NOTTINGHAM TRENT UNIVERSITY

# Wetting of Hydrophobic Beads and Sand

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# *"Conversations with a soil scientist"*

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# Overview

1. Extreme Soil Water Repellence
2. Soil as a Super-Hydrophobic Surface
3. Critical Angle for Imbibition
4. Surface Wetting versus Porosity
5. Particle Lifting and Droplet Self-Coating

# Motivation

*Extreme Soil Water Repellence*

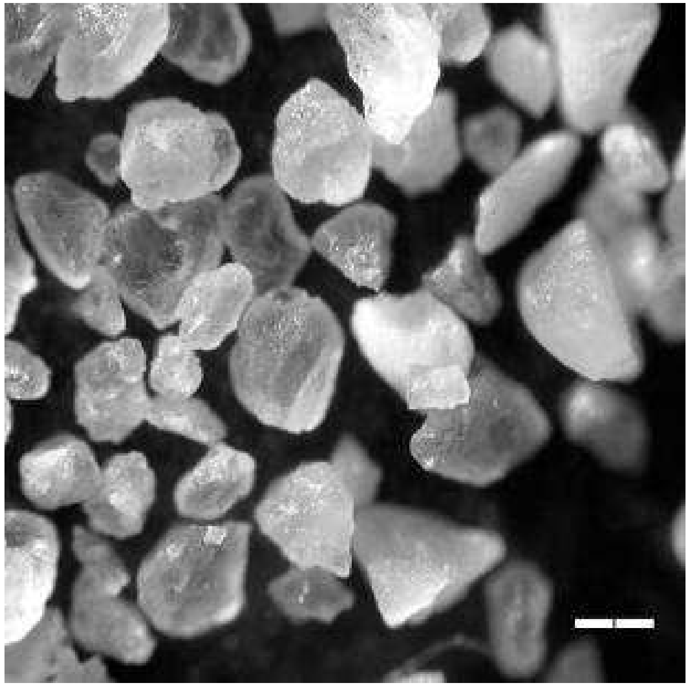
# Extreme Soil Water Repellency

## Field Conditions

1. Sandy soil can become extremely hydrophobic
   - After forest fires
   - After oil contamination
2. Problems
   - Vegetation difficult to re-establish (land remediation difficult)
   - Increased run-off
   - Land/soil erosion
3. Soil scientists use two field tests
   - Molarity of Ethanol Droplet (MED) (i.e. critical surface tension test)
     *(% ethanol needed for droplet to infiltrate within 3 seconds)*
   - Water Droplet Penetration Time (WDPT)
4. Materials scientists (and soil scientists back in the lab) may measure contact angle $\theta_{measured}$

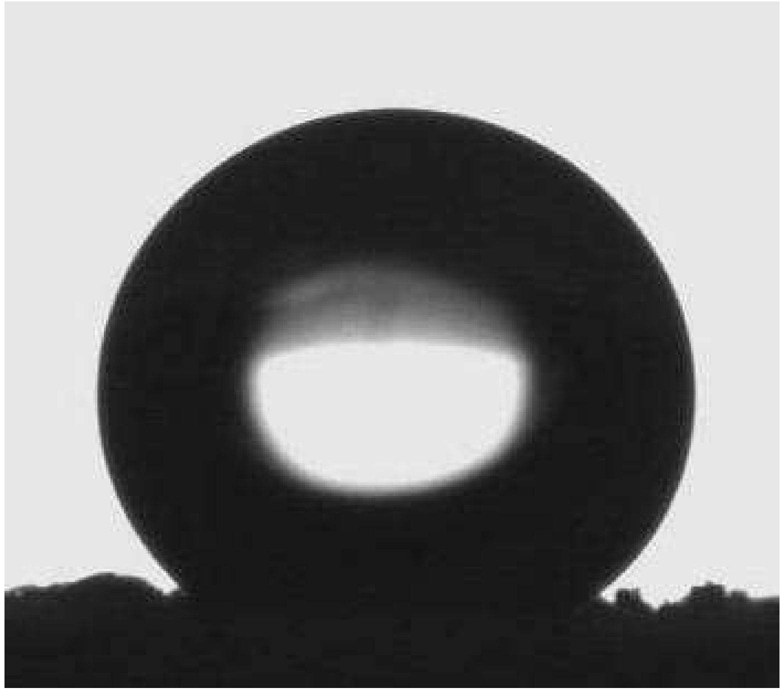
# Water Droplet on Hydrophobic Sand

Shape and Packing



200 μm

Sand with139º



# 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. Loose sandy soil is more prone to it
4. Forest fires or intense heating of soil is known to cause it - volatilised (hydrophobic) waxes from organic matter subsequently condensing and coating soil particles

