Superhydrophobicity, Spreading and Imbibition

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Overview

1. Water Repellency: Concepts
    - Insects and surface tension
    - Naturally occurring surfaces
2. Topography & Wetting: Theory
    - Surface free energy derivations: Wenzel/Cassie-Baxter equations
    - Defects and symmetric/random patterns, complex topography
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 water-repellent soil

Water Repellency: Concepts

Insects at the Water's Surface

Walking on Water

Microcosmos (Copyright: Allied Films, 1996)

Winners and Losers: *Understanding provides a competitive advantage*

Surface Tension

Liquid Surface

Molecules at a surface have fewer neighbours

Liquid surface ("skin") behaves as if it is in a state of tension

For a free "blob", the smallest area is obtained with a sphere

http://www.brantacan.co.uk

Size Matters

Surface tension force ∝ length

e.g. Force~$R\gamma_{LV}$

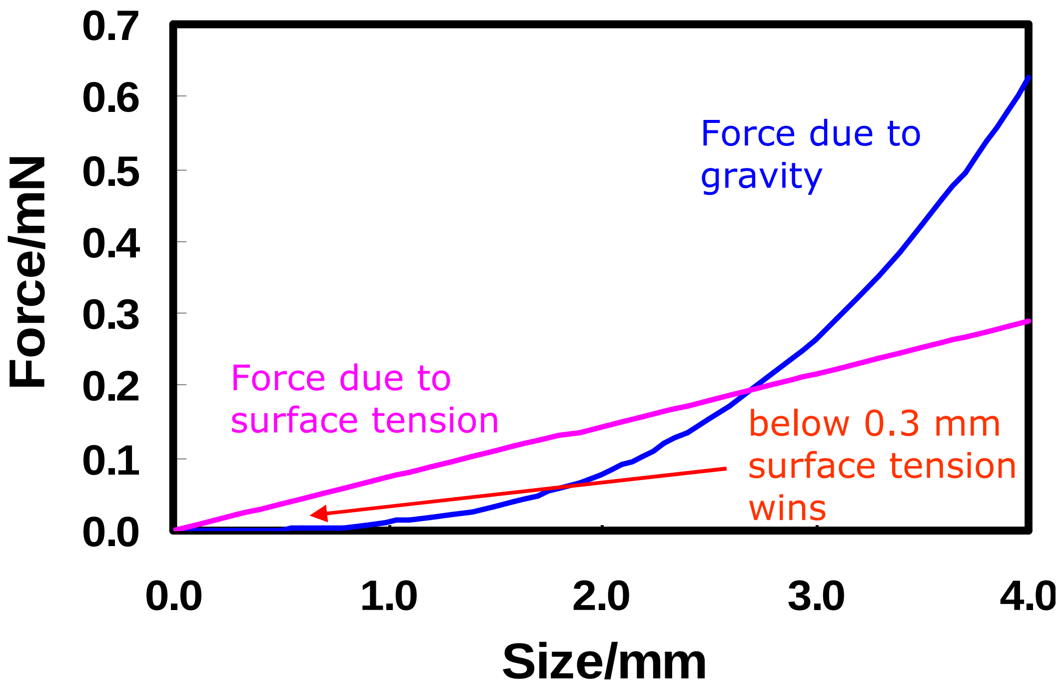
Gravity forces ∝ length^3

e.g. Force~$R^3\rho g$

Small size ⇒ surface tension wins

Small means<<capillary length

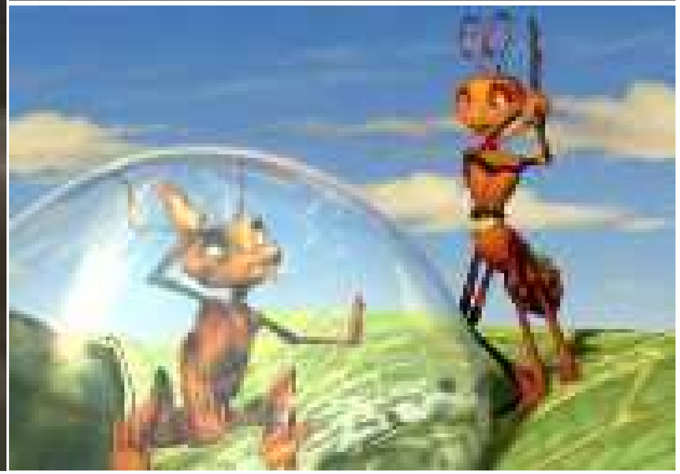
$\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2}$ ~ 2.73 mm (water)



Size Matters: Fiction or Fact?

The Movie – Antz (1998)

Courtesy: BigWave Productions



Is it just imagination?

Or could it happen?

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

The Sacred Lotus Leaf

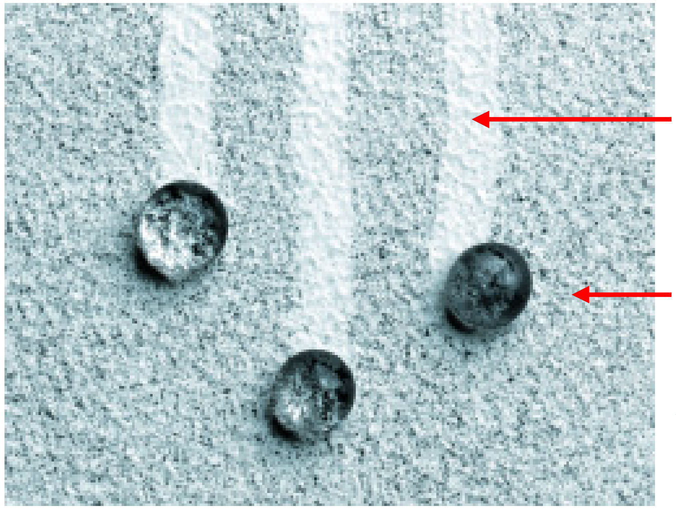
Plants

- 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

Acknowledgement Neinhuis and Barthlott

Self-Cleaning



Dust cleaned away

Dust coated droplet

A "proto-marble"

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.

Hydrophobicity and Superhydrophobicity

Surface Chemistry

Terminal group determines whether surface is water-liking or water-fearing

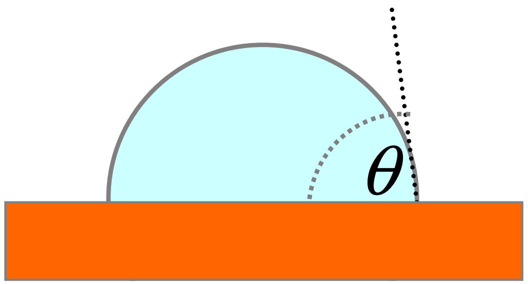
Hydrophobic terminal groups are Fluorine (CF_x) and Methyl (CH_3)

Contact Angles on Teflon

Characterize hydrophobicity

Water-on-Teflon gives ~ 115°

The best that *chemistry* can do



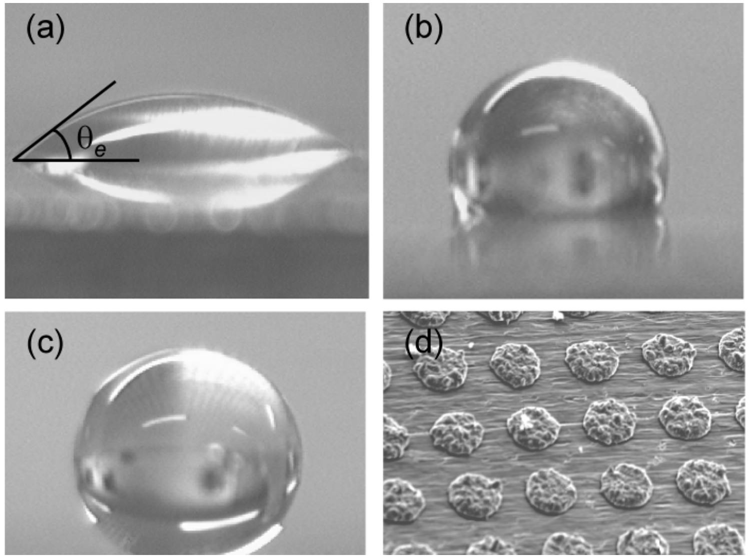
Enhancement by Topography

(a) is water-on-copper

(b) is water-on-fluorine coated copper

(c) is a super-hydrophobic surface

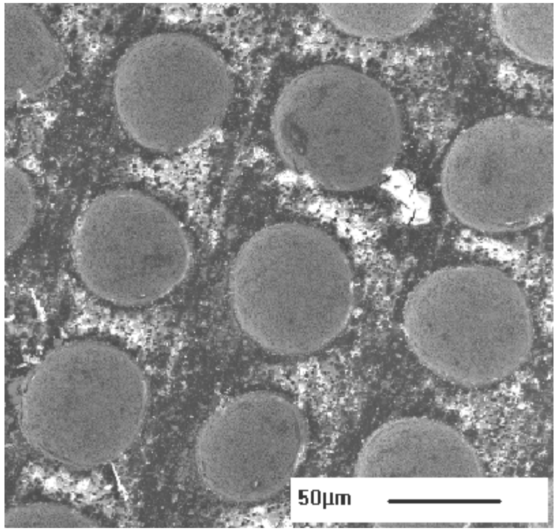
(d) “chocolate-chip-cookie” surface

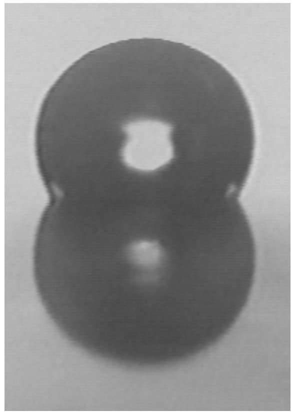


Superhydrophobicity is when $\theta > 150^o$
and a droplet easily rolls off the surface
(low contact angle hysteresis)

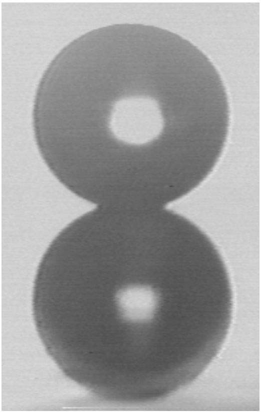
Superhydrophobicity - Man-Made Examples

Etched Metal



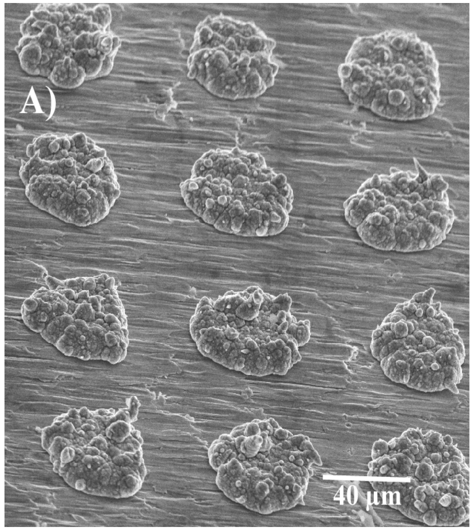


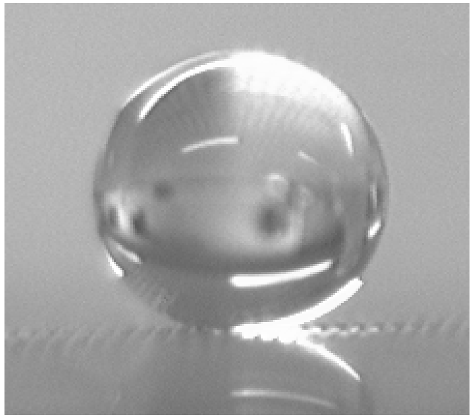
Flat & hydrophobic



Patterned & hydrophobic

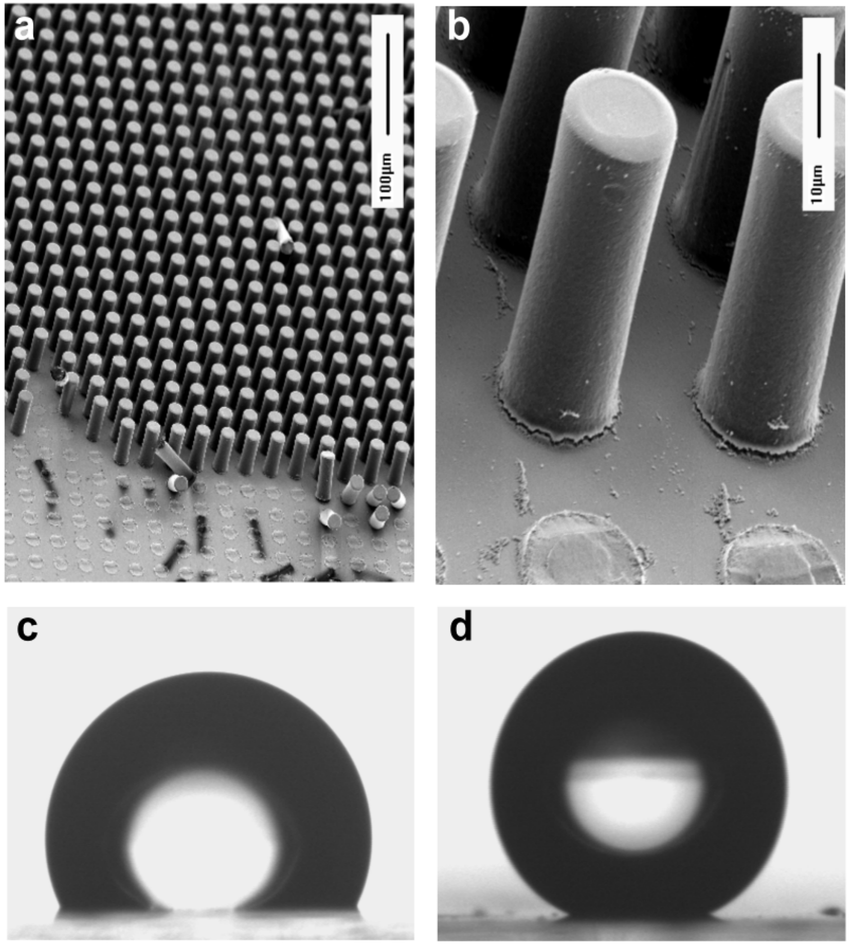
Deposited Metal





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.

