Soil Water Repellency
A Materials View

Glen McHale, Neil J. Shirtcliffe,
Michael I. Newton & F. Brian Pyatt

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

Overview

1. Materials Science Experiments

- Super-hydrophobicity
- Penetration-to-skating transition
- Similarities to soil water repellence

2. Naïve Model of Soil

- Hydrophobic granular system
- Model: Calculations
- Experiments: Glass beads and sand

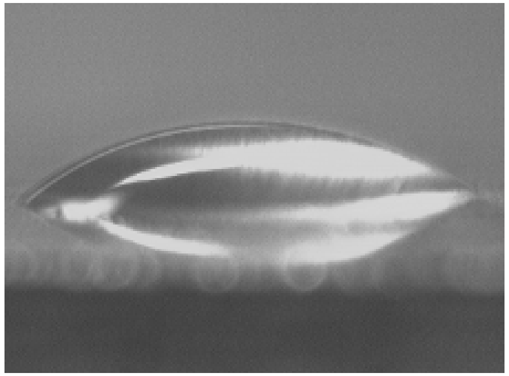
NOTTINGHAM
TRENT UNIVERSITY

Hydrophobic Effects

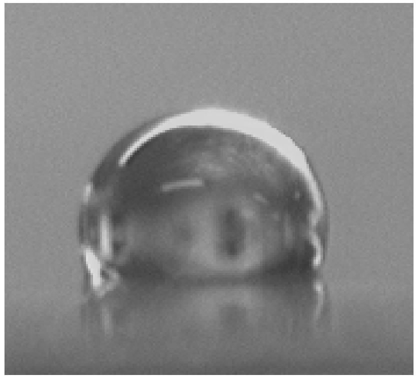
Materials Science Experiments

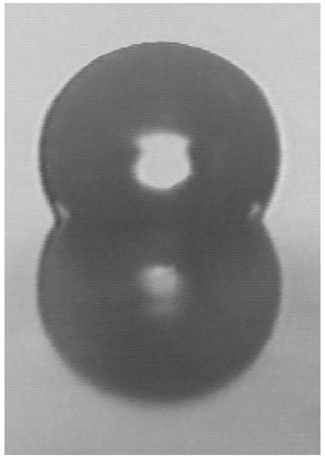
Super-hydrophobic Surfaces

Water Drop (~ 2 mm) on Cu

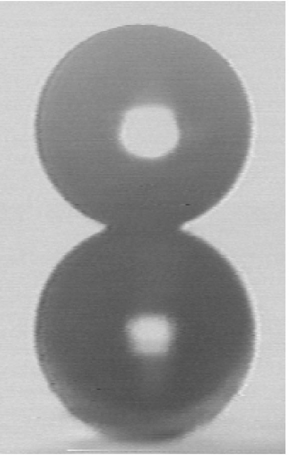


Smooth Cu surface





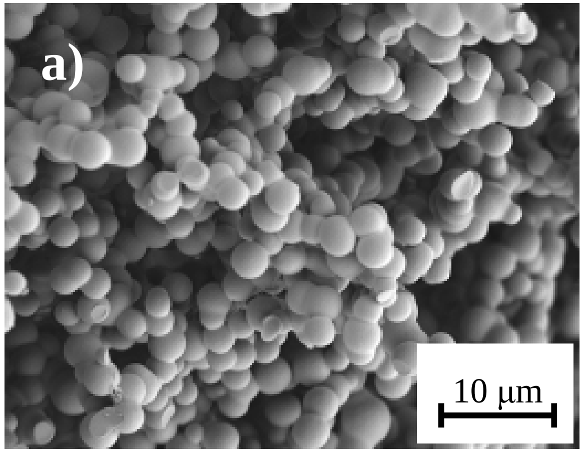
Hydrophobic and smooth Cu surface



Hydrophobised Cu etched surface

Porous Material (MTEOS Sol-Gel)