### *A Non-Soil Scientist View*

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

*Soil can be a super-hydrophobic surface*

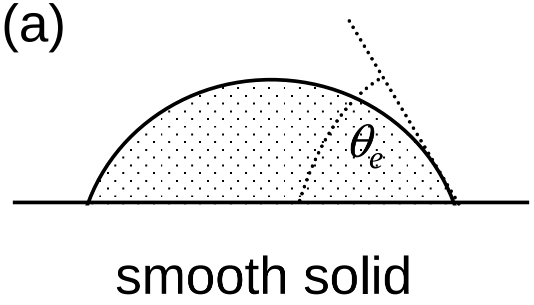
# Super-hydrophobic Model

# Super-hydrophobic Surfaces

## Smooth Surface

Young's equation summarises the surface chemistry

(a)

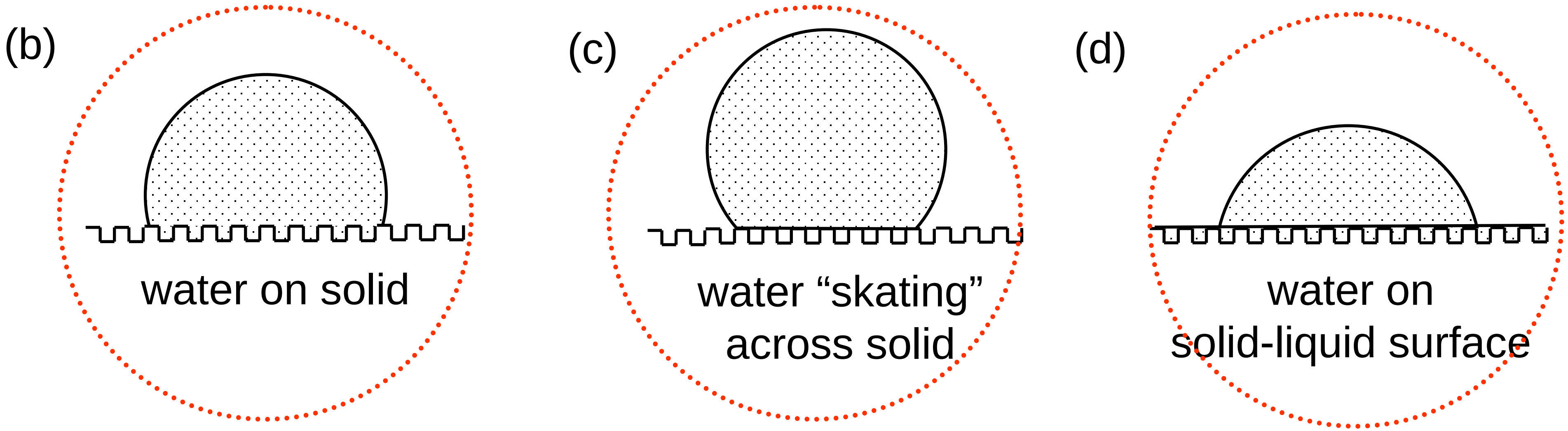



$$\cos\theta_e = \frac{(\gamma_{SL} - \gamma_{SV})}{\gamma_{LV}}$$

## "Rough" Surfaces

Identical surface chemistry

*Wenzel* *Cassie-Baxter*




*Wenzel ("Sticky")*

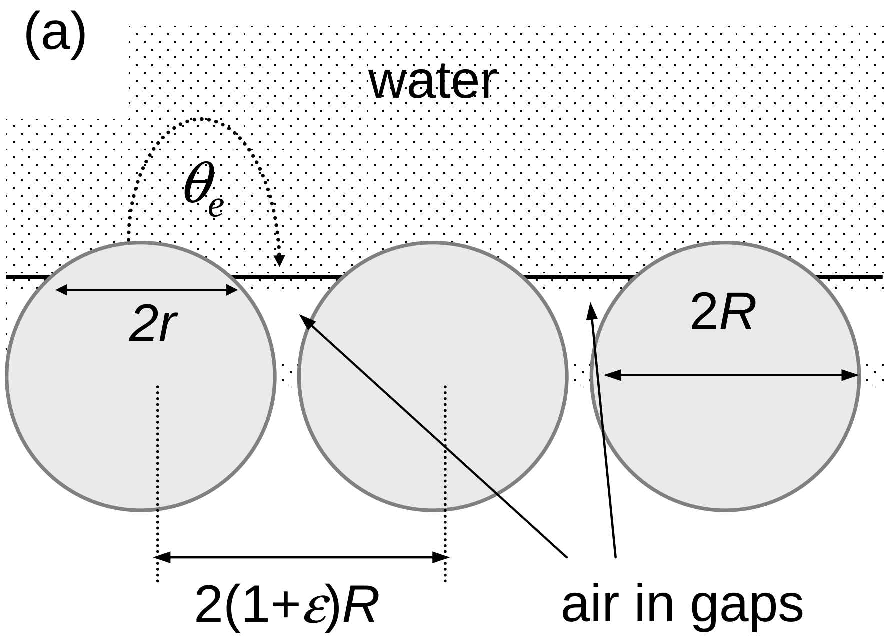
*Cassie-Baxter ("Slippy")*

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

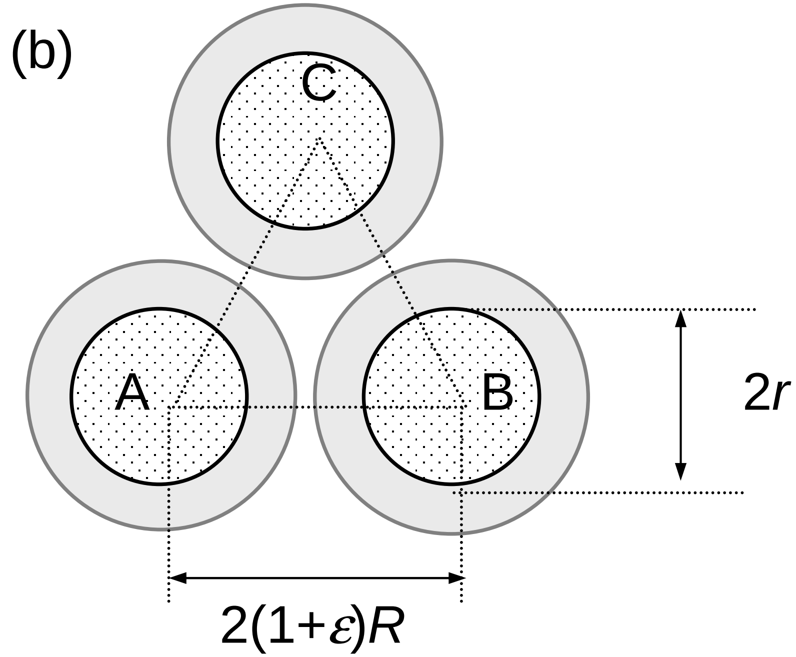
$$\cos\theta_{CB} = f\cos\theta_e - (1 - f)$$