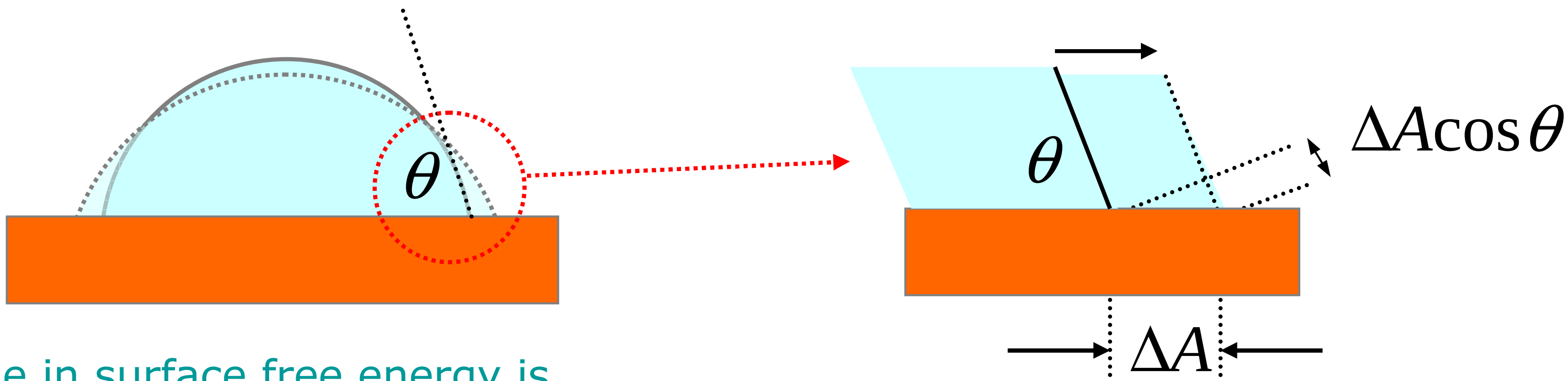
Topography & Wetting: Theory

Surface Free Energy Derivations

Minimum Surface Free Energy

Young’s Eq. – The Chemistry

What contact angle does a droplet adopt on a flat surface?



Change in surface free energy is

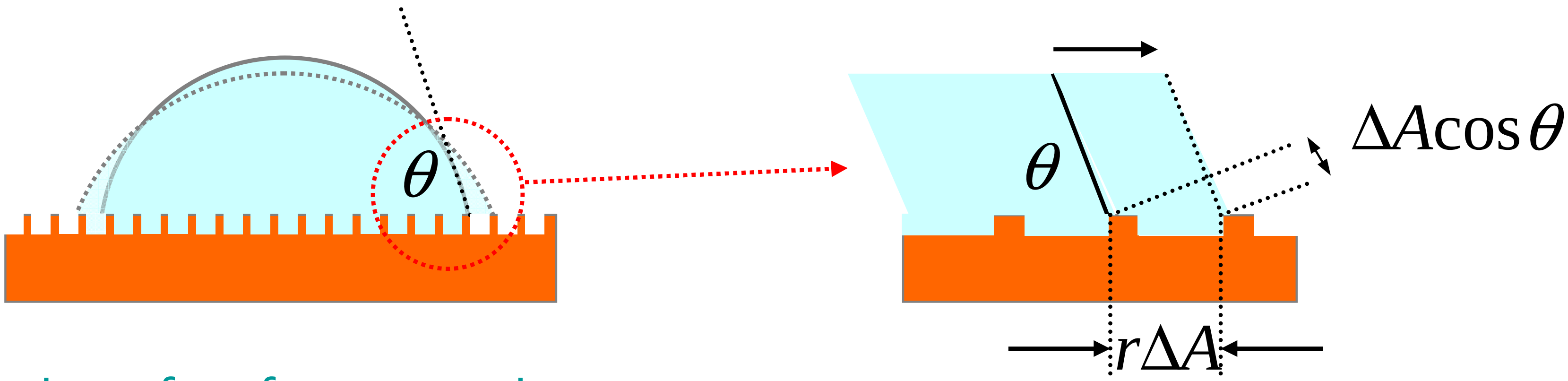
solid-liquid energy per unit area	×	gain of substrate area	-	solid-vapor energy per unit area	×	loss of substrate area	+	liquid-vapor energy per unit area	×	gain of liquid-vapor area

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

Equilibrium is when $\Delta F(x)=0$ $\Rightarrow$ $\boxed{\cos\theta_e=(\gamma_{SV}-\gamma_{SL})/\gamma_{LV}}$ Young’s Eq.

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

$$\boxed{\cos\theta_W(x) = r(x)\cos\theta_e}$$

Wenzel Eq

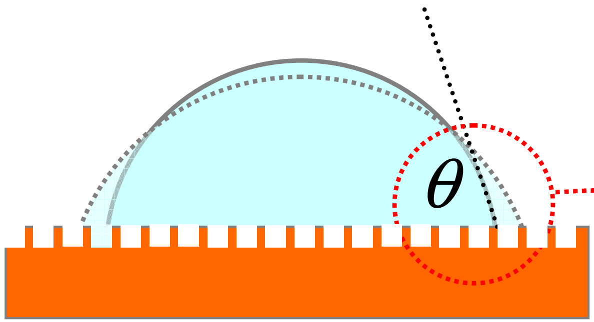
Topography $\Rightarrow$ $r(x)$ = roughness factor

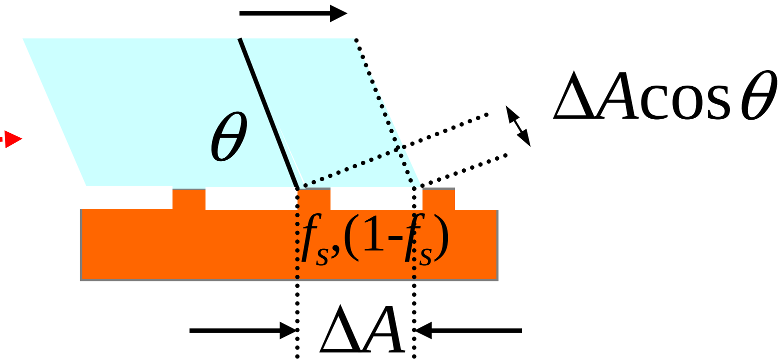
Chemistry $\Rightarrow$ Young's Eq. θ_e

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 Eq. θ_e

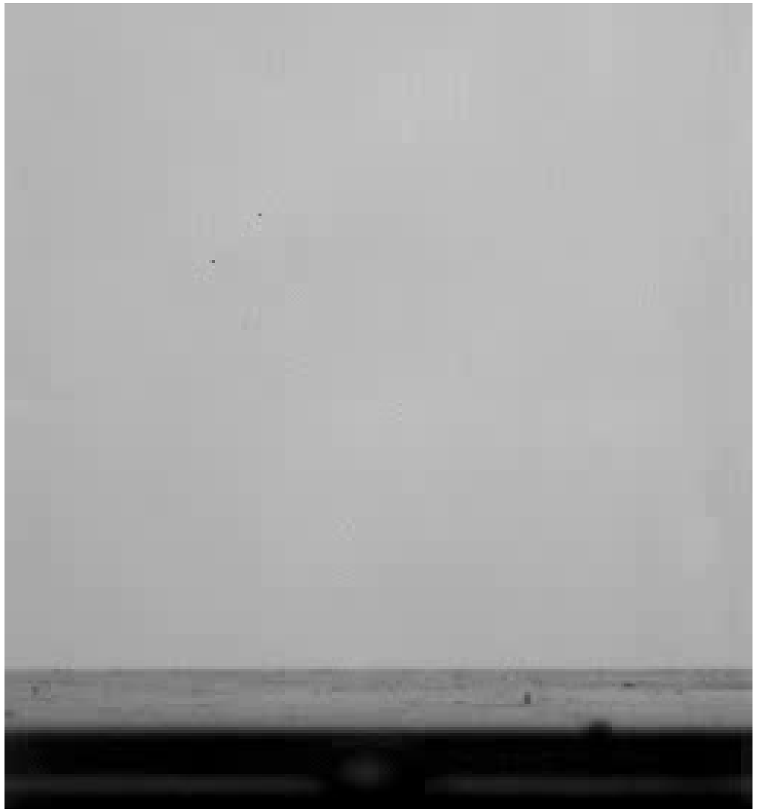
Air gaps $\Rightarrow$ cos(180°) = -1

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 (and Bouncing Droplets)



Acknowledgement: Dr Hind & Ms Fretwell (NTU)

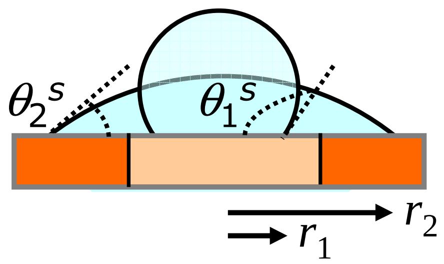
Courtesy: Prof. David Quéré, ESPCI

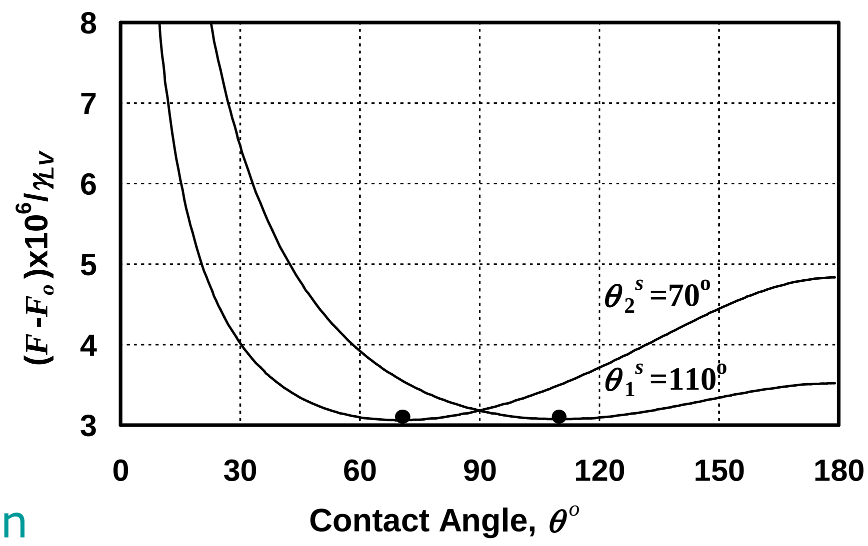
But …. liquid skin interacts with solid surfaces and "nails" do not need to be equally separated. A useful analogy, but it is not an exact view.

Importance of the Three-Phase Contact Line

Isolated Defect Surface

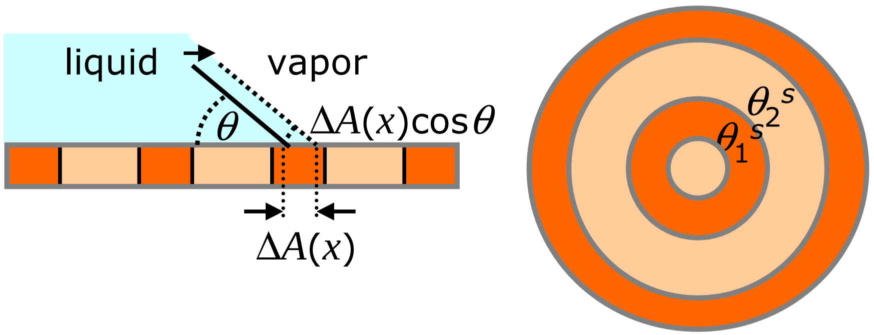
Surface has θ_1^s=110°, θ_2^s =70°



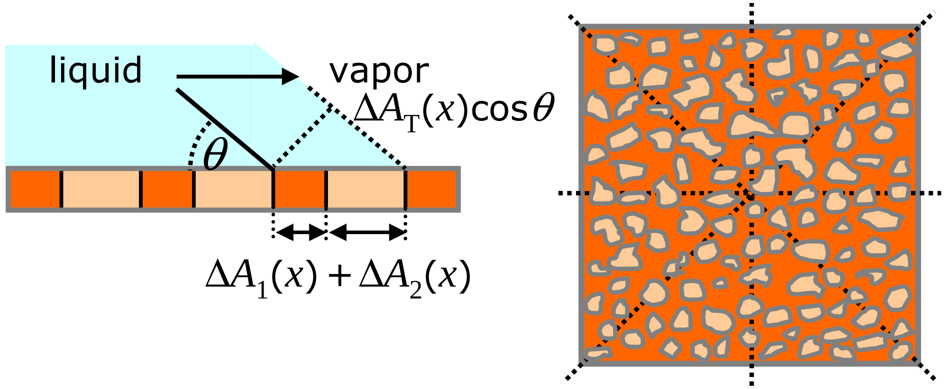


Two droplet configurations exist with min in their local surface free energy corresponding to the same droplet volume

Radial Symmetry



Random Surface



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

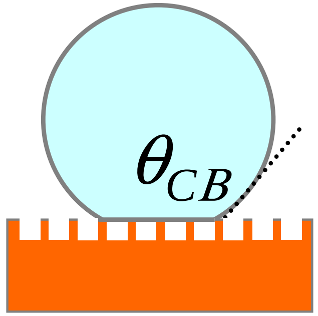
Local and not Global Differential Parameters

Cassie-Baxter

Define surface fractions: $f_i(x)=\Delta A_i(x)/(\Delta A_1(x)+\Delta A_2(x))$

$$\cos\theta_c(x) = f_1(x)\cos\theta_1 + f_2(x)\cos\theta_2$$

for a simple post-type superhydrophobic surface $\Rightarrow$

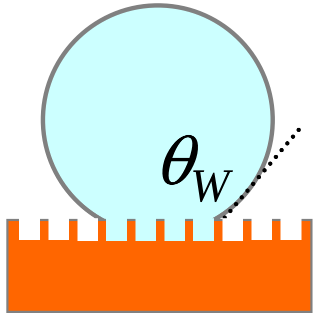


$$\boxed{\cos\theta_{CB}(x) = f_s(x)\cos\theta_e - (1 - f_s(x))}$$

where $f_s(x)$ is the solid surface fraction and the x indicates values at the three-phase contact line ($\theta_e = \theta_e(x)$ is also local to the three-phase contact line)

Wenzel

Define roughness: $r(x)=\Delta A_{wetted}(x)/\Delta A_{projected}(x)$



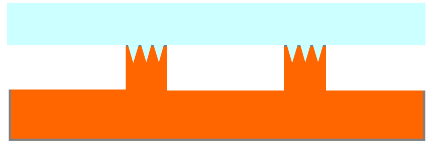
$$\boxed{\cos\theta_W = r(x)\cos\theta_e}$$

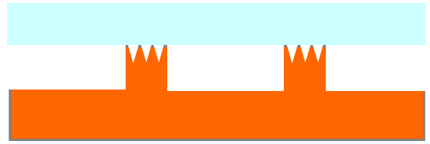
Reference McHale, G. Langmuir 23 (2007) 8200-8205.

