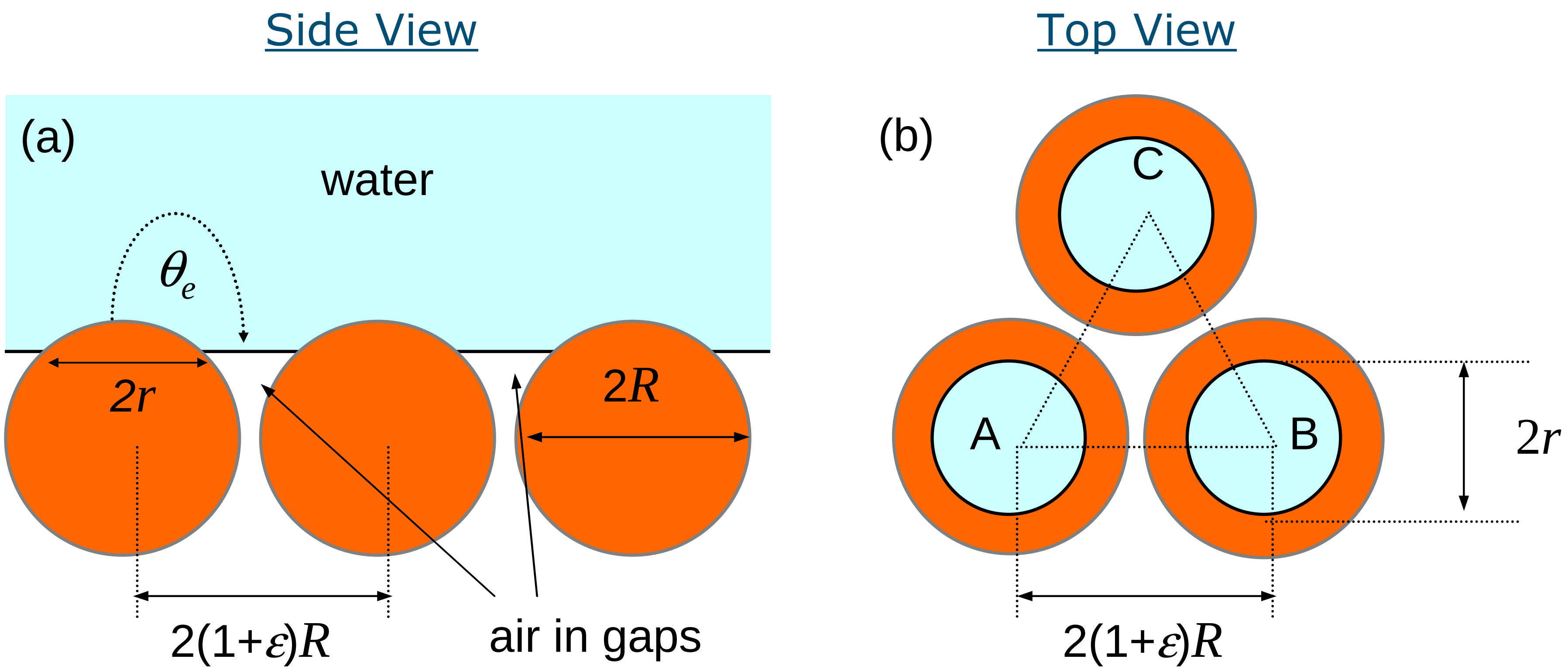
$$h_c = \sqrt{\frac{8}{3}}R = 1.63R$$

$\theta_c = 50.73^o$

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

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

Model of Bead Pack/Soil



Assumptions

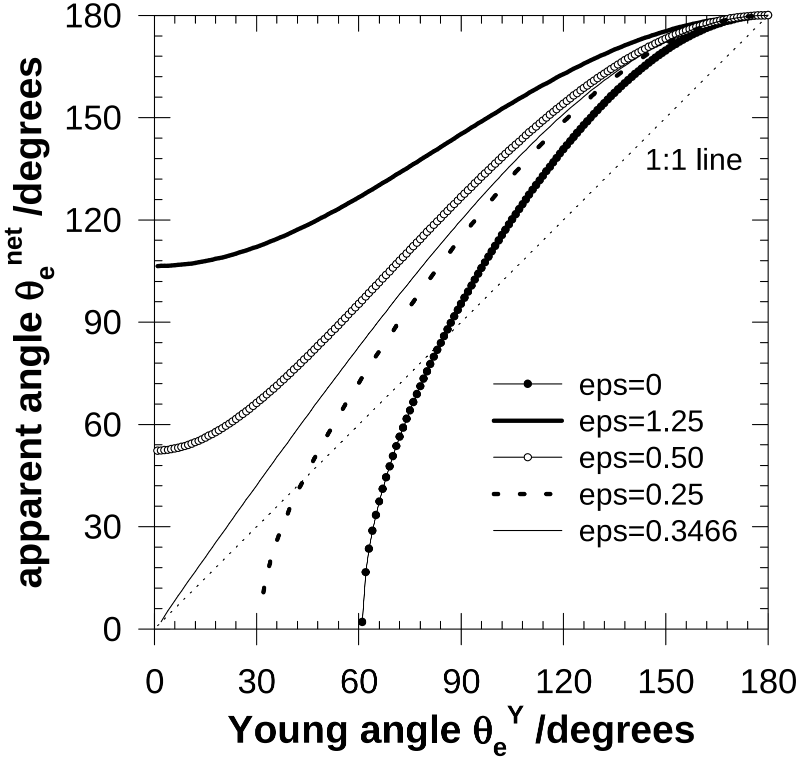
1. Uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges air gaps horizontally between spheres
3. Capillary (surface tension) dominated size regime of gaps<< κ^{-1}=2.73 mm

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).

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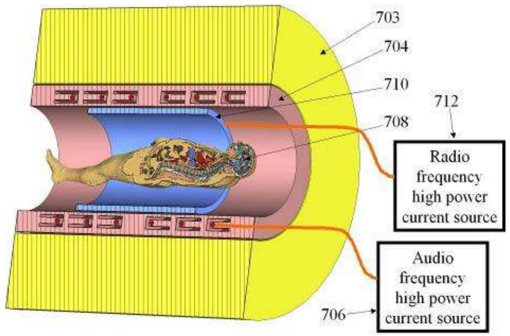
Unilateral NMR/MRI

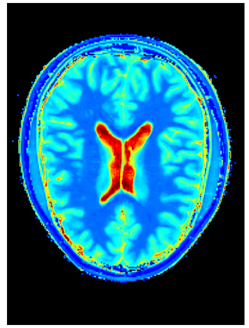
Liquid Penetration and Imbibition

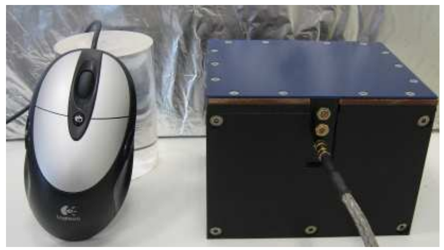
 Reference Bencsik, M.; Adriaensen, H.; Brewer, S.A.; McHale, G. J. Mag. Res. 193 (2008) 32.

NMR, MRI and MR Microscopy

- Nuclear Magnetic Resonance (NMR)
  - Uses intrinsic magnetic moment of nucleus (e.g. proton in hydrogen)
  - Align with external field
  - “Kick-out” out of alignment using rf field
  - Monitor signal recovery
  - Recovery depends on environment
- Magnetic Resonance Imaging (MRI)
  - Use magnetic field gradients to resolve spatially
  - Signal can be deconvolved into an image
  - Most familiar from medical imaging applications
- Magnetic Resonance Microscopy
  - NMR and MRI made small (down to 10 microns)
  - Relatively inexpensive equipment (£30k-£60k)
  - Portable and benchtop use possible
  - Unilateral MRI (e.g. NMR MOUSE®)