# A Simple Model of Soil

## Side View




## Top View

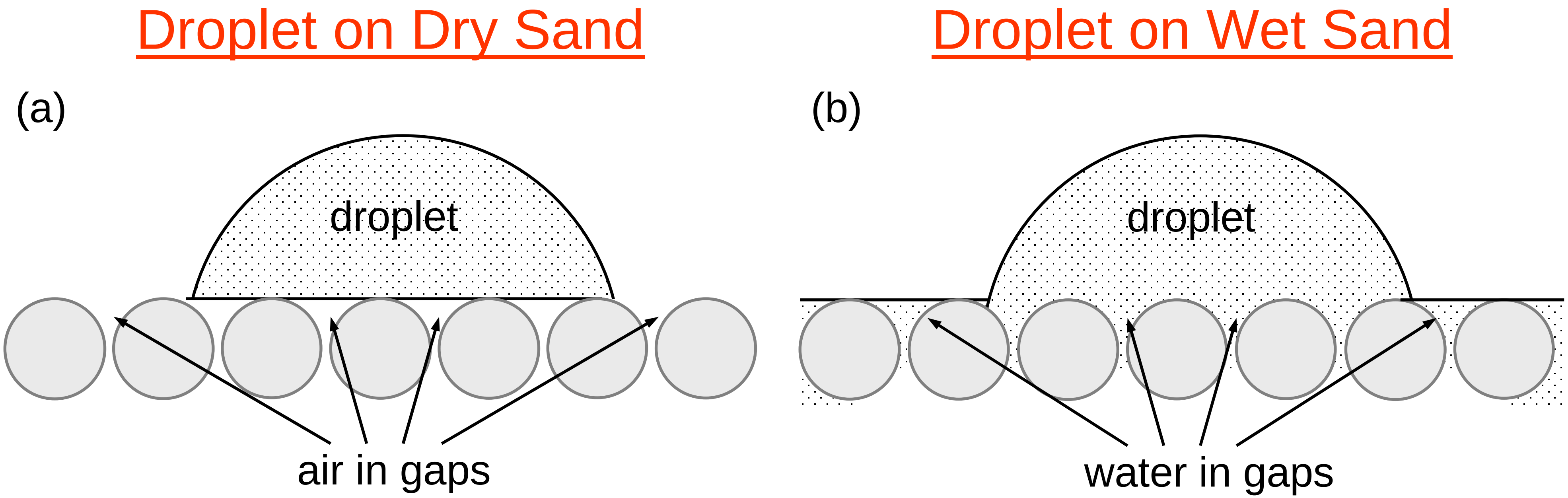



## Assumptions

1. Uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges horizontally between spheres
3. Capillary (surface tension) dominated size regime

Reference: McHale *et al*, Eur. J. Soil. Sci. 56 (2005) 445-452; Hydrological Processes (2006).