"Skating" to "penetrating" transition

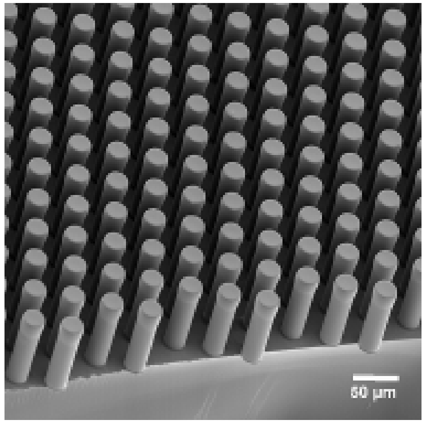


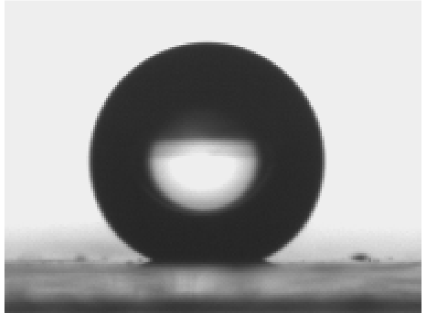
Penetration-to-Skating Transition

Micro-Structured Surface

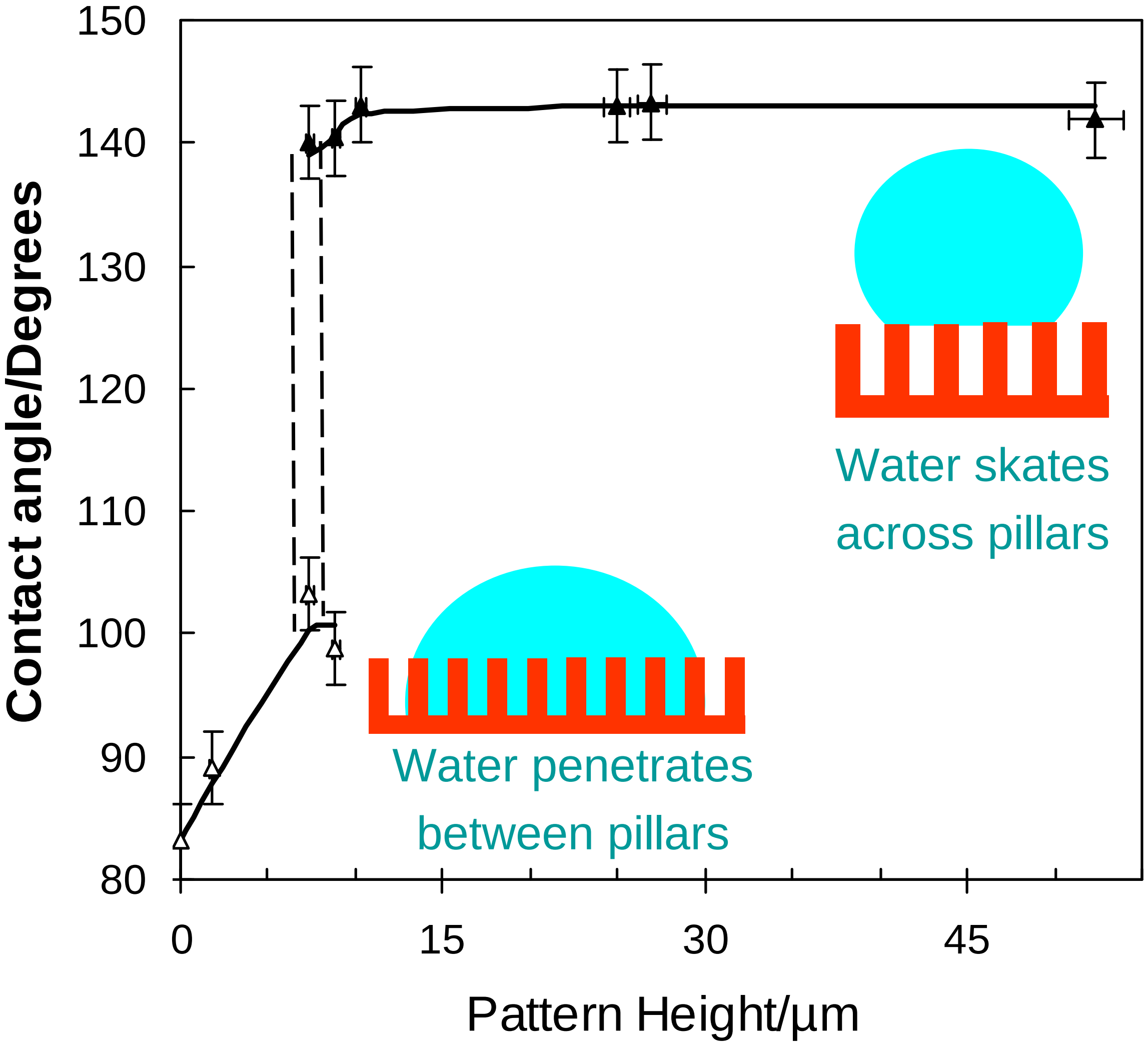
Polymer pillars 15 μm

Hydrophobic treatment





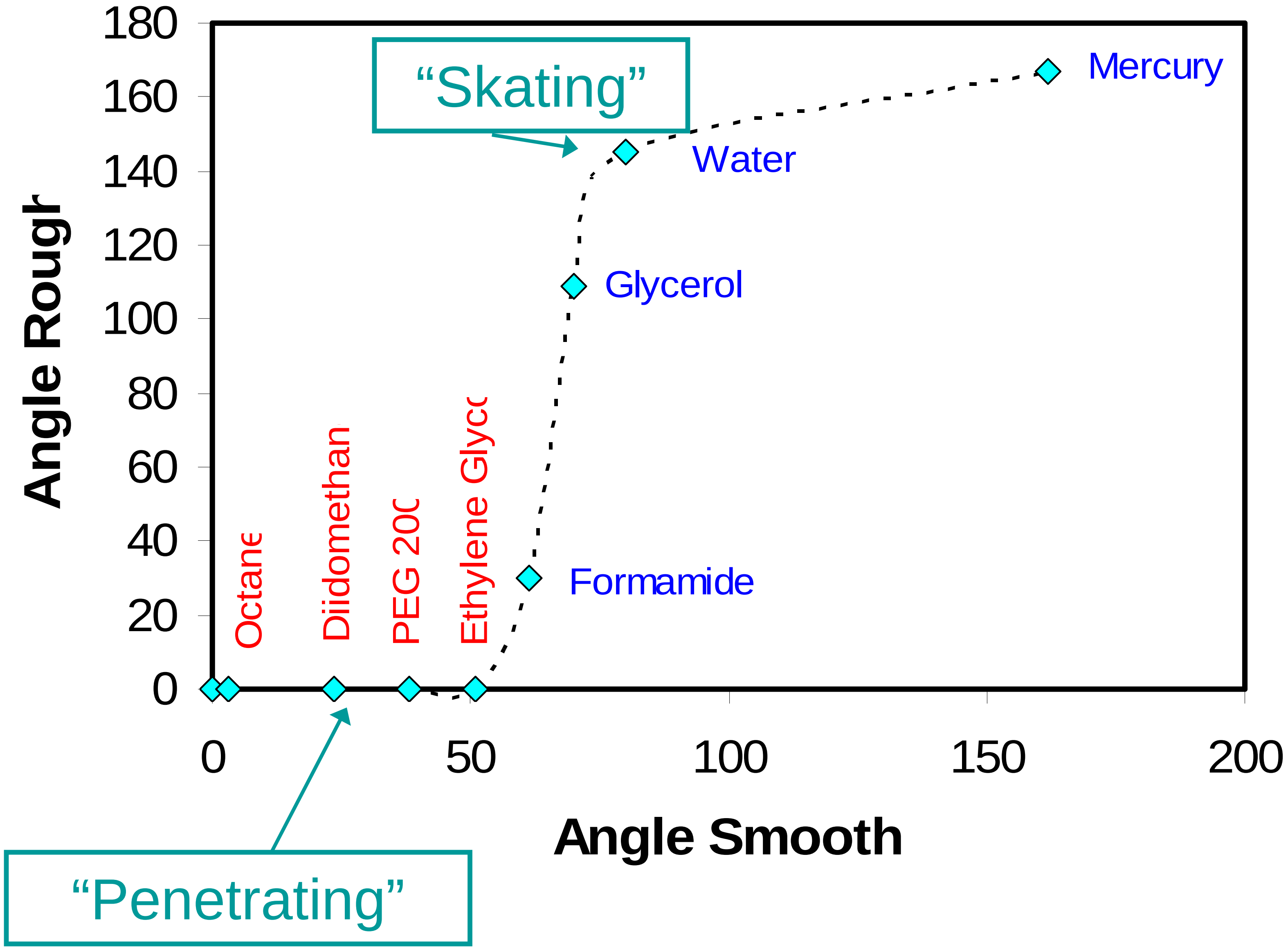
Change of Pillar Height



Water skates across pillars

Water penetrates between pillars

Different Liquids on a Super-H Surface



“Skating”

“Penetrating”

Pillar Surface - SU-8 photoresist (*D* =15 µm, *L* = 2*D*, *h* = 43 µm)

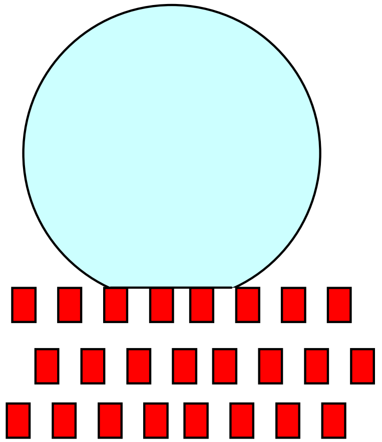
Porous Materials

No Penetration

Water droplet skates across pores

Contact angle is weighted average of θ_s

and 180° using fractions *f* and (1-*f*)

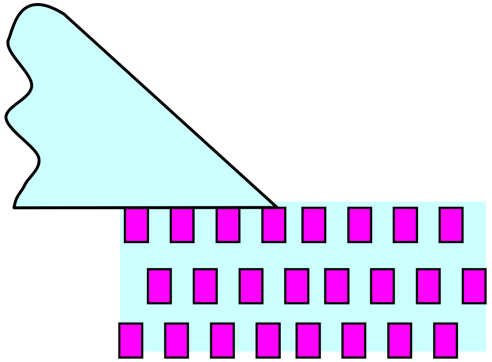


Pre-Existing Penetration

Water droplet on grains and filled pores

Contact angle is weighted average of θ_s

and 0° using fractions *f* and (1-*f*)