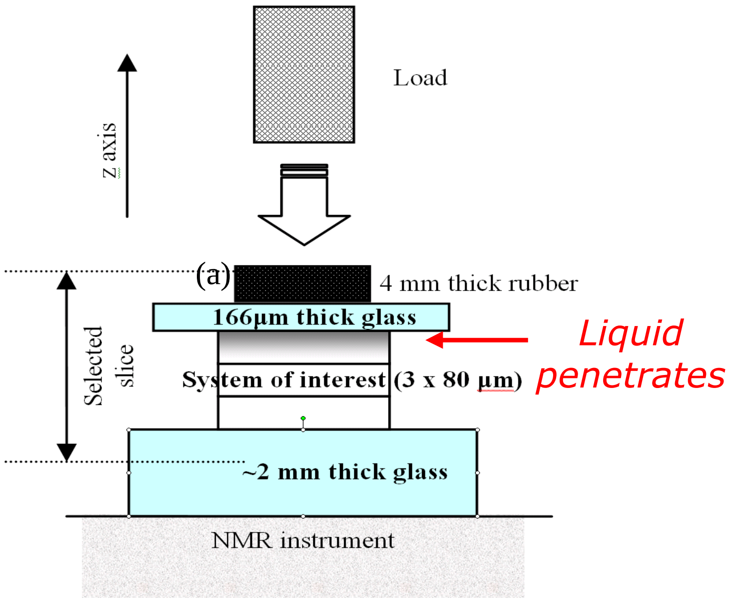


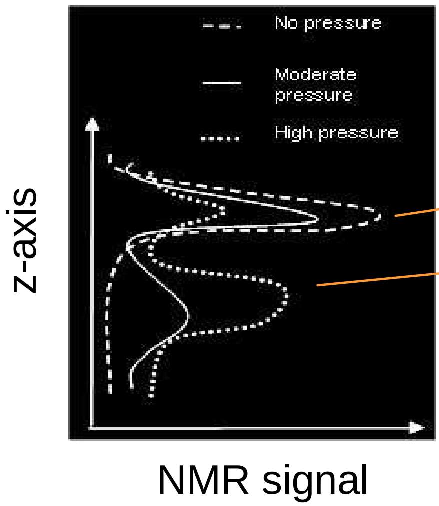


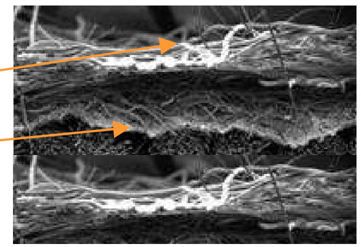
3D imaging of a small volume above it, with a region of interest 15 mm x 15 mm x 10 mm.

Application 1: Assessment of Textile Substrates

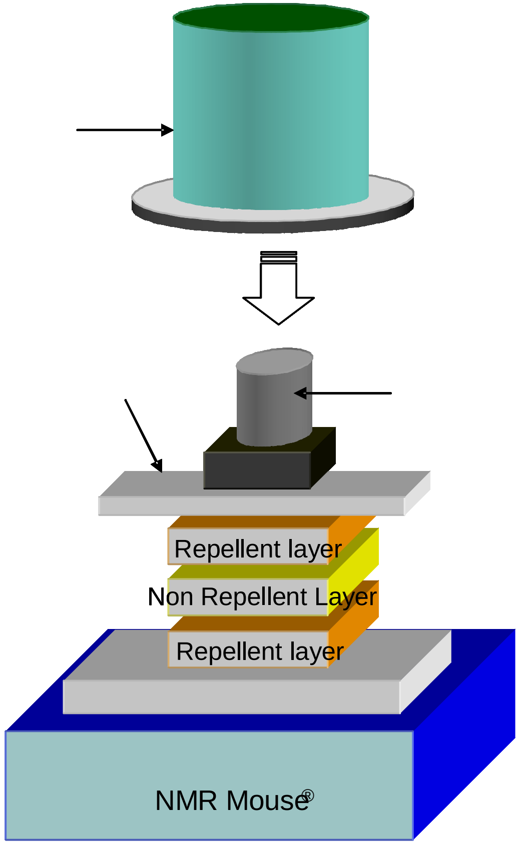
- Textiles that provide protection against toxic chemicals need to prevent the ingress of aerosols, vapours and liquids
  - Aerosols: particle capture
  - Liquid: repellent and wicking layers
  - Vapour: activated carbon
- Test methods that image a textile's performance are desirable