# Dry and Wet Soil




## Notes

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

# 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

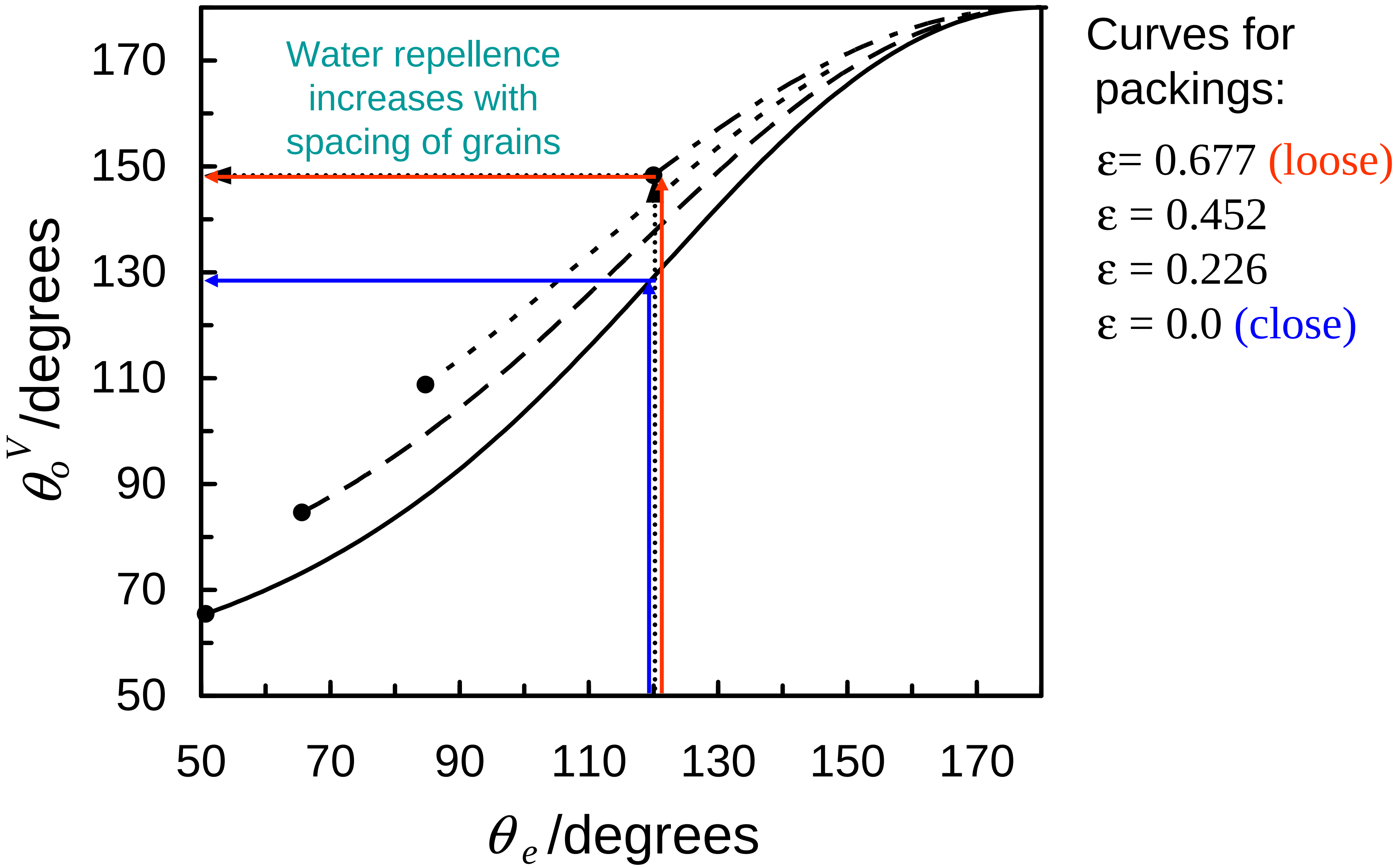
$$\cos\theta_W^C = f\cos\theta_e + (1-f)$$