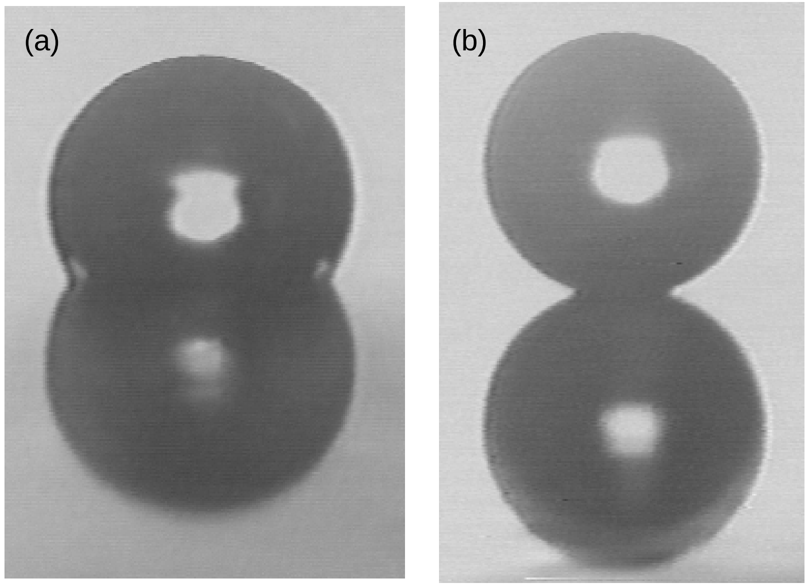


Small solid fraction f leads to either θ_r=180° *or* θ_r=0° via

$$\cos\theta_r = f\cos\theta_s \mp (1-f)$$

Requirements for Super-hydrophobicity

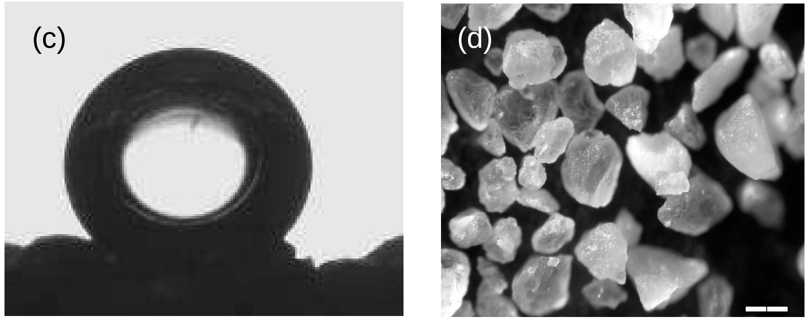
1. Surface Topography
   - roughness, hairs/fibers, surface texture, porosity, sharp features
2. Hydrophobic Surface Chemistry
   - reduction of capillary penetration



Hydrophobised Sand

Water on hydrophobised sand

Sand grains ~ 100-400 μm



Can ideas explaining transformation of a) to b) also apply to c)?

If so, does this occur naturally in sandy soil?

Soil Science Literature

Extreme Water Repellence

1. Soil exhibiting it is within the upper part of the soil profile
2. Promoted by drying of soil
3. Established via natural processes or oil contamination
4. Loose sandy soil is more prone to it
5. Forest fires or intense heating of soil is known to cause it - volatilised (hydrophobic) waxes from organic matter subsequently condensing and coating soil particles

Non-Soil Scientist View

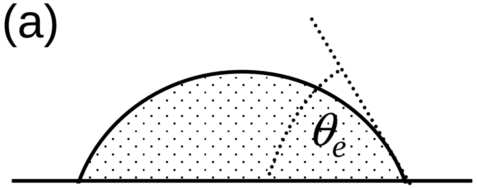
Soil is a convoluted surface consisting of a porous/granular material coated with hydrophobic compounds

Contact Angles & Topography

Smooth Surface

Young's equation summarises the surface chemistry

(a)



smooth solid

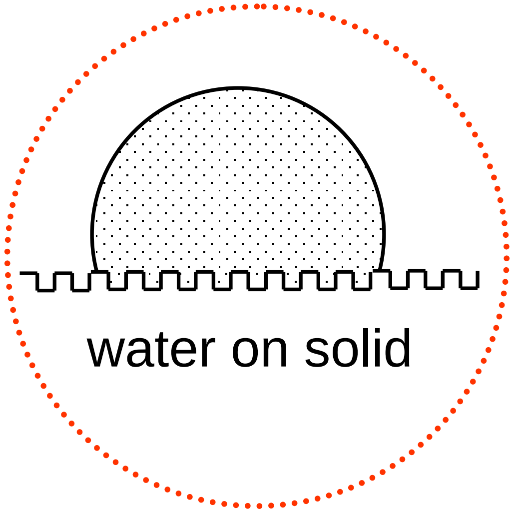
$$\cos\theta_e = \frac{(\gamma_{SL} - \gamma_{SV})}{\gamma_{LV}}$$

Rough Surfaces

Identical surface chemistry

Wenzel

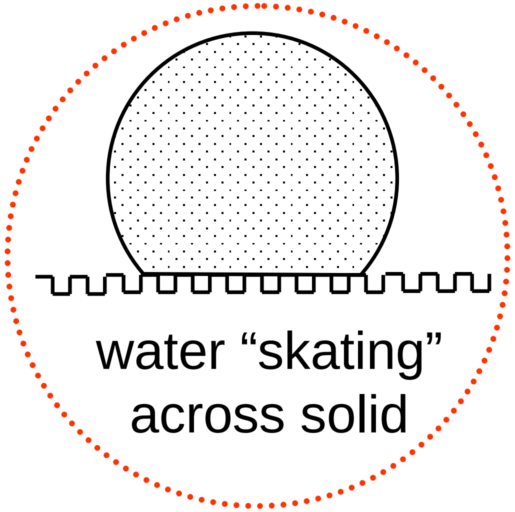
(b)



water on solid

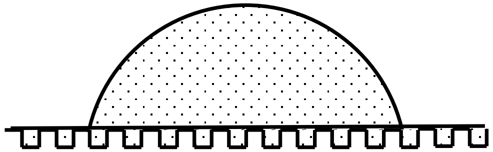
Cassie-Baxter

(c)



water "skating" across solid

(d)



water on solid-liquid surface

Wenzel ("Sticky")

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

Cassie-Baxter ("Slippy")