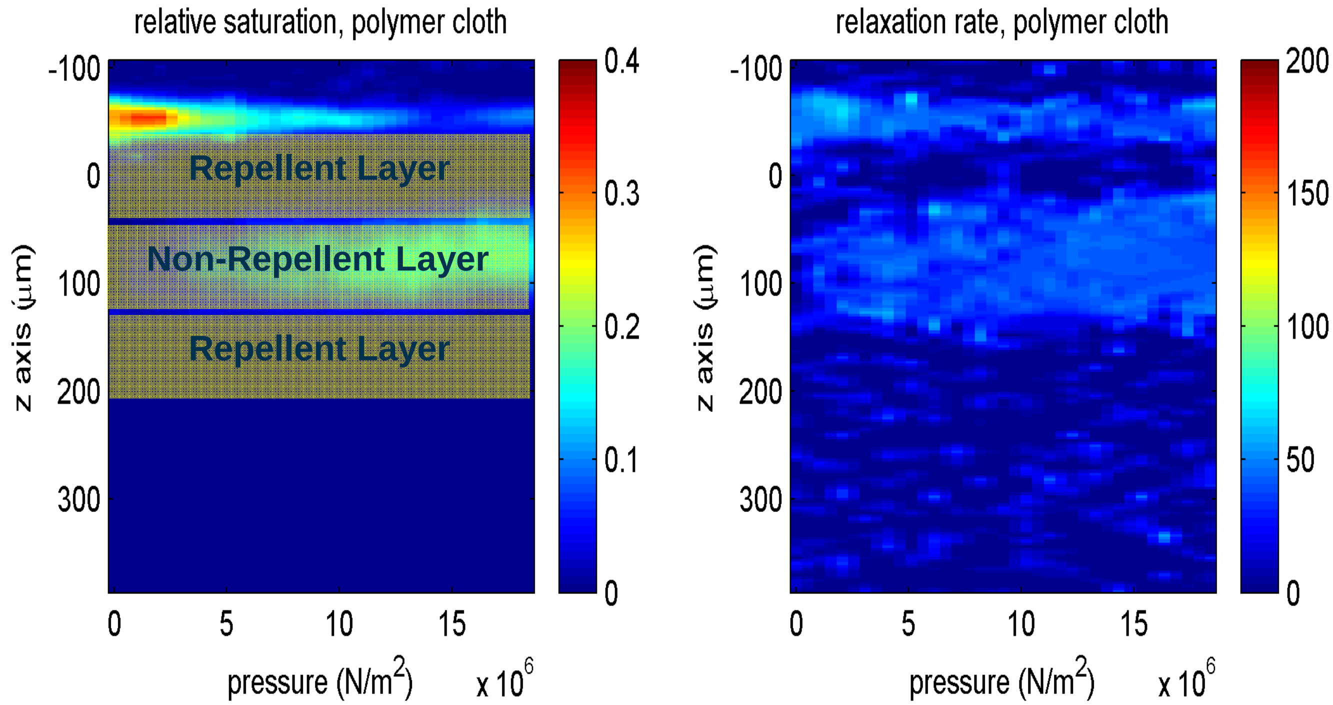




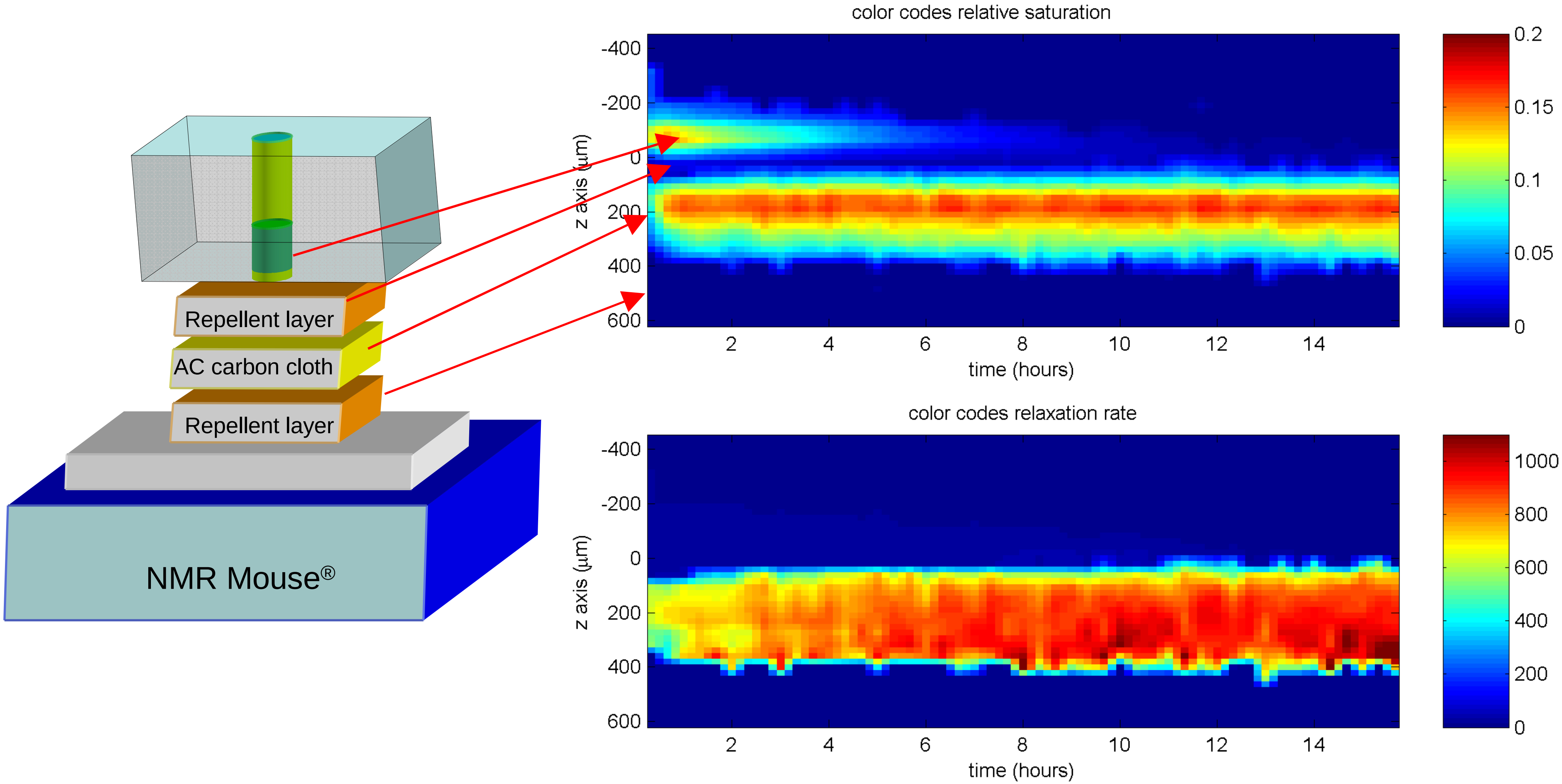


Spatially Resolved Measurement





Spatially Resolved Measurement of Vapour Uptake through a Repellent Layer



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. 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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PDRA’s	Dr Neil Shirtcliffe, Dr Dale Herbertson, Dr Carl Evans, Dr Paul Roach, Dr Yong Zhang
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