Complex Topography

Roughness on Top of Features

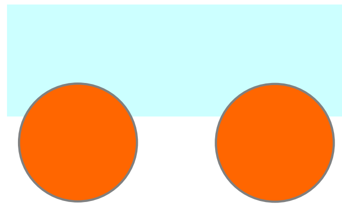
- Liquid filled case: Create Wenzel angle and use in Cassie-Baxter equation $\theta_e \rightarrow \theta_W(\theta_e) \rightarrow \theta_{CB}(\theta_W)$
- Non-filled case: Create CB angle for top and use in CB for large scale structure $\theta_e \rightarrow \theta_{CB}(\theta_e) \rightarrow \theta_{CB}(\theta_{CB})$

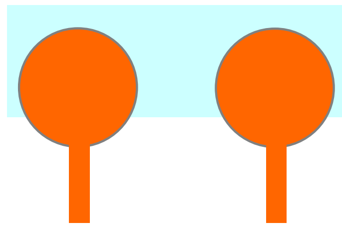




Curved Features

- 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

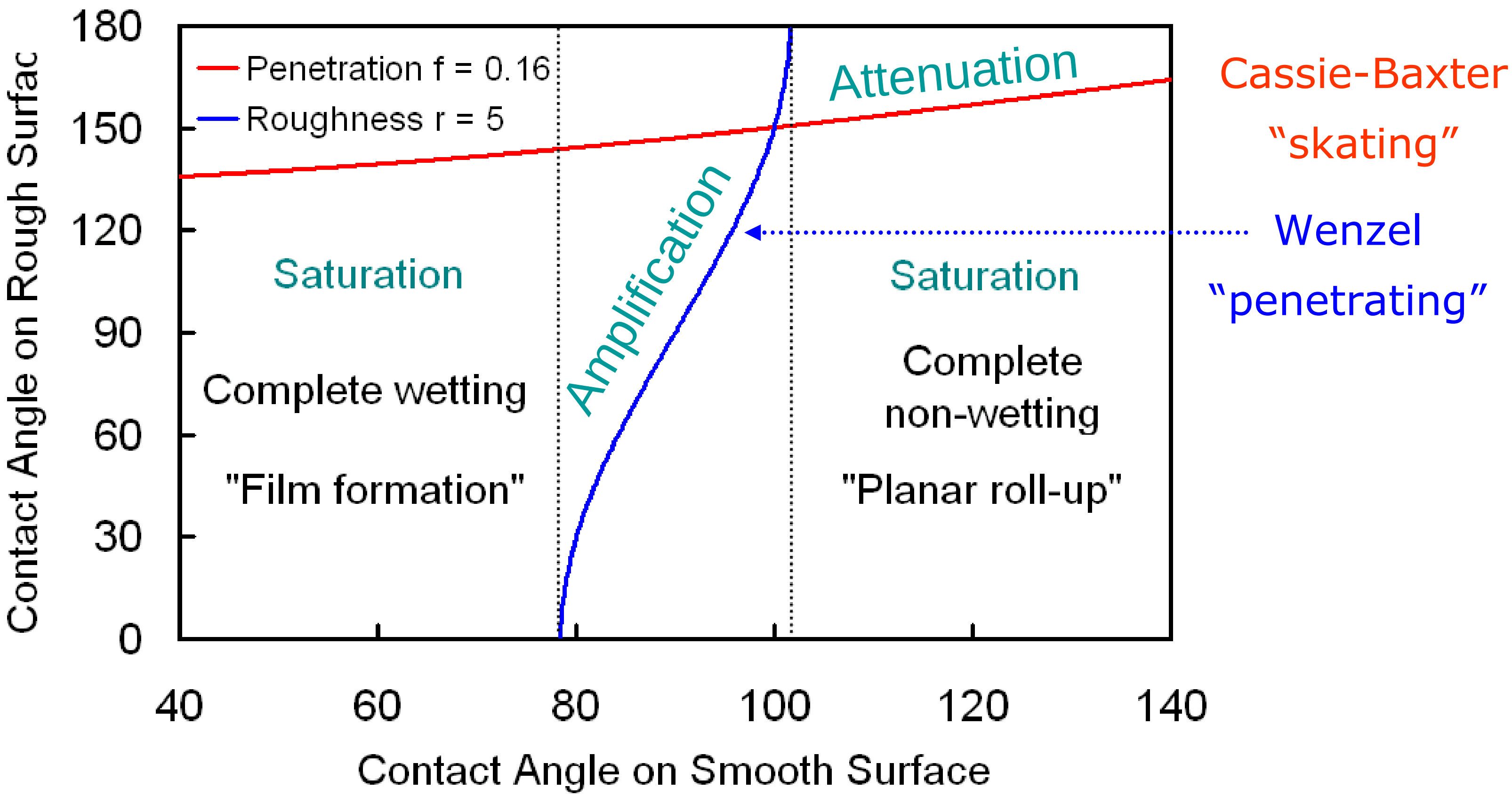
- Roughness, $r(x)$, and solid surface fraction, $f_s(x)$, become dependent on contact line position[4], x
- Can create gradients in superhydrophobicity[5]

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

Concepts: Amplification, Attenuation, Saturation



Roughness/Topography

θ_e^s > threshold ⇒ enhances repellence

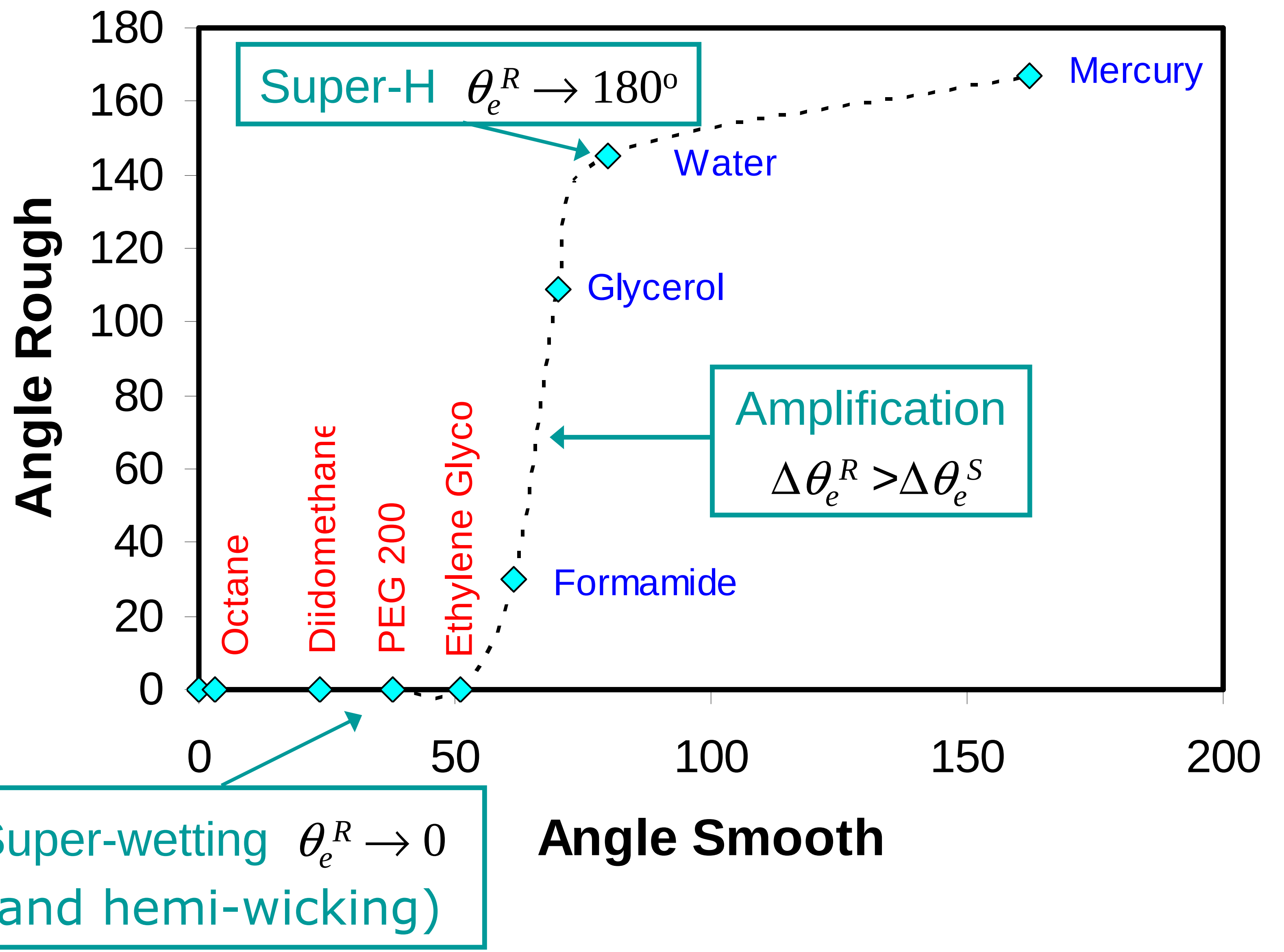
θ_e^s < threshold ⇒ enhances film formation

Superhydrophobic

"Skating case" ⇒ most existing examples

Pressure ⇒ transition to penetrating

Liquids on a Superhydrophobic Surface



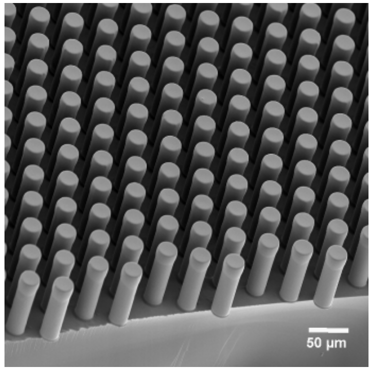
References McHale, G. *et al.*, Analyst 129 (2004) 284-287; Langmuir 20 (2004) 10146-10149.

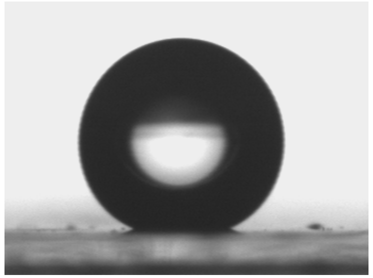
Skating-to-Penetrating Transition

Micro-Structured Surface

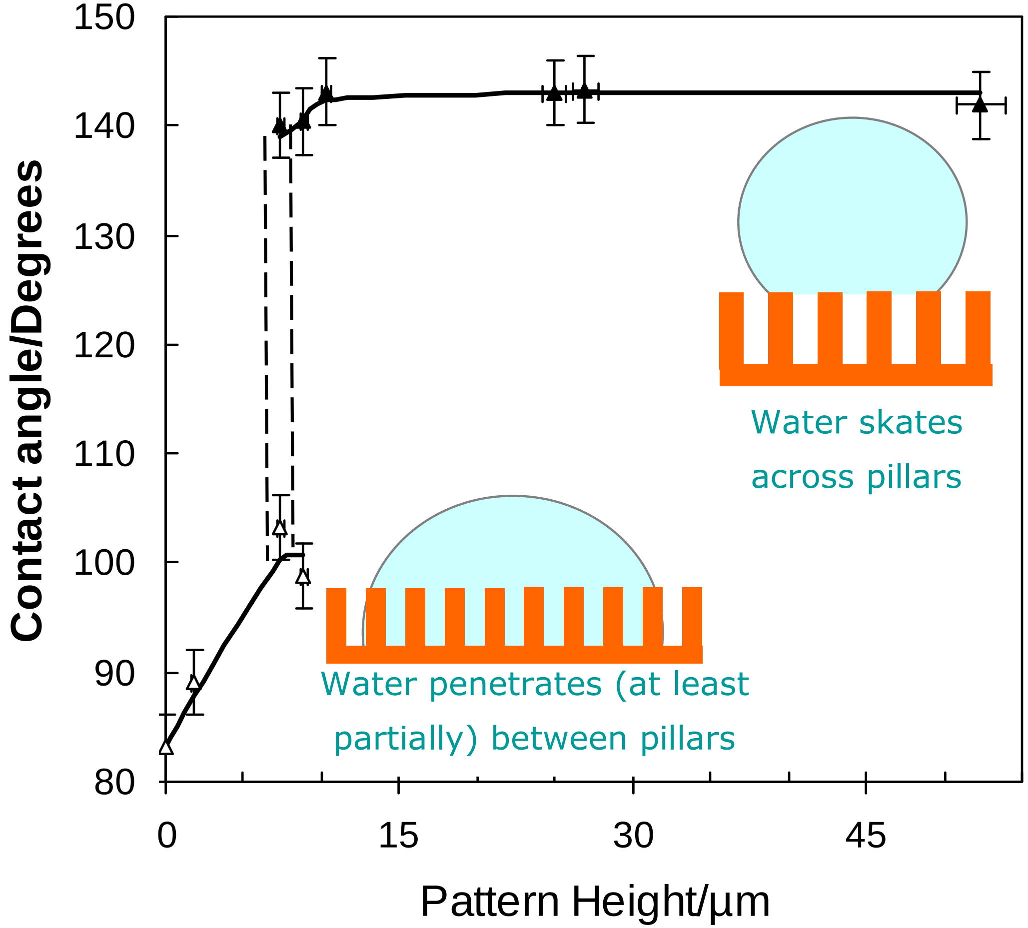
SU-8 pillars[1] 15 μm

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.