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

Hydrophobic Effects

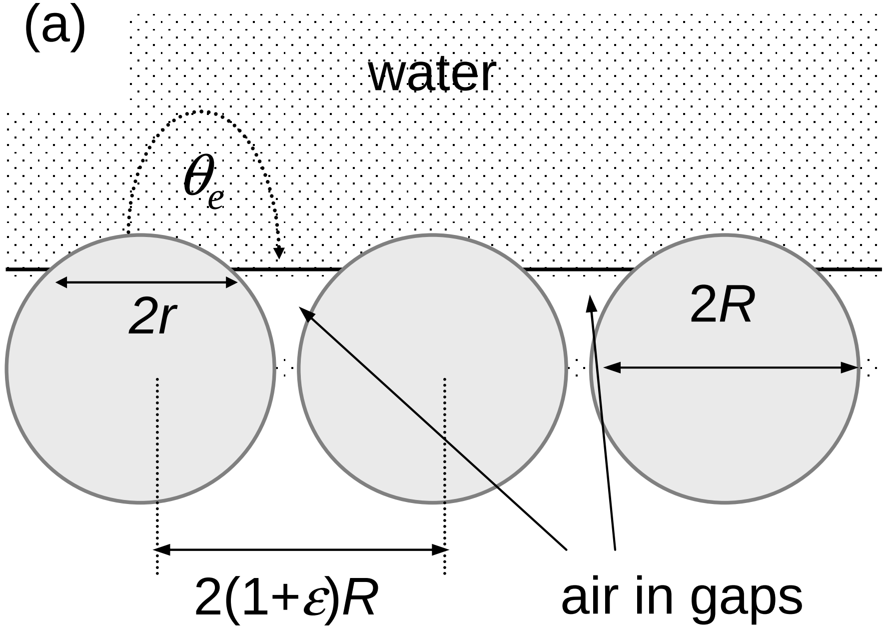
Model & Results

A Naïve Model of Soil

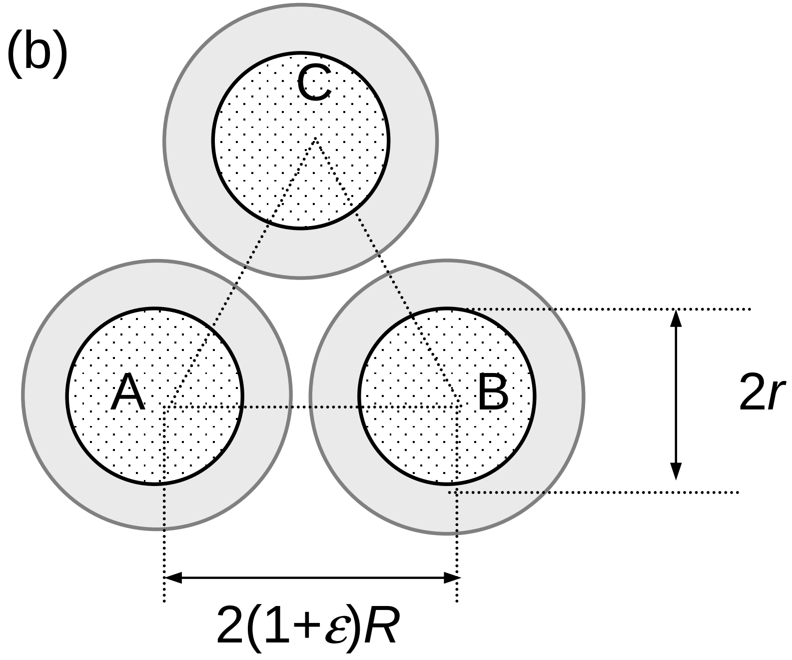
Assumptions

1. Uniform size, smooth spheres
2. Water bridges horizontally between spheres
3. Capillary (surface tension) dominated size regime
3. Ignore complex grain/pore structures, micro- or macro-aggregates with differing hydrophobicity, water flow and transport properties of soil

Side View



Top View



Pre-Existing Dry and Wet Soil

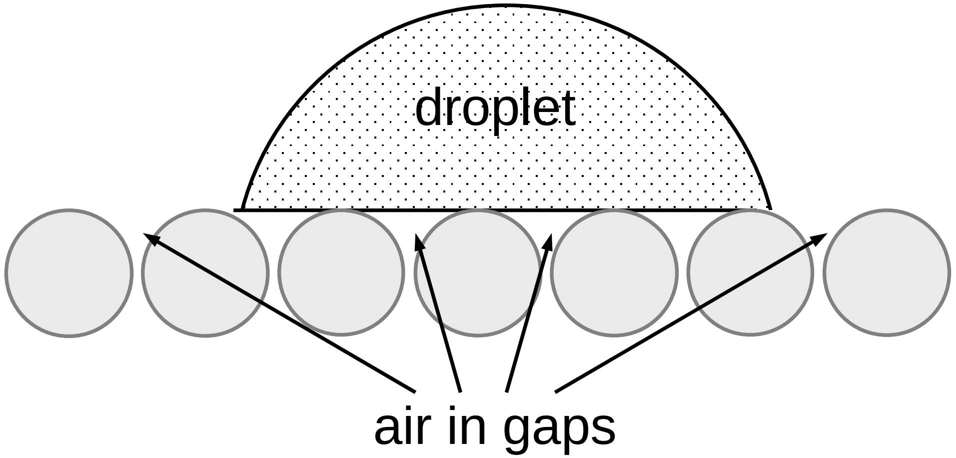
Cassie- Baxter or Wenzel?

1. Cassie-Baxter state is often a metastable state
2. Water can be forced into pores by applying pressure
3. Water vapour condensing can form Wenzel state whereas a droplet may deposit in a Cassie-Baxter state

Droplets Deposited onto Dry/Wet Sand will be Different

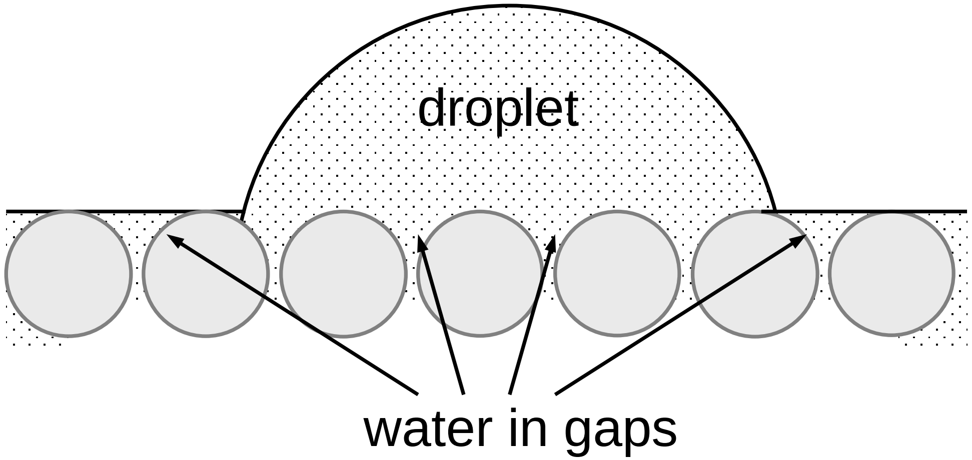
Droplet on Dry Sand

(a)



Droplet on Wet Sand

(b)