Appendices

Additional References

Book

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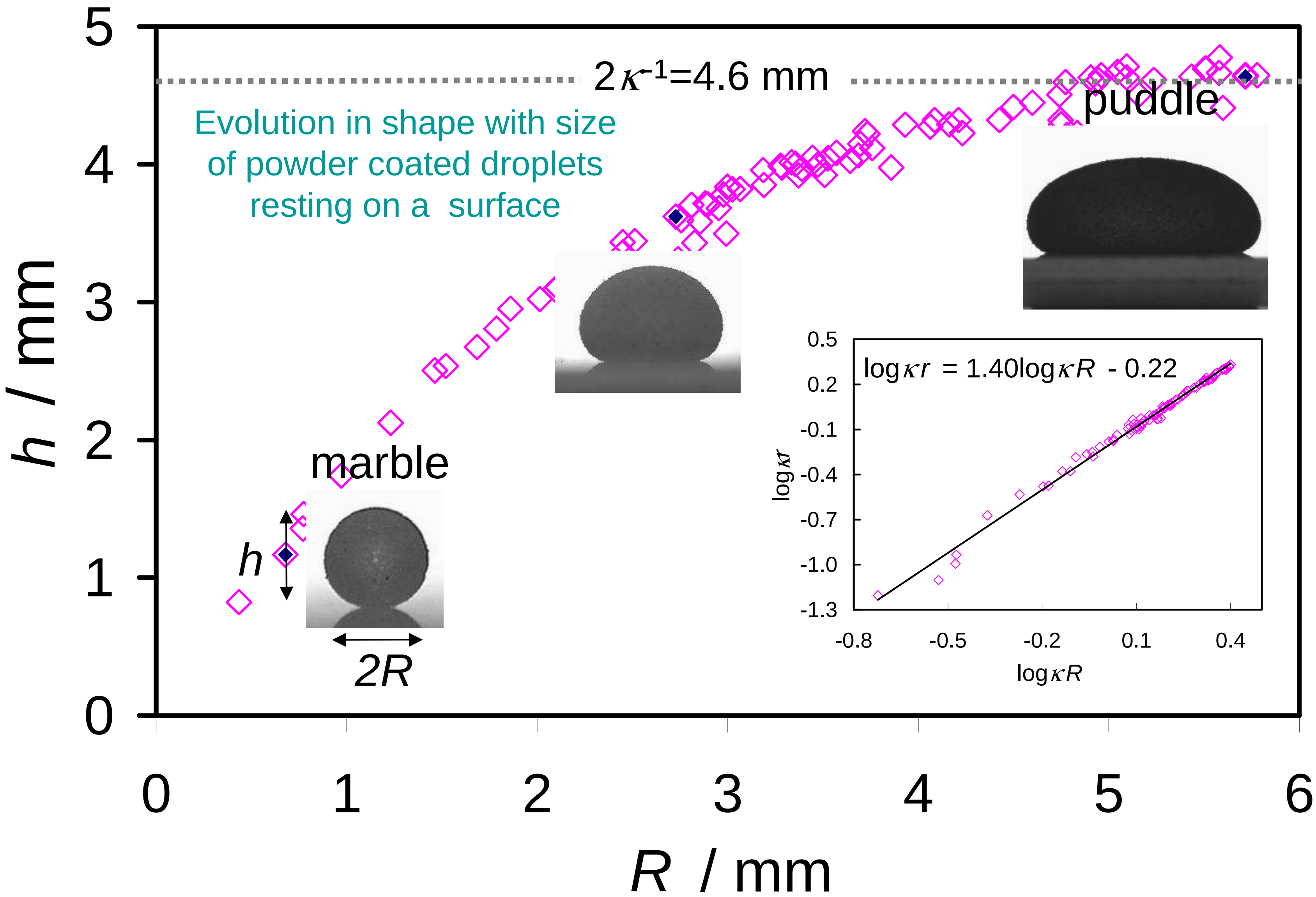
Liquid Marble Size Data (Lycopodium)