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]

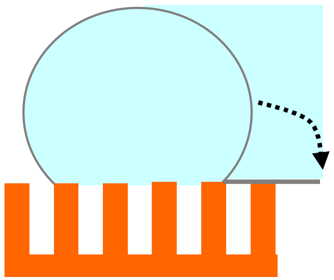
Assumes contact area changes are dominant effect and amplify an intrinsic hysteresis of the surface

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



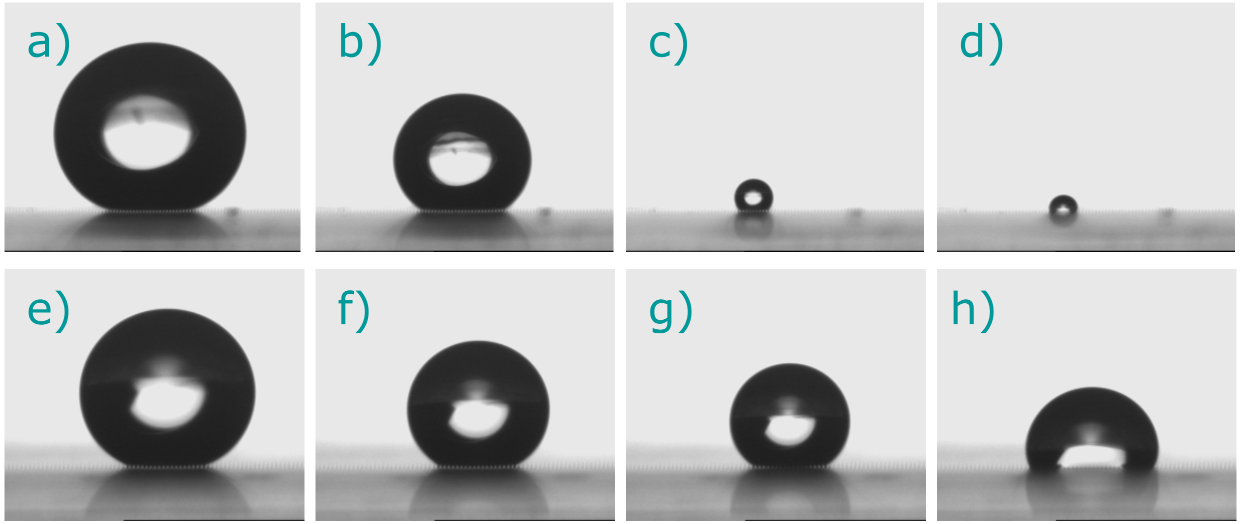
References [1]Quéré, D.; Lafuma, A.; Bico, J. Nanotechnology 14 (2003) 1109-1112. [2] Öner, D.; McCarthy, T.J. Langmuir 16 (2000) 7777-7782; 22 (2006) 6234-6237. [3]McHale, G. *et al*., Langmuir 20 (2004) 10146-10149. [4]Kusumaatmaja, H.; Yeomans, J.M. Langmuir 23 (2007) 6019-6032,): Reyssat, M.; Quéré, D.; J. Phys, Chem. B 113 (2009) 3906-3909

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

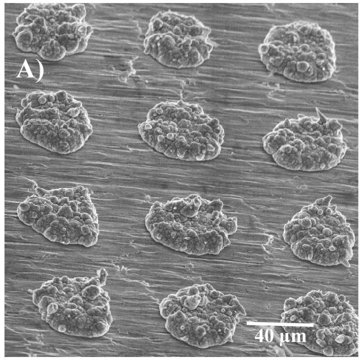
Yeomans[2] suggests three processes during evaporation:

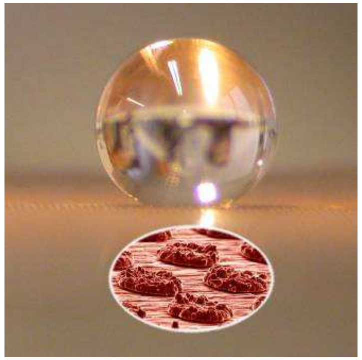
1. the contact line retreats inwards across the surface
2. the free energy barrier to collapse vanishes and the drop moves smoothly down the posts (long posts)
3. the drop touches the base of the surface patterning and immediately collapses (short posts) – critical curvature of droplet $\propto b^2/h$,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

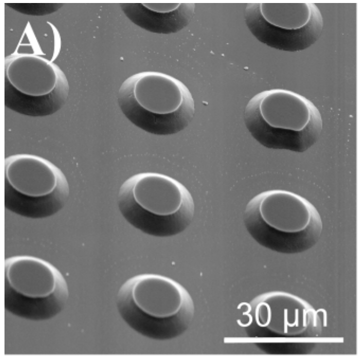
3D simulation suggests the drop can depin from all but the peripheral posts, so that its base resembles an inverted bowl.

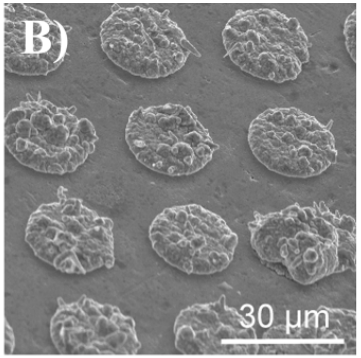
References [1]McHale, G. *et al.*, Langmuir 21 (2005) 11053–11060. [2] Kusumaatmaja, H. *et al.*, Euro. Phys. Lett. 81 (2008) art. 36003. Reyssat, M.; Yeomans, J.M.; Quéré, D. Euro. Phys. Lett. 81 (2008) art. 26006. Moulinet, S.; Bartolo, D. Euro. Phys. J. E24 (2007) 251-260. Bartolo D., *et al.*, Europhys.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

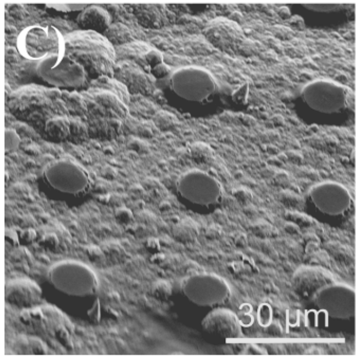
Double Length Scale Systems

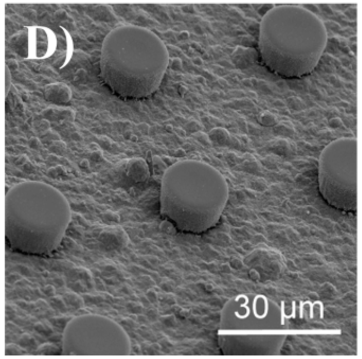






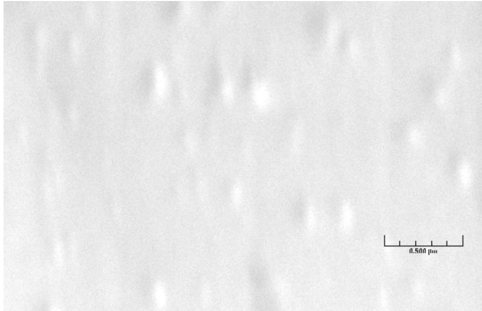


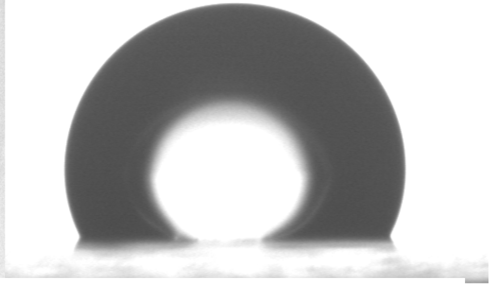




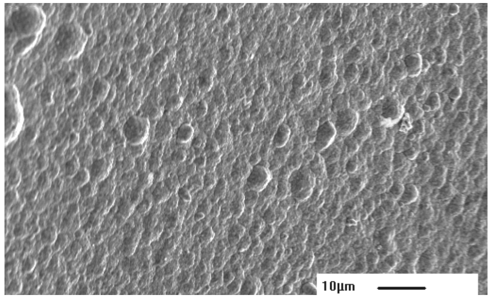
Two length scales is extremely effective

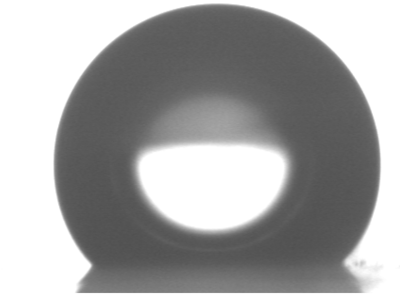
Smooth and hydrophobised: 115°



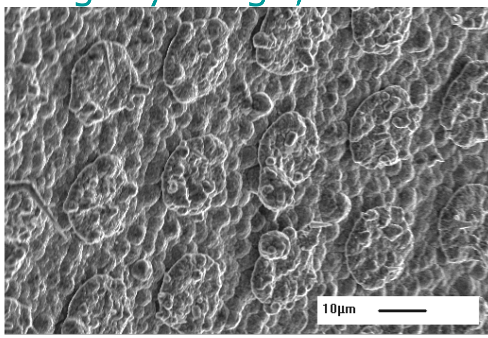


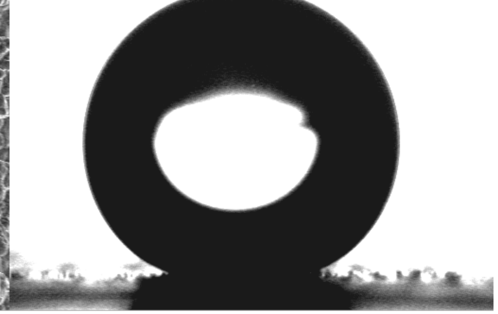
Slightly rough and hydrophobised: 136°





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

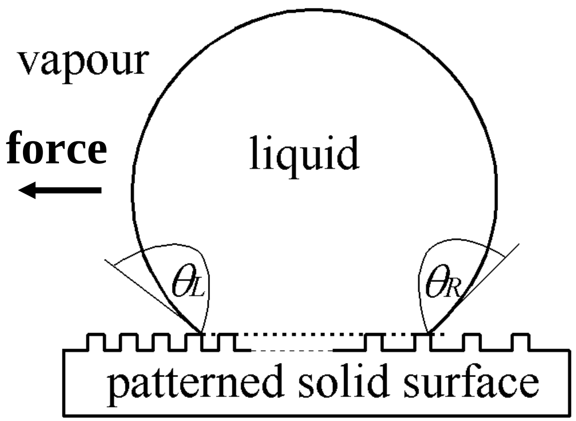
Make contact angle depend on position and surface chemistry $\theta(\underline{x}, \theta_e^s)$

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, G. *et al*, in 'Contact Angle, Wettability and Adhesion' Koninklijke Brill NV, vol. 6, 219-233.; Quéré, D. Europhys. Lett. (2009).

Superhydrophobicity

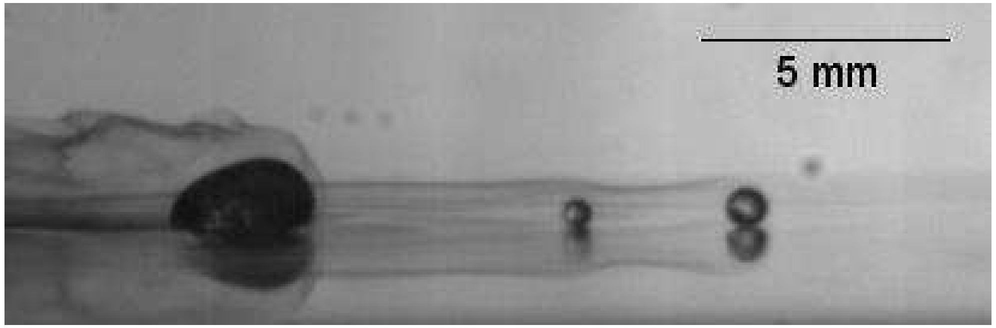
Unexpected superhydrophobicity?

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

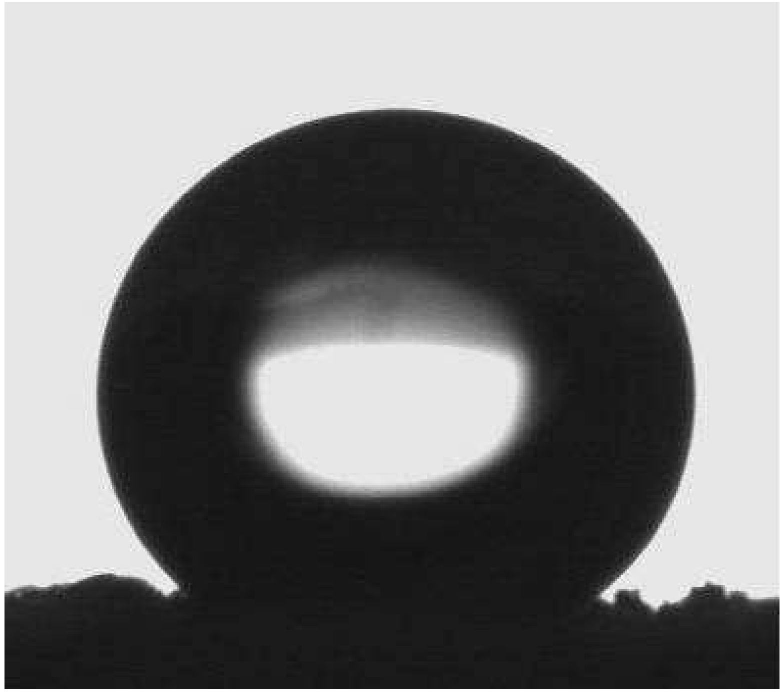
Leidenfrost Puddle

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

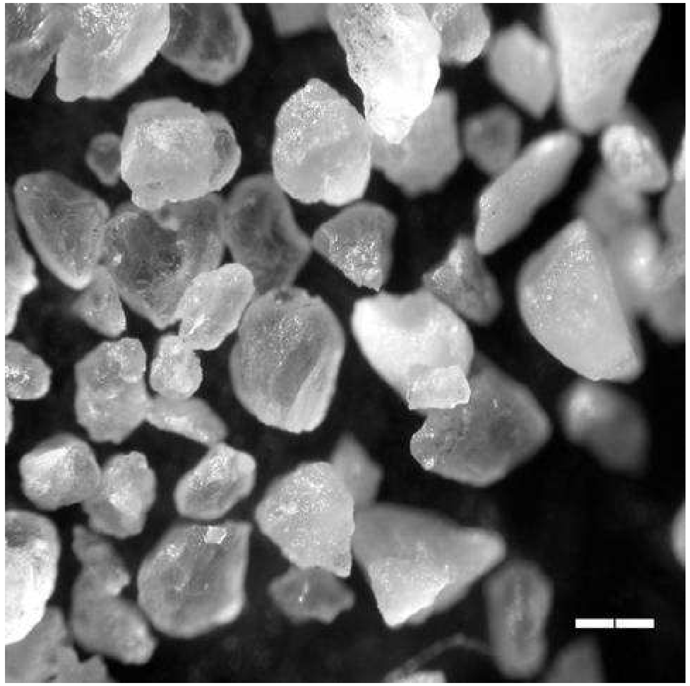
Reference Biance, A.L.; Clanet, C.; Quéré, D. Phys. Fluids. 15 (2003) 1632-1637.
http://www.pmmh.espci.fr/fr/gouttes/recherche/