Principles of Calculation

Dry Soil

Cassie-Baxter equation with
composite solid-vapour surface

$$\cos\theta_V^C = f\cos\theta_e - (1-f)$$

Soil with Water in Gaps

Cassie-Baxter equation with
composite solid-water interface

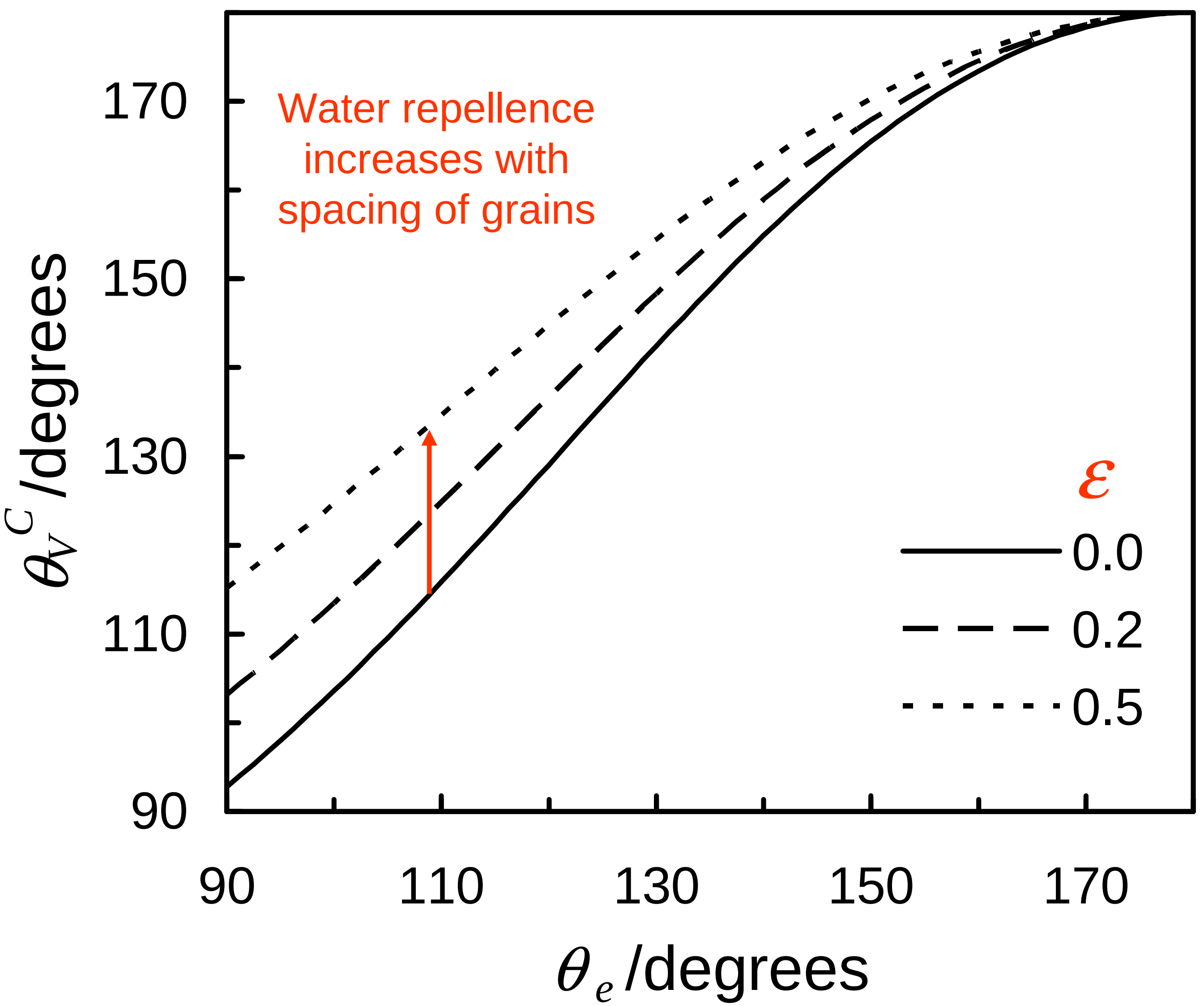
$$\cos\theta_W^C = f\cos\theta_e + (1-f)$$

Solid Surface Fraction

Use geometry
Grains not close-packed
Centre-to-centre separation
between spheres is $2(1+\varepsilon)R$
where, ε, is a spacing constant

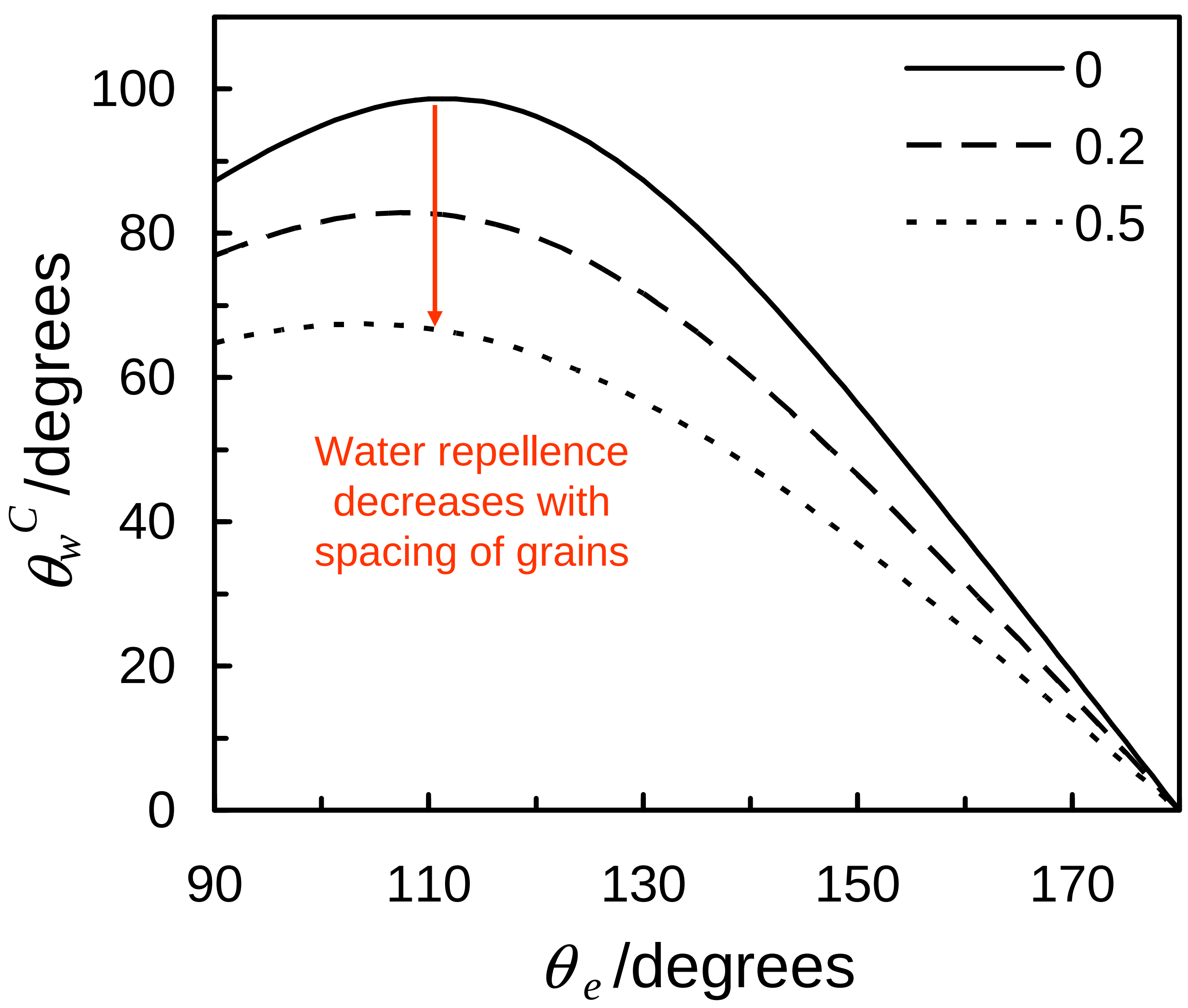
$$f(\varepsilon) = \frac{1+\cos\theta_e}{1+\cos\theta_e + \sqrt{3}(1+\varepsilon)^2 \Big/ \pi - \frac{1}{2}\sin^2\theta_e}$$