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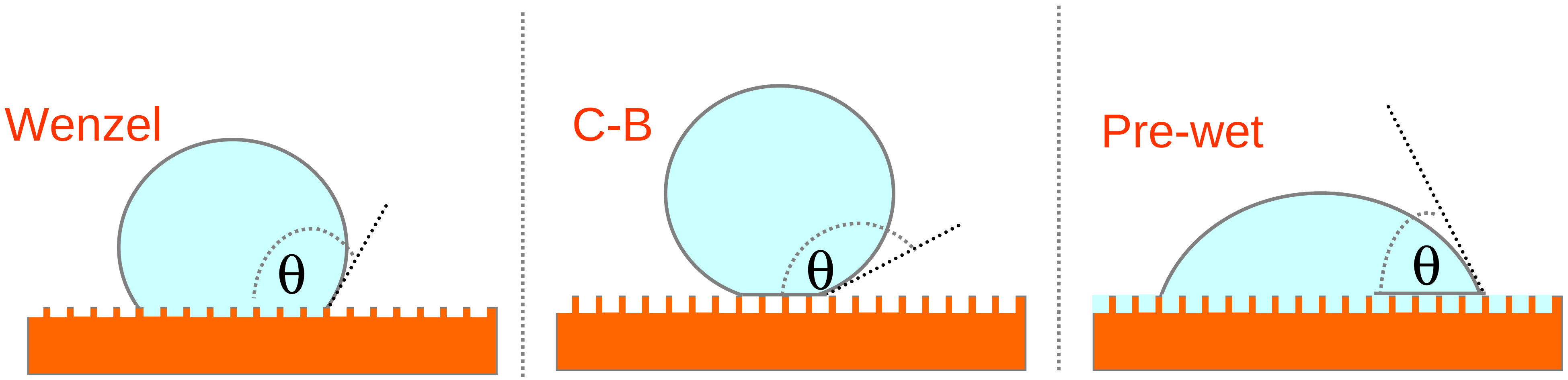
Pre-existing Wetness



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

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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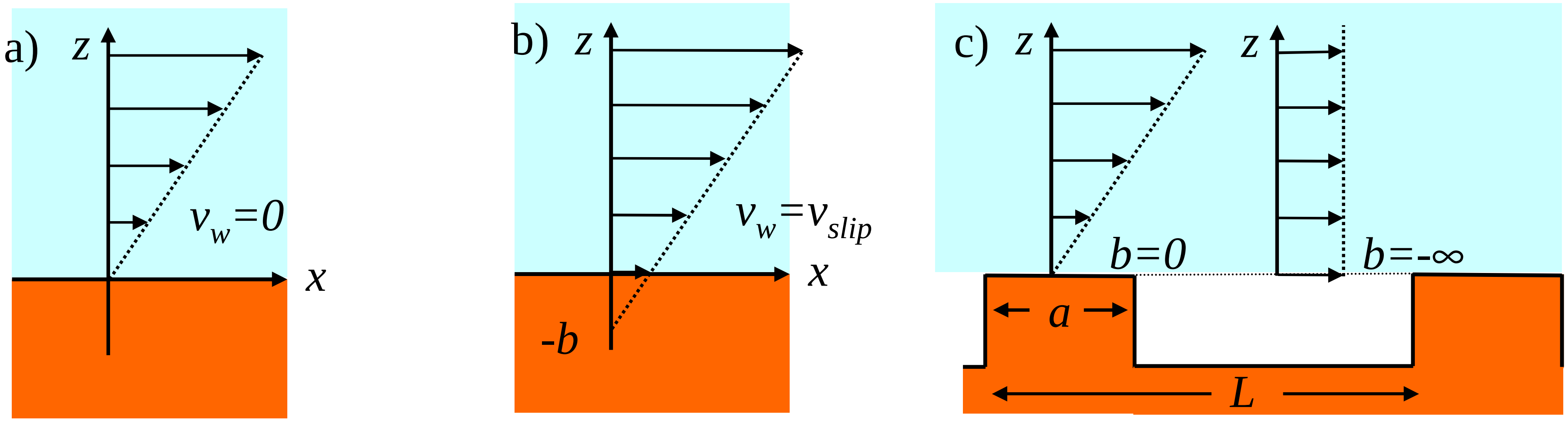
Slip by Simple Newtonian Liquids

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%

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