Super Water-Repellent Sand/Soil

<u>Sand with 139°</u>



<u>Shape and Packing</u>



200 μm

<u>Comments</u>

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)

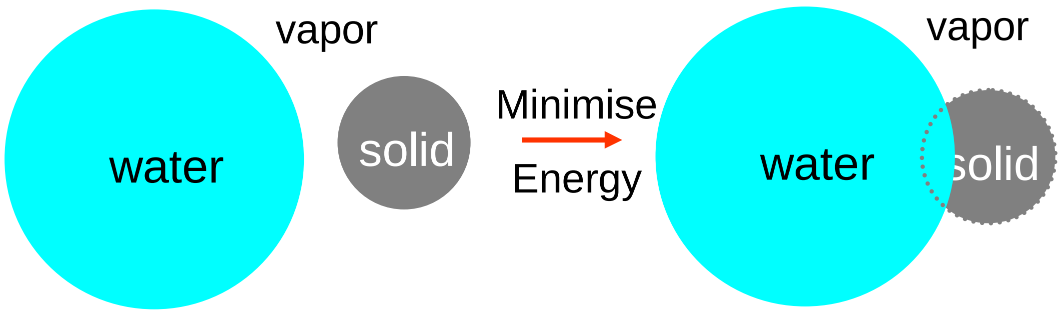
<u>References</u> McHale, G. *et al.*, Eur. J. Soil Sci. <u>56</u> (2005) 445-452; McHale, G. *et al.*, Hydrol. Proc. <u>21</u> (2007) 2229-2238. Bachmann, J. & McHale, G. Eur. J. Soil Sci. <u>60</u> (2009) 420-430.

Liquid Marbles

Loose Surfaces

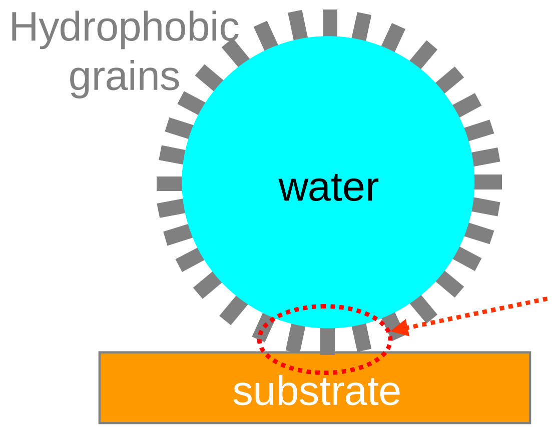
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

Hydrophobic Grains and Water

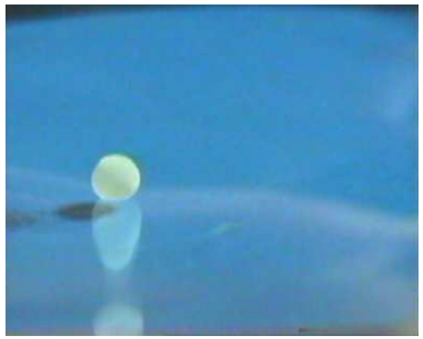


$$\Delta F = -\pi R_g^2 \gamma_{LV}(1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment



Similar to pillars, but solid conformable to liquid

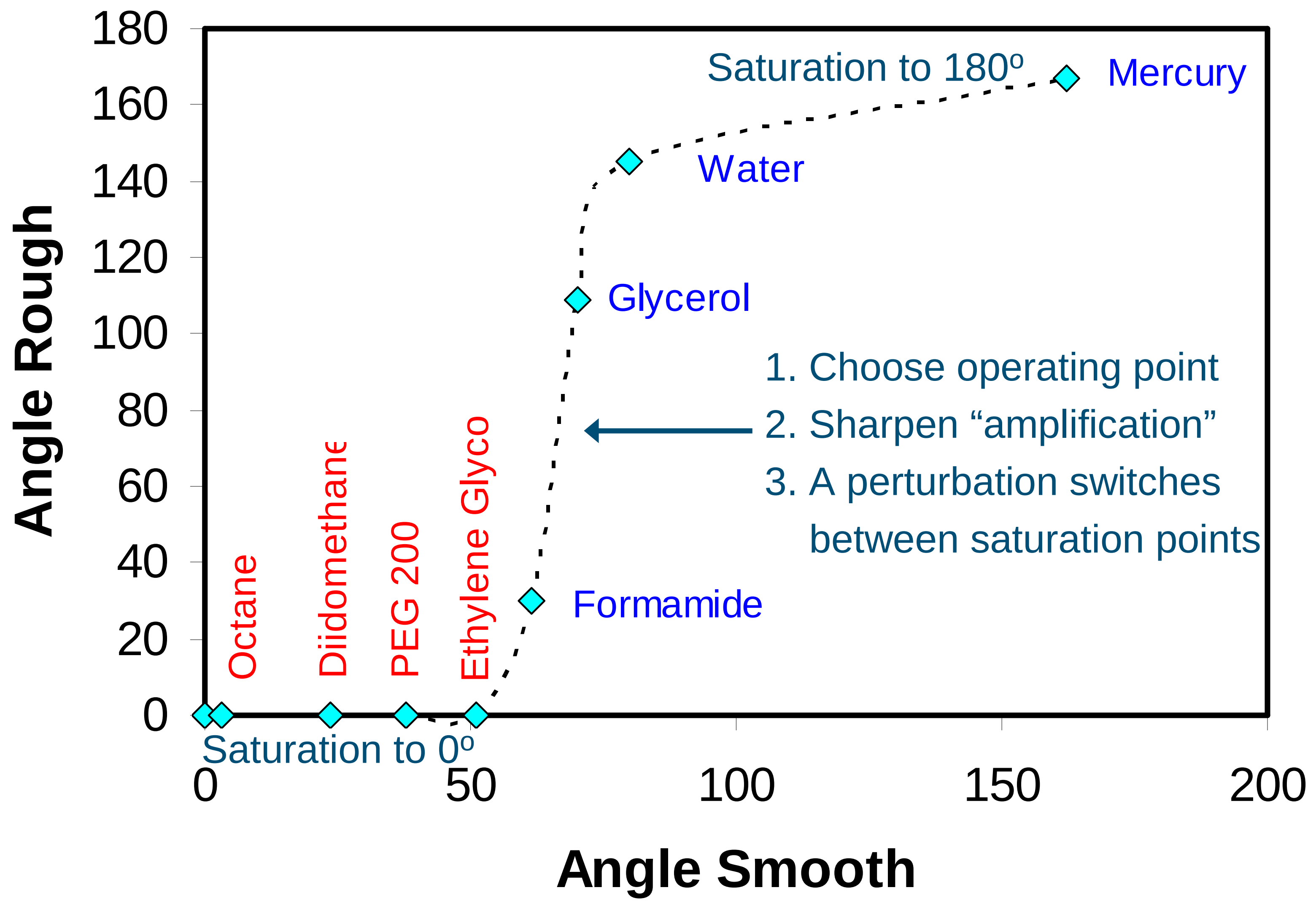


References Aussillous, P.; Quéré, D. Proc. Roy. Soc. A462 (2006) 973-999; Nature 411 (2001) 924-927. McHale, G., *et al*. 23 Langmuir (2007) 918-924. Newton, M.I., *et al*. J. Phys. D40 (2007) 20-24. Gao, L.C.; McCarthy, T.J. Langmuir 23 (2007) 10445-10447.

Porosity, Spreading and Imbibition

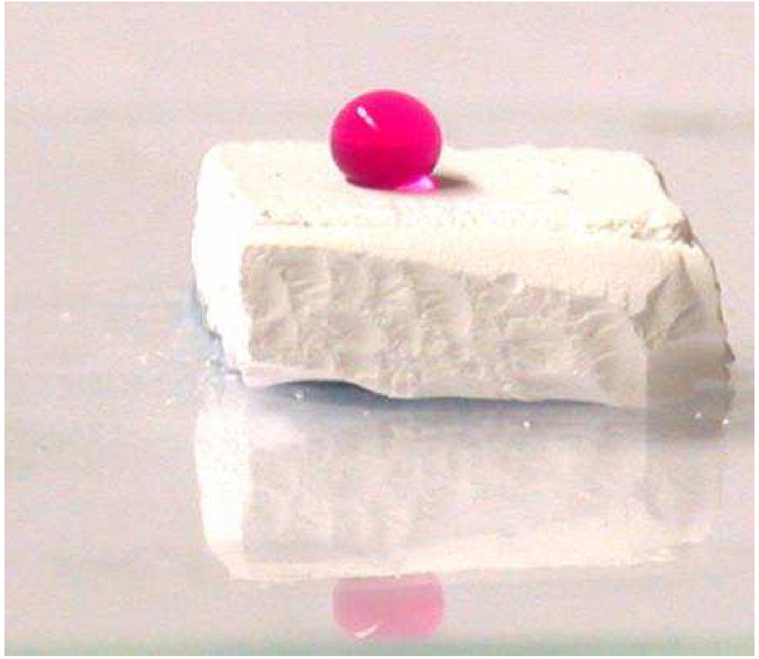
Superwetting, Superspreading, Hemi-wicking and Porosity

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

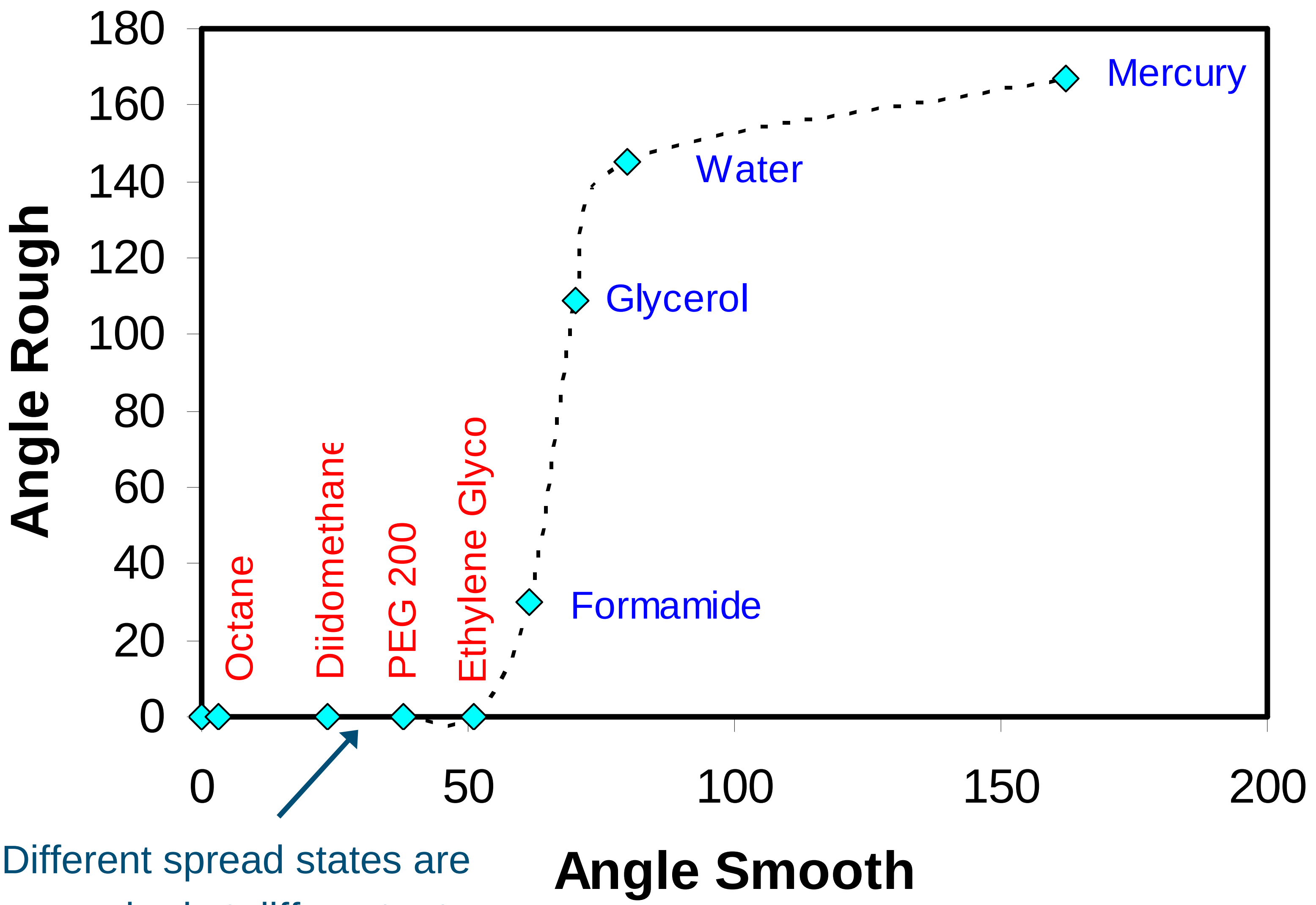
Mechanisms for Switching

- Temperature history of substrate
- Surface tension changes in liquid (alcohol content, surfactant, …)
- Electrowetting

Switch could trigger a large change ⇒ Sensor based on hydrophobicity

References Shirtcliffe, N.J. *et al.*, Chem. Comm. (25) (2005) 3135-3137 (Nature News "*Quick change for super sponge*" On-line 20/7/05). Shirtcliffe, N.J., *et al.*, Maters. Chem. & Phys. 103 (2007) 112–117.