Dry Soil - Water Repellence Enhancement



Water repellence increases with spacing of grains

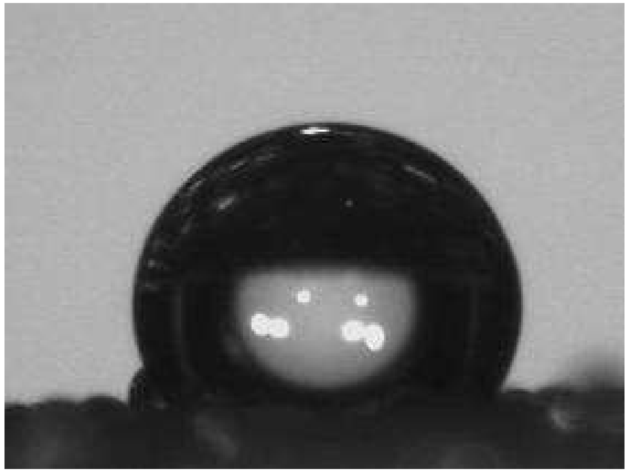
Wet Soil - Water Repellence Reduction



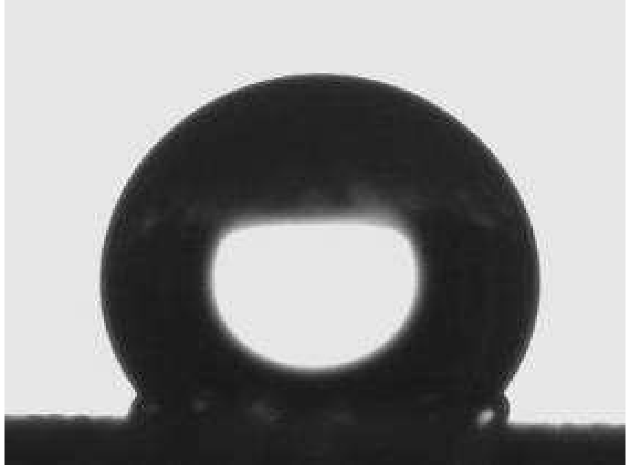
Water repellence decreases with spacing of grains