## Solid Surface Fraction

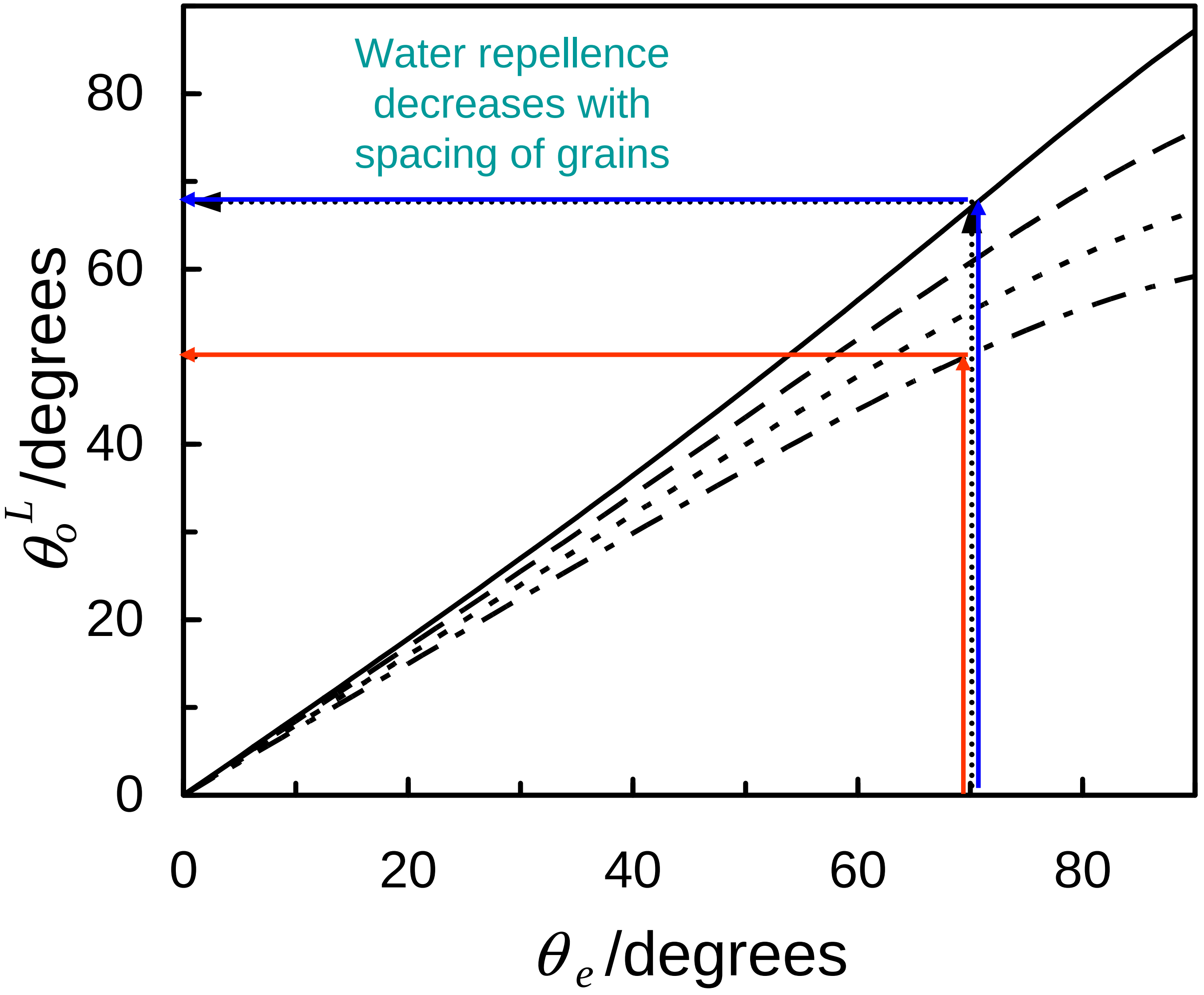
Use geometry
Grains not close-packed
Centre-to-centre separation
between spheres is $2(1+\varepsilon)R$
where, $\varepsilon$, is a spacing constant