Super-spreading



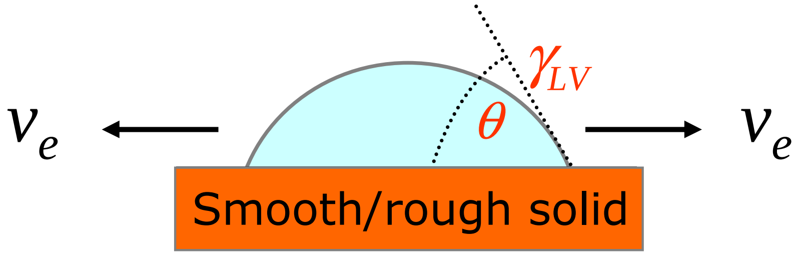
Different spread states are approached at different rates

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

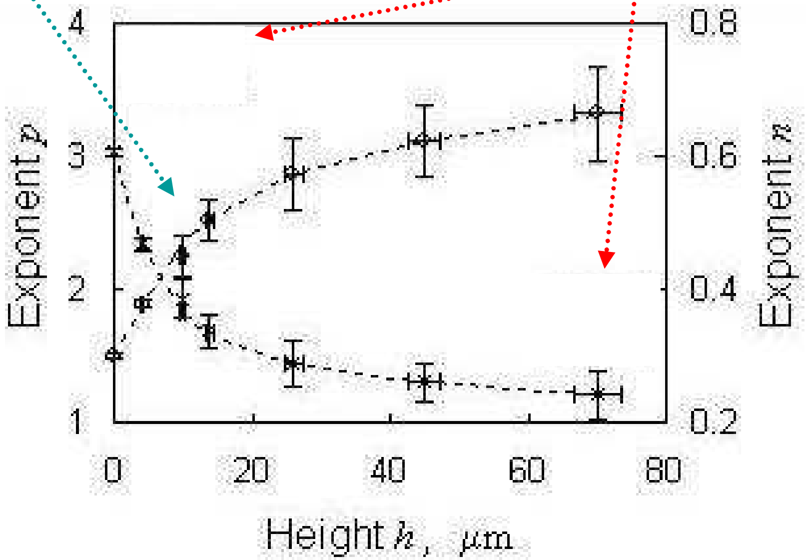
Tanner's Law exponents *p* and *n*

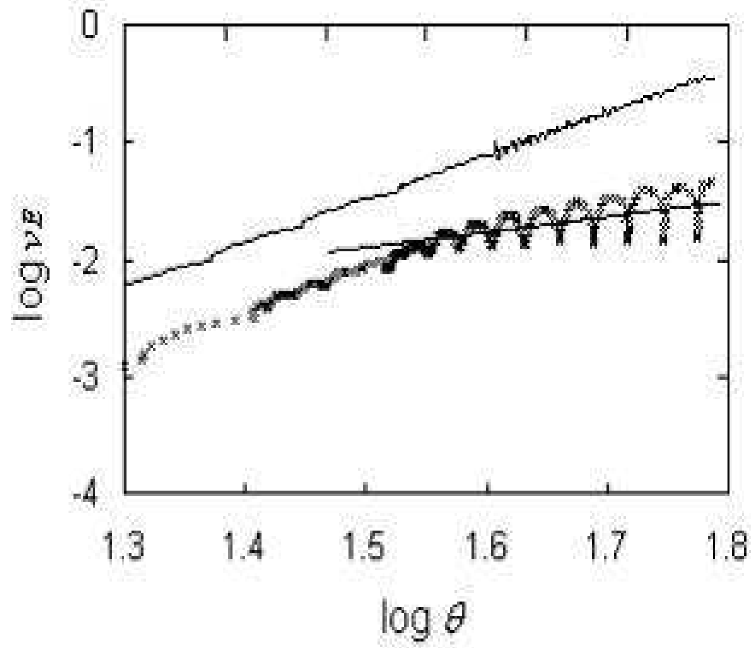
(cubic to linear transition)

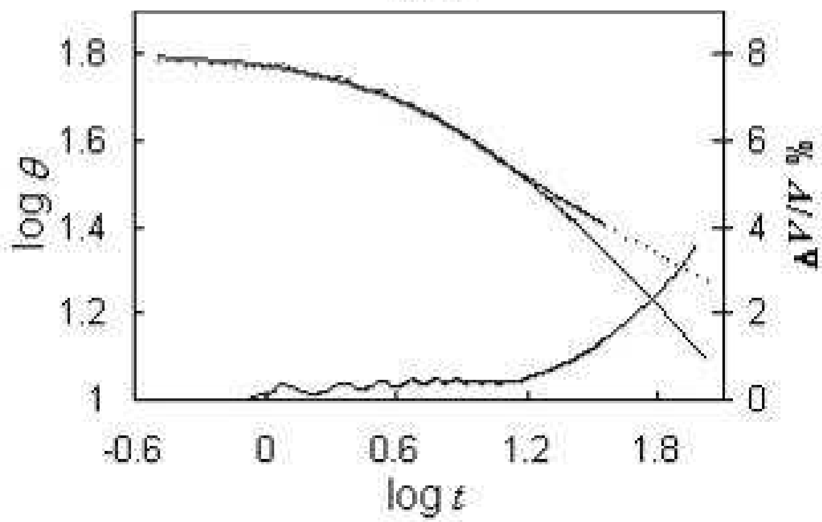
$$v_E \propto v^* \theta^p \qquad \theta \propto \left(\frac{V^{1/3}}{v^*}\right)^n \frac{1}{(t+t_o)^n}$$

Effect of substrate on PDMS

Effect of substrate on water

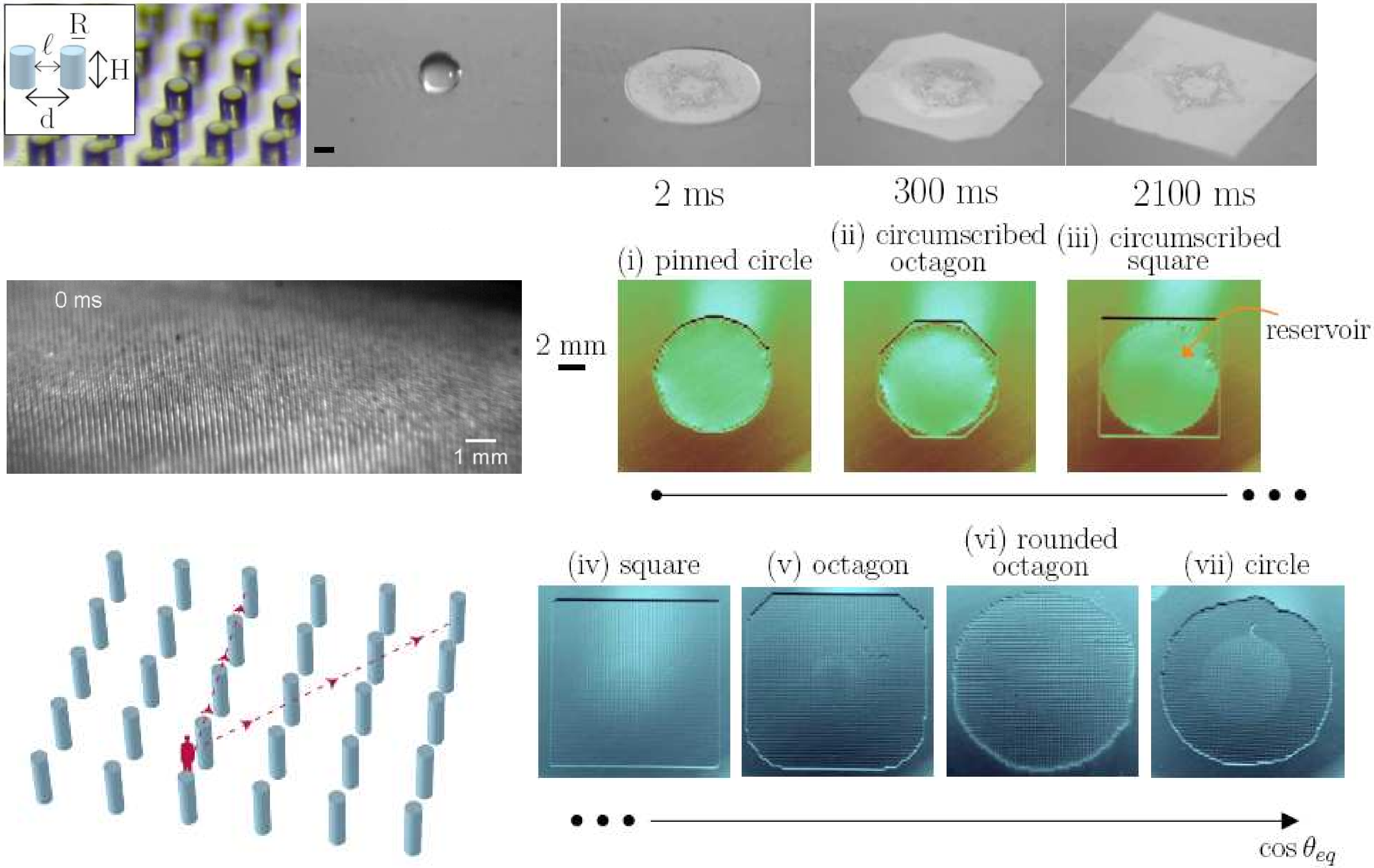






Reference McHale□, G. *et al.*, Phys. Rev. Lett. 93 (2004) art. 036102.

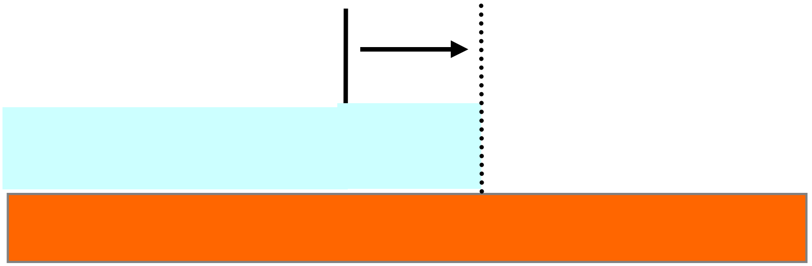
Topography Induced Wetting: Hemi-Wicking



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

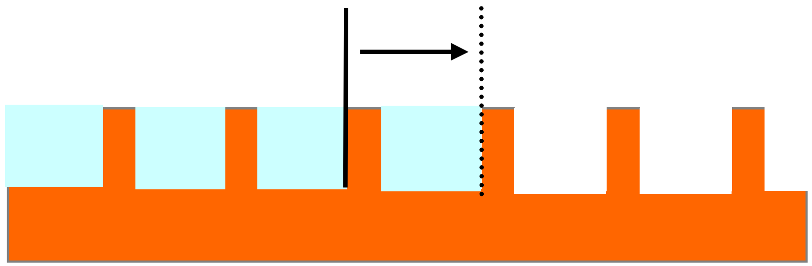
Spreading is when $\Delta F < 0 \quad \Rightarrow$

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

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 0^o and 90^o

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

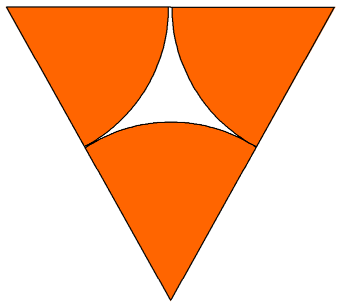
References Bico, J. *et al.*, Coll. Surf. A206 (2002) 41-46. Quéré, D. Physica A313 (2002) 32-46.

Transition from Wetting to Porosity

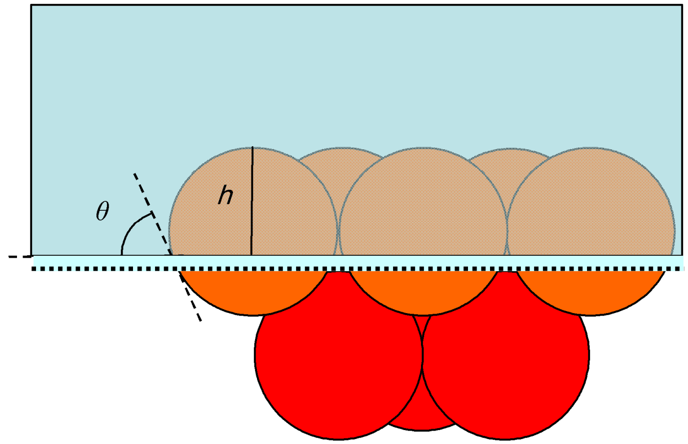
Assumptions

1. Spherical particles radius R
2. Fixed & hexagonally packed
3. Planar meniscus with Young's eq. contact angle, θ_e
4. Minimise surface free energy, F

Top View



Side View



Results for Close Packing

1. Change in surface free energy with penetration depth, h, into first layer of particles
2. Equilibrium exists provided liquid does not touch top particle of second layer
3. If liquid touches second layer at depth, h_c, then complete infiltration is induced
4. Critical contact angle, θ_c, when h_c reached[1,2]

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

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

$\theta_c = 50.73^o$

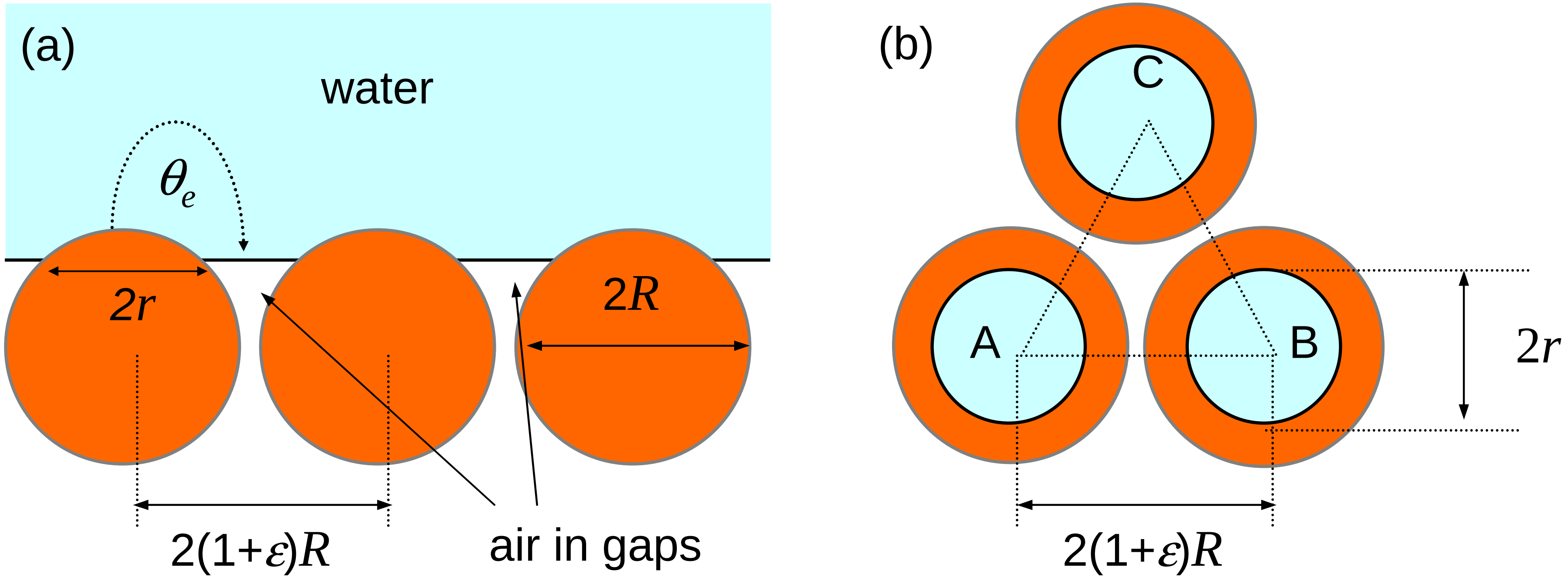
Creating superhydrophobic surfaces with curved features allows liquids to be supported even when $\theta_e < 90^o$ – so-called re-entrant surface features[3]

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.