Experiments on TMSCL Treated ($\theta \sim 108^{o}$) Glass Beads

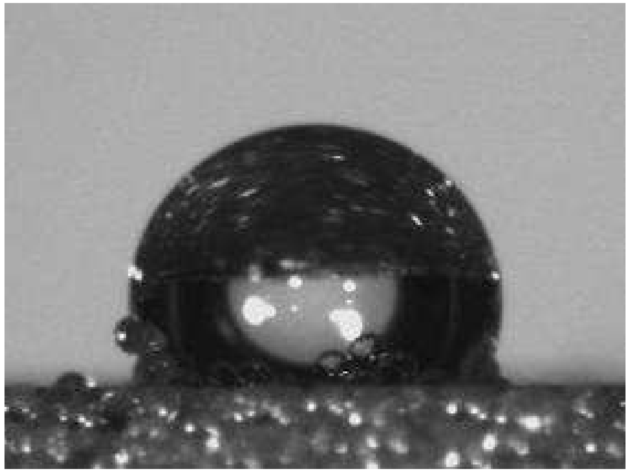
600 μm and 126°



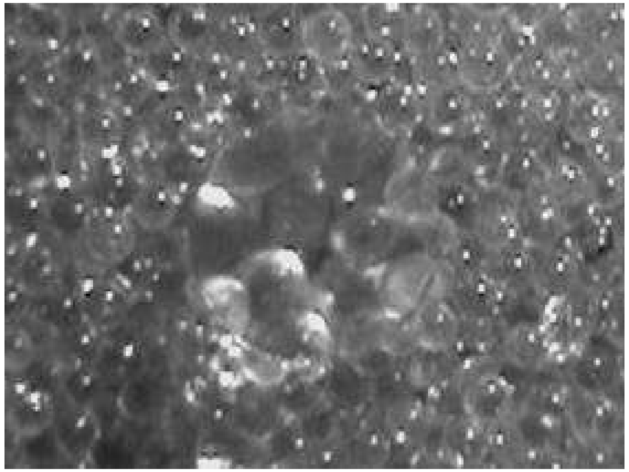
250 μm and 140°



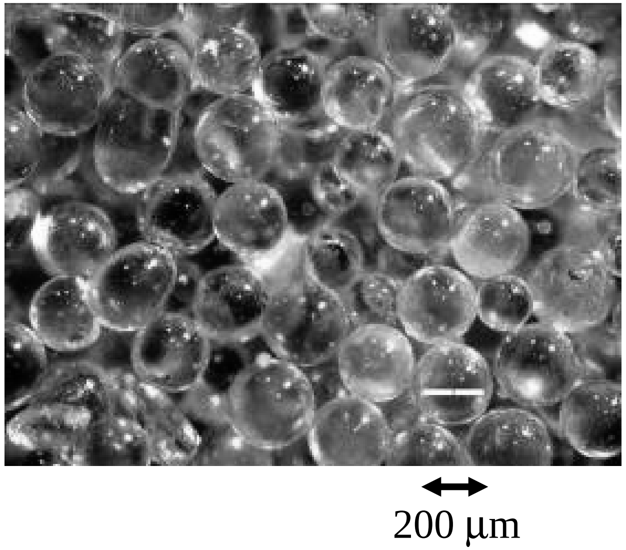
Forward Tilt View



Top View

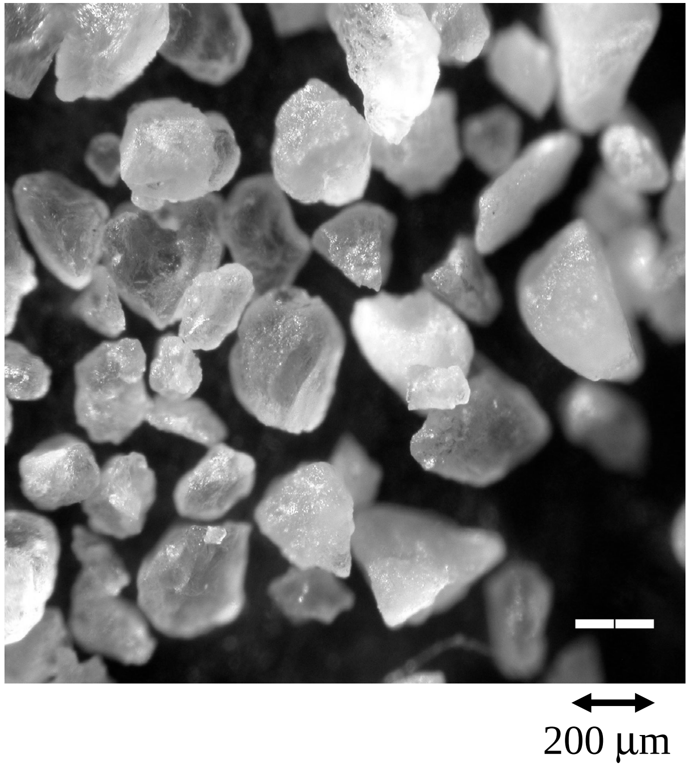


Packing

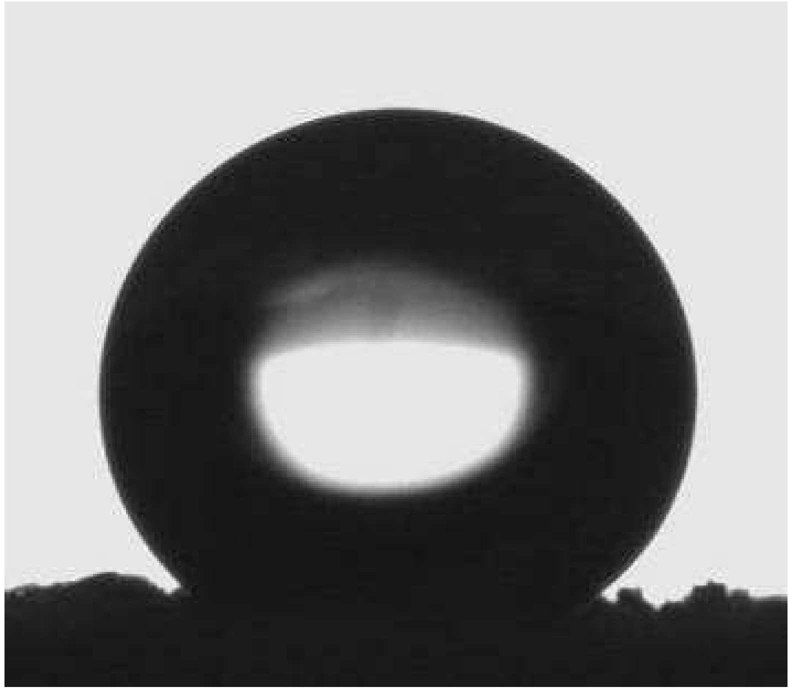


Experiments on Hydrophobic Sand

Shape and Packing



Sand with139°



Experiments Performed or In Progress

1. *MED and WDPT comparisons to contact angles*
2. *Systems with mixed sizes of glass beads*
3. *Systems with mixtures of hydrophobised and non-hydrophobised beads/sand*

Conclusions

1. Naïve model predicts hydrophobic enhancements
2. Packing effect is consistent with loose/fluffy soil
3. Size range of grains is plausible for super-hydrophobicity
4. Relative humidity/wet soil would reduce water repellence
5. Sharp features on sand would have a dramatic effect
6. Microstructure of any wax could have a strong effect
7. Run-off and raindrop splash erosion would be enhanced
8. MED (Cassie-Baxter to Wenzel transition) and WDPT (Wenzel infiltration routes) will not measure the same effects

Acknowledgements

- Professor Loveland, Editor of EJSS
- Dr Stefan Doerr, Swansea University
- EPSRC EP/C509161/1 *(Extreme Soil Water Repellency)*
- EPSRC GR/R02184/01 *(Systematic Physical and Chemical Design of Surfaces with Controlled Super-Hydrophobicity/Hydrophilicity)*
- Professor Carole Perry (Sol-gel surfaces)
- Gregoire Chabrol, Saana Aqil, Carl Evans, Dr Dale Herbertson

Key References

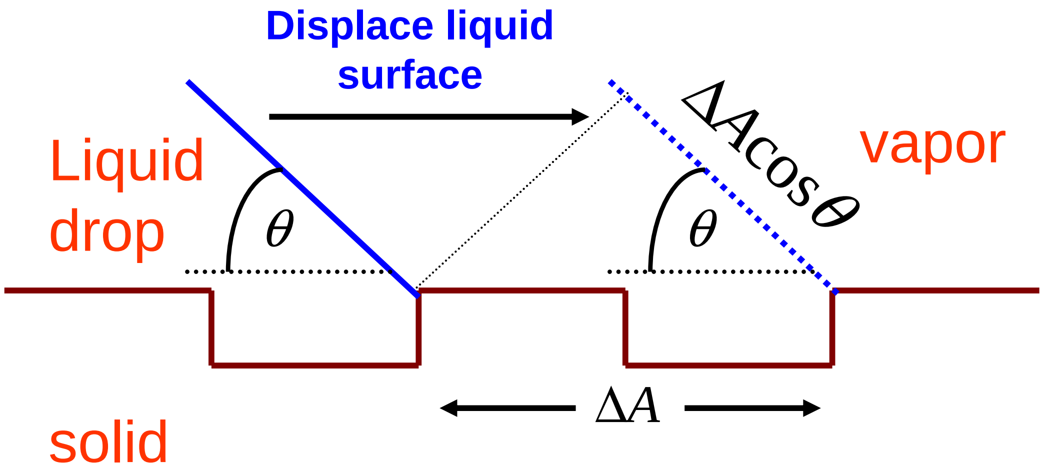
1. McHale G, Newton MI, Shirtcliffe NJ, *Water repellent soil and its relationship to granularity, surface roughness and hydrophobicity: a materials science view*, EJS (2005)
2. Shirtcliffe NJ, McHale G, Newton MI, Chabrol G, Perry CC, *Dual-scale roughness produces unusually water-repellent surfaces*, Adv. Maters. 16, 1929 (2004)
3. McHale G, Shirtcliffe NJ, Newton MI, *Super-hydrophobic and super-wetting surfaces: Analytical potential?*, Analyst, 129, 284 (2004)
4. Shirtcliffe NJ, McHale G, Newton MI, Perry CC, *Intrinsically superhydrophobic organosilica sol-gel foams*, Langmuir, 19, 5626 (2003)

The End

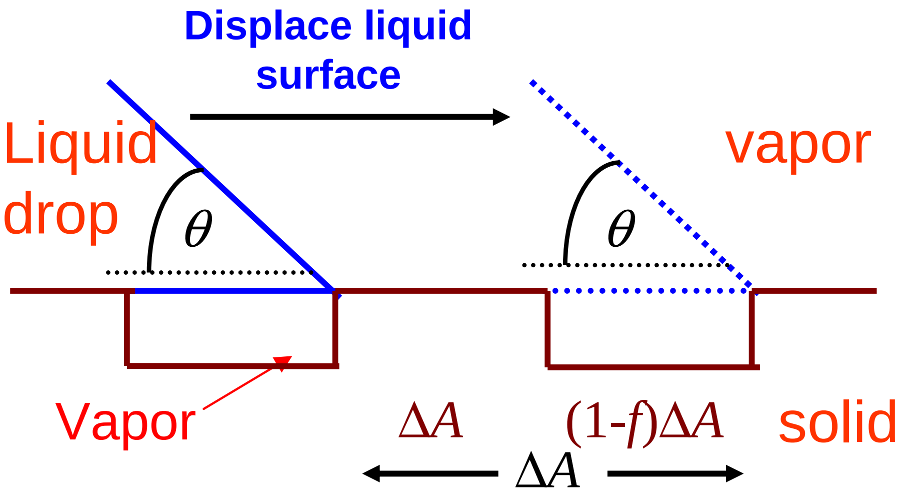
The End

Wetting and Topography

Complete Penetration



Air “Trapping”



Surface Free Energy Changes

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

Wenzel’s Eqn

$$\cos\theta_e^R = r(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} = r\cos\theta_e^s$$

$r = \Delta A_{\text{true}}/\ \Delta A$ = roughness factor

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

Modified (Cassie Style) Eqn

$$\cos\theta_e^R = f\cos\theta_e^s - (1-f)$$

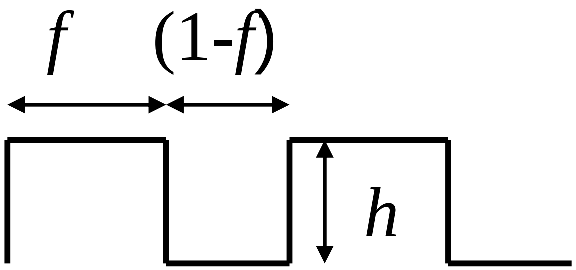
f = fraction of “rough” surface wet

Effect of Topography - Air “Trapping”