Model Extreme Water-Repellent Soil

Side View

Top View



Comments

1. Effect occurs naturally (forest fires in sandy areas, grey water usage, …)
2. Can model using uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges air gaps horizontally between spheres – Mixed Wenzel/CB system

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

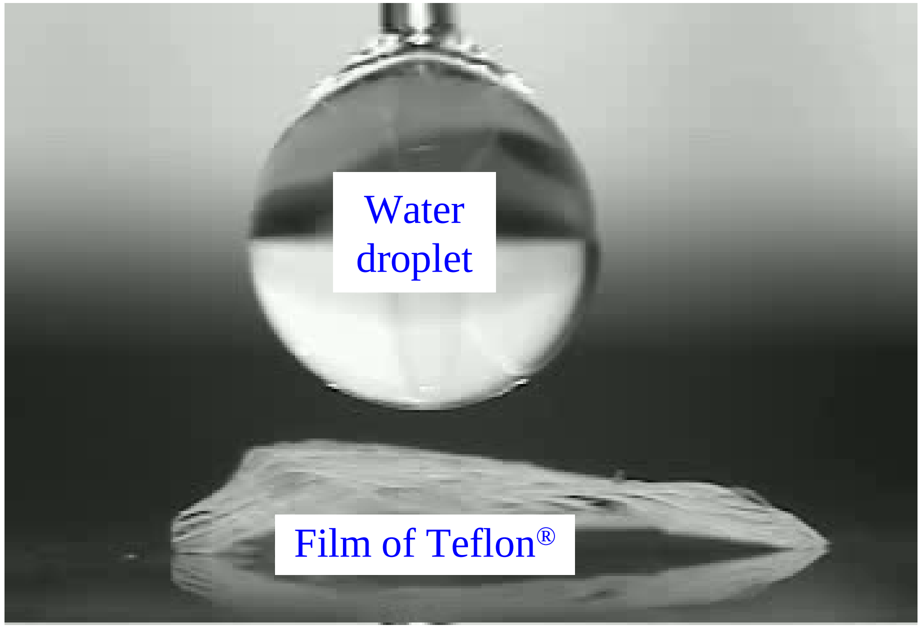
References McHale, G. *et al.*, Eur. J. Soil. Sci. 56 (2005) 445-452. Bachmann, J. & McHale, G. Eur. J. Soil Sci. 60 (2009) 420-430.

One Last Thought

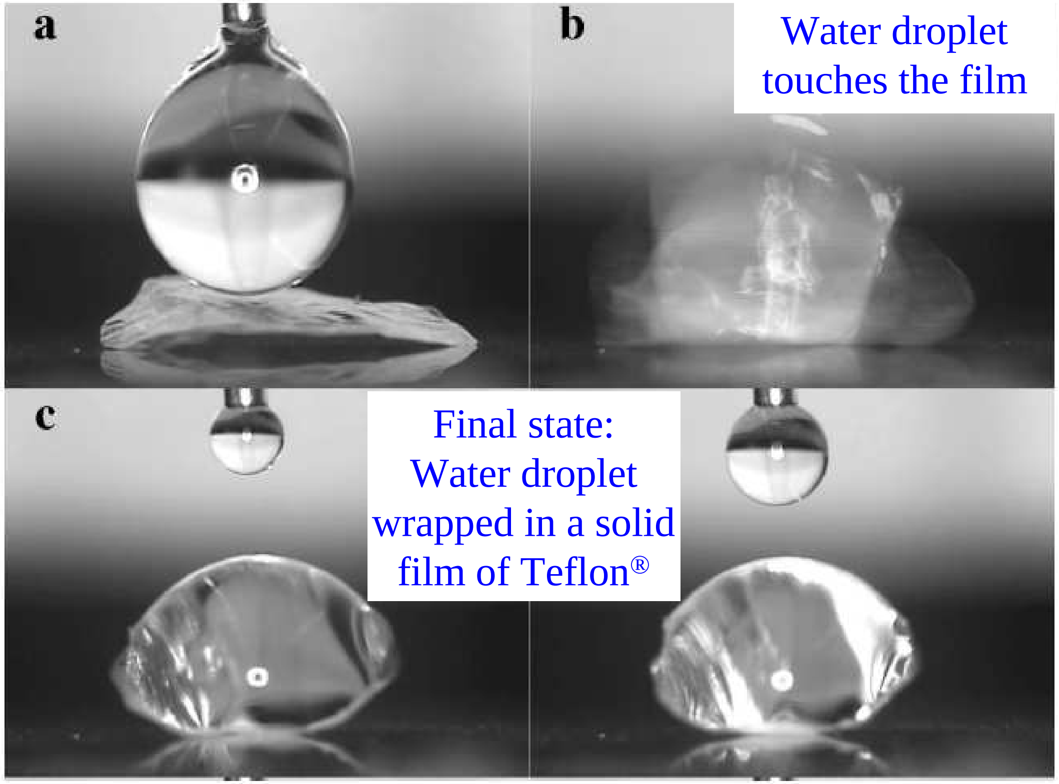
Do Hydrophobic Surfaces Exist?

1. We all know Teflon® is a hydrophobic solid and gives a non-stick surface …..
2. Consider a thin, 3.7 μm, film of Teflon® AF2400 contacted by a droplet of water

Droplet Wrapping Video



Stills from Video



Courtesy: Prof. Tom McCarthy (UMass, Amherst)

If a droplet wraps itself up in Teflon® … is this consistent with Teflon® being hydrophobic?

References Gao, L.; McCarthy, T.J. Langmuir 24 (2008) 9183-9188. McHale, G. Langmuir 25 (2009) 7185-7187.

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
   - Slip, drag reducing and functional properties are now being seriously investigated (See our contributed paper)

The End

Acknowledgements

Collaborators

Academics	Dr Mike Newton, Prof. Carole Perry (Chemistry), Prof. Brian Pyatt (Life Sciences)
	Prof. Mike Thompson (Toronto), Dr Stefan Doerr (Swansea), Dr Stuart Brewer (Dstl)
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

Funding Bodies

GR/R02184/01 – Superhydrophobic & superhydrophilic surfaces

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

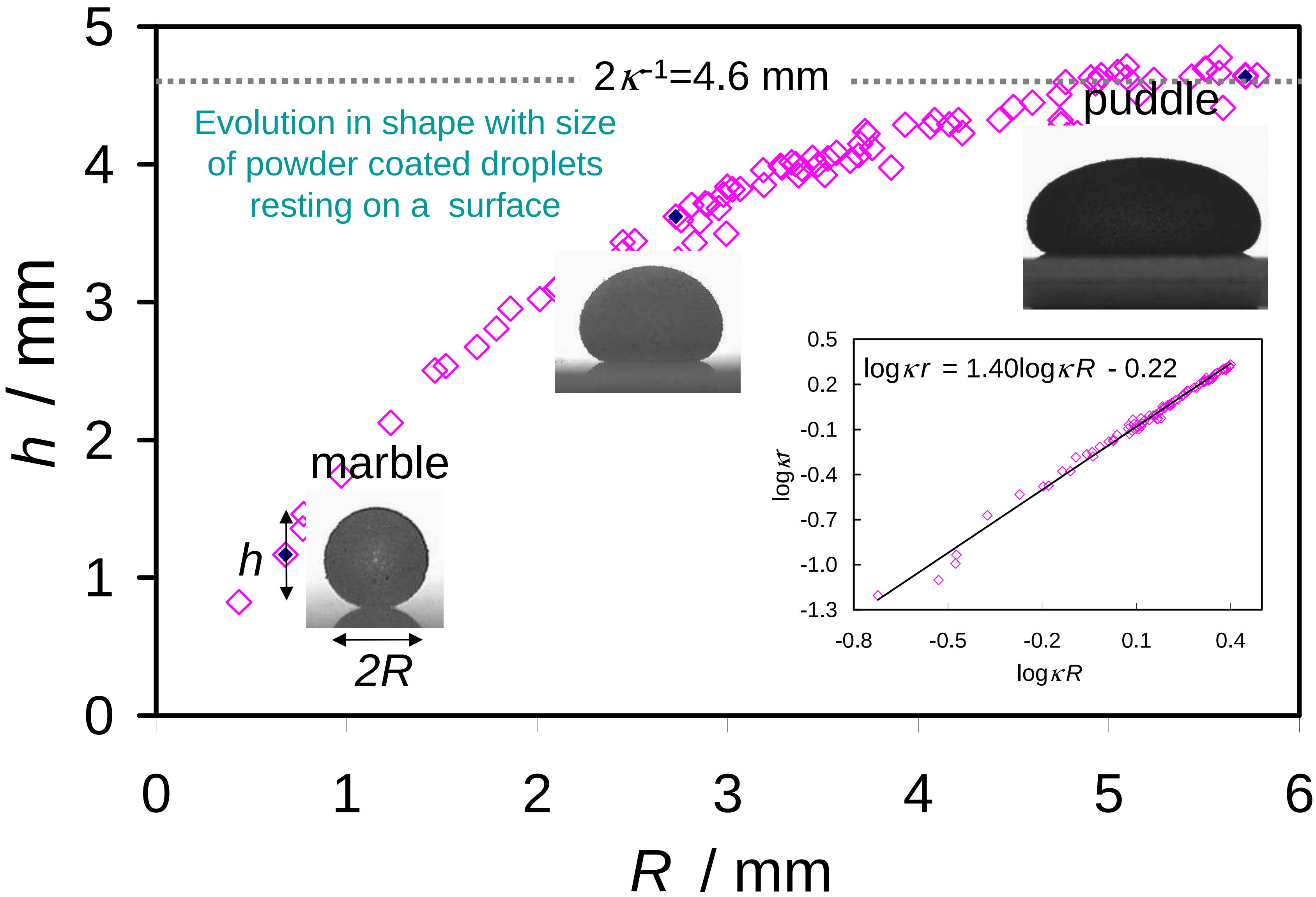
EU COST Action P21 - Physics of droplets

NATURAL ENVIRONMENT RESEARCH COUNCIL

Engineering and Physical Sciences Research Council

Appendices

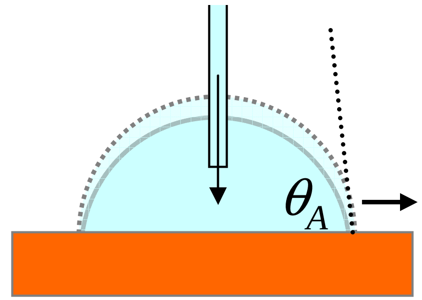
Liquid Marble Size Data (Lycopodium)

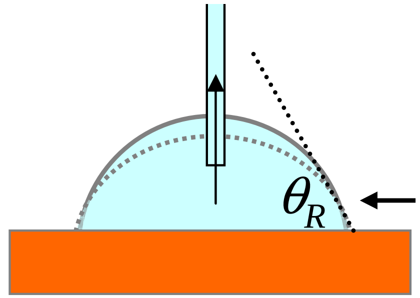


References Aussillous P, Quéré D. Proc. Roy. Soc. A462 (2006) 973-999; Nature 411 (2001) 924-927. McHale G., *et al*. 23 Langmuir (2007) 918-924. Newton, M.I., *et al*. J. Phys. D40 (2007) 20-24.

Contact Angle Hysteresis

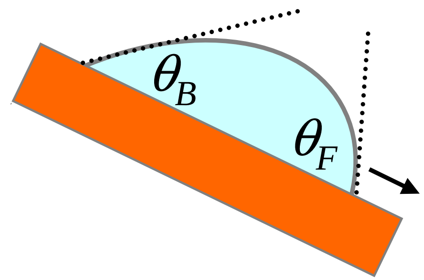
Advancing and Receding Contact Angles





- 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



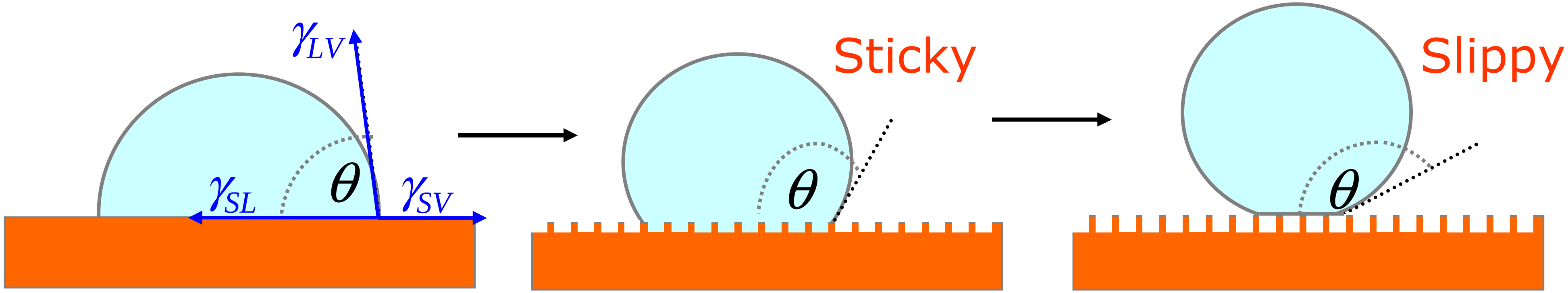
- Tilt platform and measure forward, θ_F, and backward, θ_B, contact angles
- At instant before motion assume these give advancing and receding angles
- There is no proof that these are equivalent
- Sliding angle is lowered by superhydrophobicity[1]

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

Topography & Wetting

Droplets that Impale and those that Skate

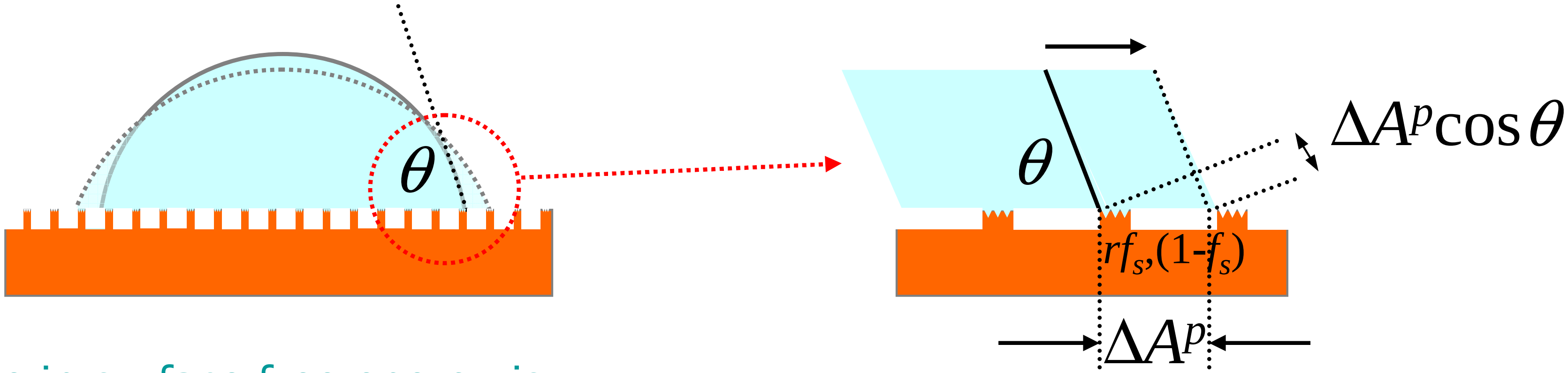
What contact angle does a droplet adopt on a "rough" surface?



Young's Eq.	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 Eq. 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.

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

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

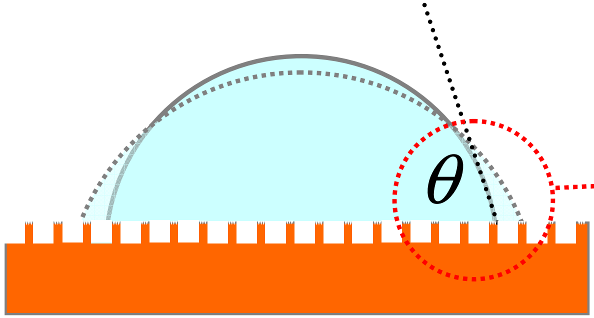
Topography $\Rightarrow$ $f_s = \Delta A_{SL}{}^{P}/(\Delta A_{SL}{}^{P} + \Delta A_{LV}{}^{P})$ = solid surface fraction from planar projections

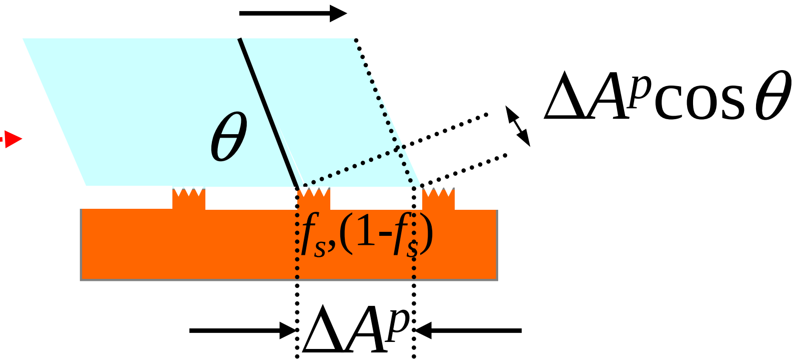
$r = \Delta A_{SL}/\Delta A_{SL}{}^{P}$ = roughness of "tops" of features

Transformation via Wenzel eq. 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. Eur. J. Soil Sci. 60 (2009) 420-430.

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 $\Delta F = 0$ $\Rightarrow$

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

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

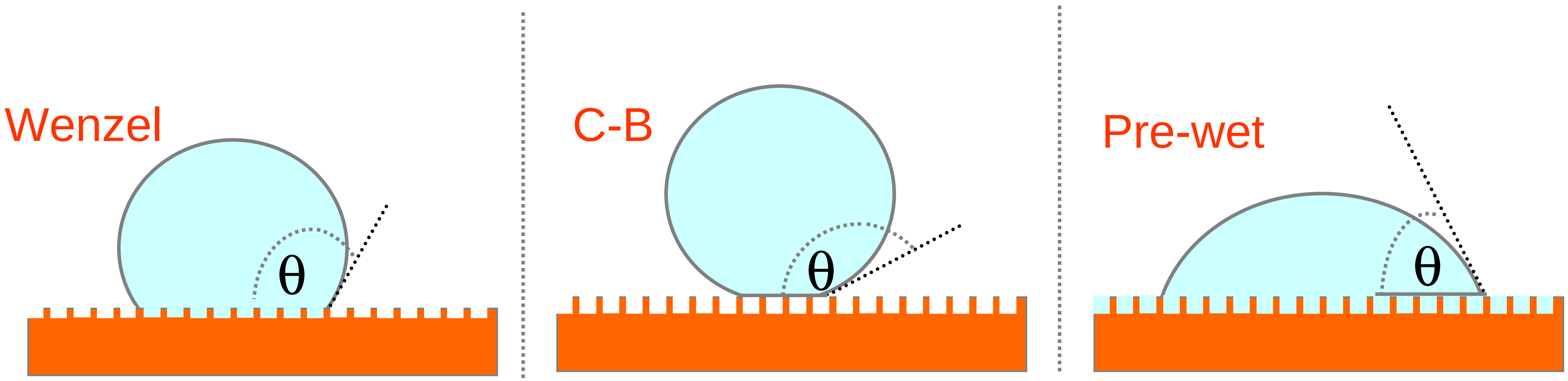
f_s^{large} = solid surface fraction for large scale structure

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. Eur. J. Soil Sci. 60 (2009) 420-430.

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

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

sign has been switched to +ve from -ve

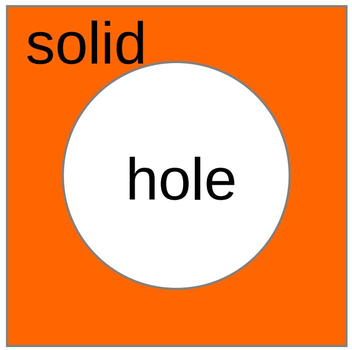
References Bico, J. *et al.*, Coll. Surf. A206 (2002) 41-46. Quéré, D. Physica A313 (2002) 32-46; McHale, G. *et al.*, Eur. J. Soil. Sci. 56 (2005) 445-452; Shirtcliffe, N.J. *et al.*, Chem. Comm. (25) (2005) 3135-3137

Cylindrical Model for Capillary Infiltration

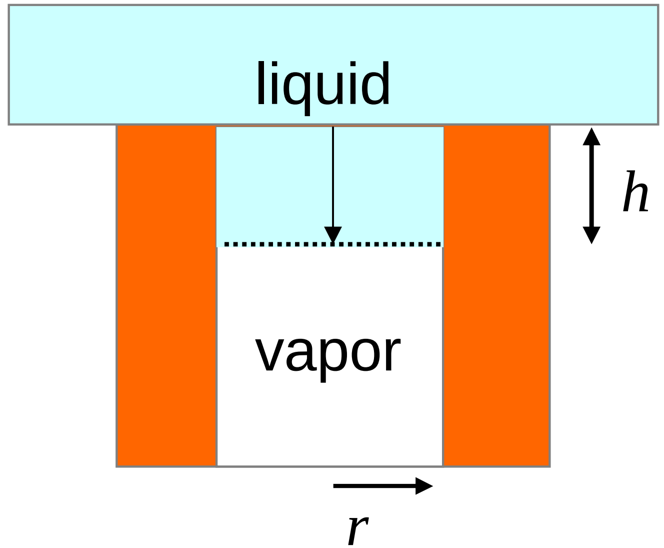
<u>Assumptions</u>

1. Fixed cylindrical pipe
2. Meniscus with Young's eq. 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

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

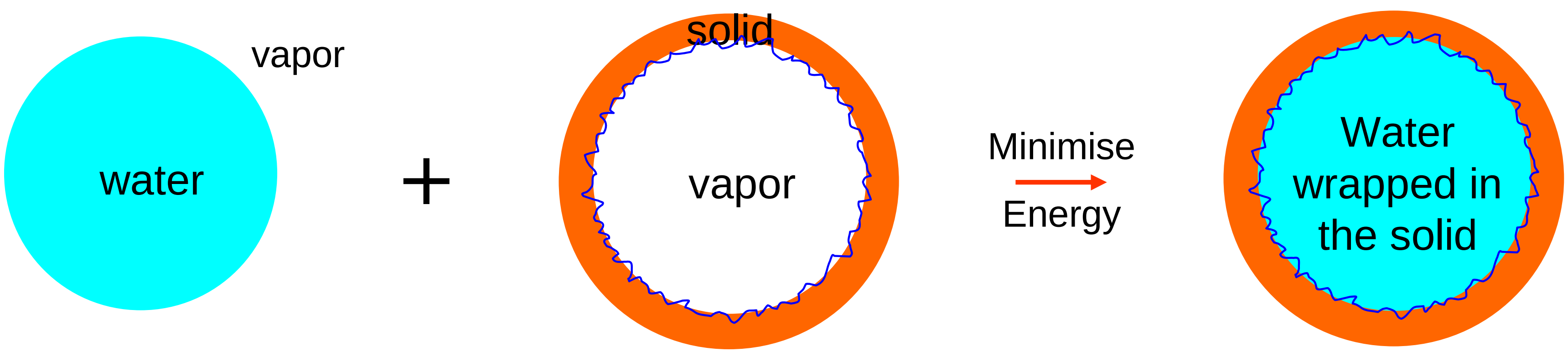
Spontaneous infiltration when ΔF is negative $\Rightarrow$ $\theta_e < 90^o$

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

Aren't all Solids with θ_e<180º Hydrophilic?

1. Assume energy in deforming solid is zero
2. Assume solid is smooth
3. Under these conditions surface free energy always favors solid wrapping up a droplet providing the Young's eq. contact angle is less than 180º

<u>Hydrophobic Solid Shell (of thickness ε) and Water</u>



$$4\pi R^2\gamma_{LV} \quad + \quad r\,4\pi R^2\gamma_{SV} + 4\pi(R+\varepsilon)^2\gamma_{SV} \quad > \quad r\,4\pi R^2\gamma_{SL} + 4\pi(R+\varepsilon)^2\gamma_{SV}$$

gives $\Delta F/4\pi R^2 = r\,\gamma_{SL} - \gamma_{LV} - r\,\gamma_{SV}$ Use Young's eq. $\Rightarrow$ $= -(1 + r\cos\theta_e) < 0 \Rightarrow \theta_e <$ $\theta_e < 90^o$ $r \to \infty$

All smooth (r=1) solids with Young's eq. θ_e<180º , incl. Teflon, are absolutely hydrophilic, although those with θ_e >90º have a tendency to hydrophobicity (in a Wenzel sense)

Bead Pack/Soil Model Calculations

Surface Free Energy Considerations

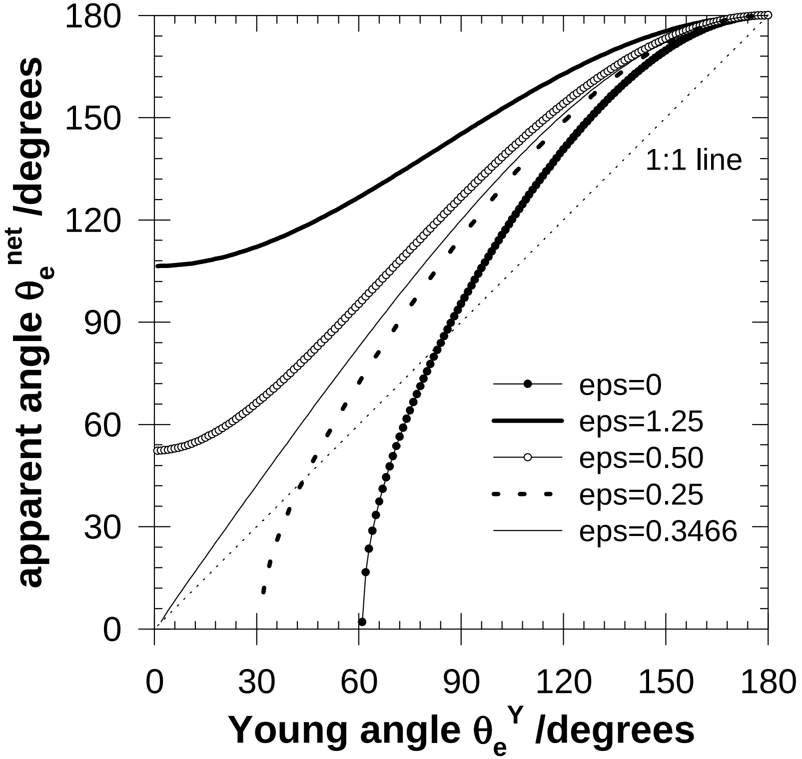
1. the curved bead surface effectively gives a roughness factor, r_s
2. the planar projection of the bead and the gap between beads forms a Cassie-Baxter system with a solid surface fraction, f_s
3. both r_s and f_s depend on the chemistry (via Young's eq.)
4. Young's contact angle is converted to a 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. Eur. J. Soil Sci. 60 (2009) 420-430.