- Liquid Penetration into Texture

  f=solid fraction, (1- f)=liquid fraction

  r = roughness



Liquid film penetrates when:

Critical angle θ_c is in 0 to 90° range

$$\cos\theta_e^S > \frac{1-f}{r-f} = \cos\theta_c$$

- “Skating” Drop

  Liquid bridges from one peak to next

$$\cos\theta_e^R = -1 + f\left(\cos\theta_e^S + 1\right)$$

- Air “Trapping” and Roughness

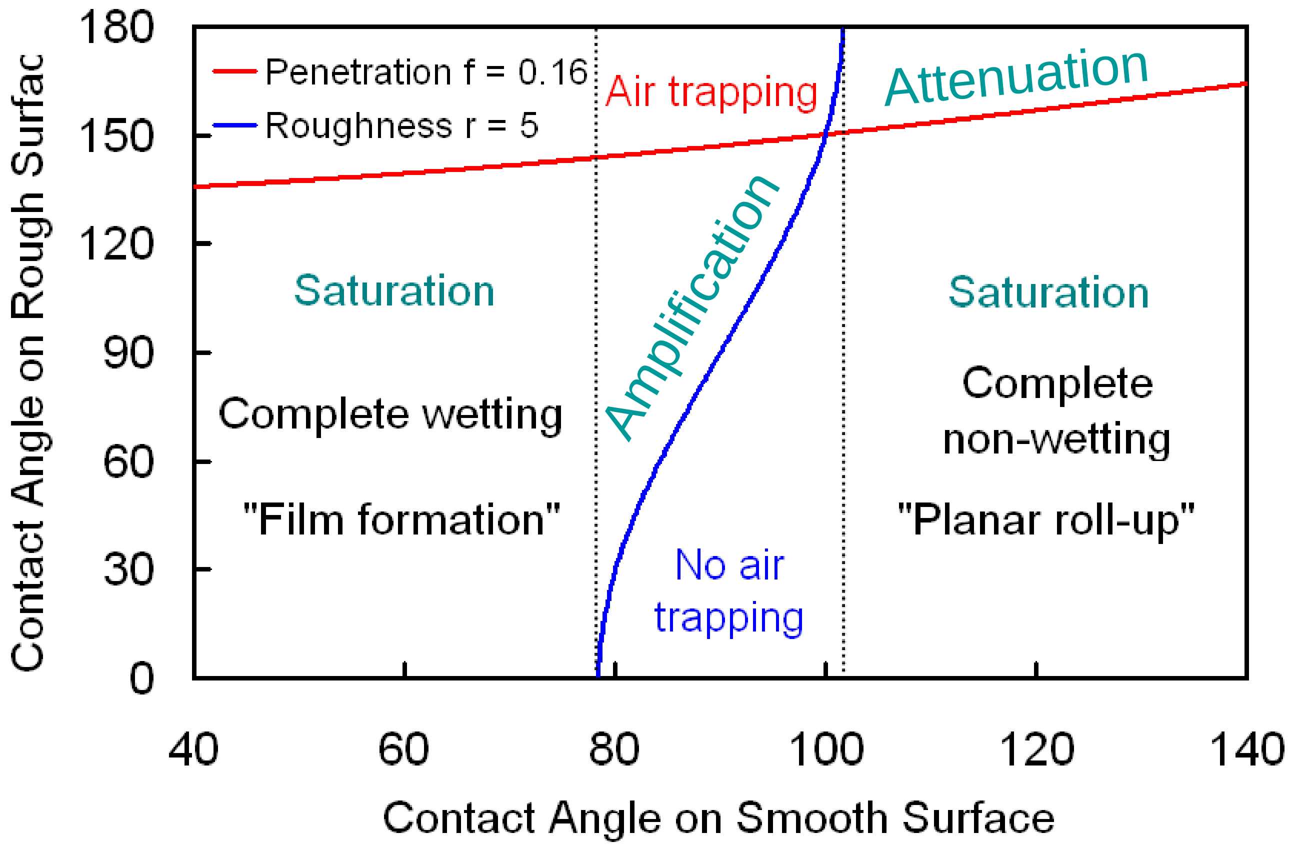
  Sinusoidal model gives critical roughness for installation of horizontal contact line

  (e.g. for 120°, r_c=1.75 $\Rightarrow$ jump in θ_e^R to > 150°)

  Also, sharp features promote “skating”

$$r_c = 1 + \frac{\tan^2\theta_e^S}{4}$$

Effect of Topography - Equilibrium



Roughness/Topography

θ_e^s > threshold

⇒ enhances hydrophobicity

θ_e^s < threshold

⇒ enhances film formation

Super-hydrophobic

Air “trapping” (“Skating case”)

⇒ most existing examples

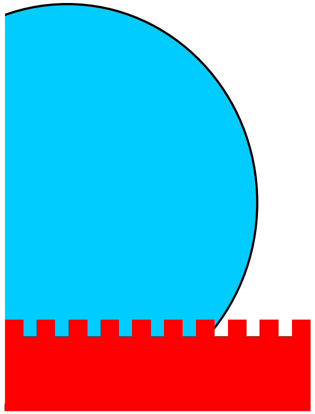
Pressure

⇒ air trapping disappears

Hydrophobic Effects

Theoretical Ideas

Wenzel Form of Super-H



Wenzel's Equation

- Based on roughness, *r*

$$\cos\theta_e^w = r\cos\theta_e^s$$

Consequences

- Saturation to non-wetting

$$\cos\theta_e^s \to -1/r$$

- Saturation to wetting

$$\cos\theta_e^s \to 1/r$$

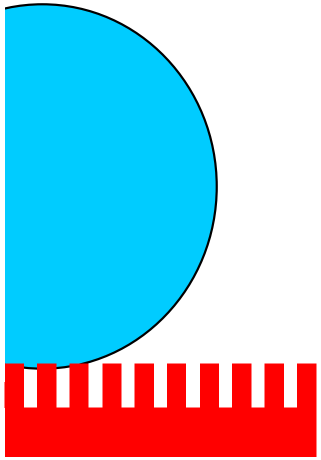
- Amplification in-between

$$\left(\frac{\Delta\theta_e^w}{\Delta\theta_e^s}\right)_{\theta_e^s} > 1$$

Contact Angle Hysteresis

- Super-H with <u>large</u> hysteresis, i.e. "<u>Sticky</u>" surface

Cassie-Baxter Form of Super-H



Cassie-Baxter Equation

- Based on composite air-solid surface, *f*

$$\cos\theta_e^C = f\cos\theta_e^S + (1-f)\cos(180)$$

Consequences

- Complete super-H of 180º only reached when $\theta_e{}^s$=180º
- Easier to obtain >150º than with Wenzel
- Transition to super-H promoted by sharp edges on features

Contact Angle Hysteresis

- Low hysteresis: "Slippy" rather than "sticky" surface

Effect of Topography - Aspect Ratio

- Penetration and Aspect Ratio

  As roughness increases system jumps from blue (Wenzel) to red (Cassie-Baxter) curve, OR

  For a given roughness, jump occurs with increasing chemical hydrophobicity