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

# Dry Soil - Water Repellence Enhancement



# Wet Soil - Water Repellence Reduction

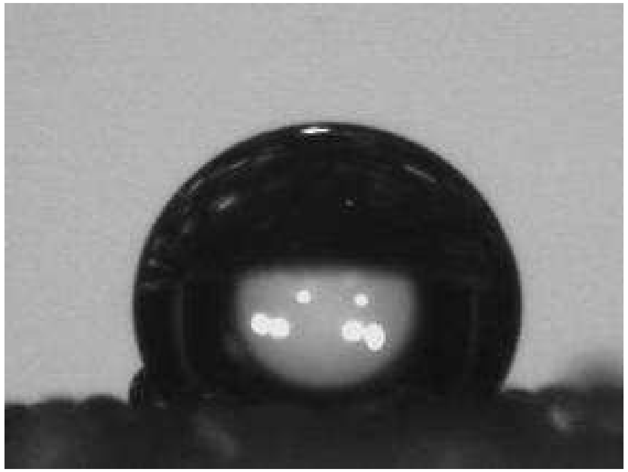



Curves for packings:

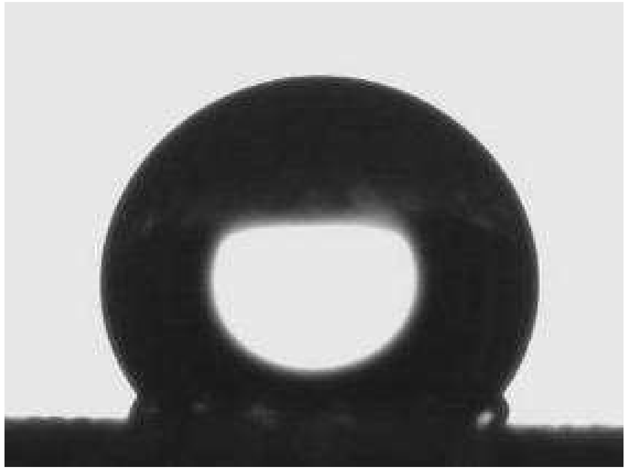
ε= 0.0 (close)
ε=0.226
ε = 0.452
ε = 0.677 (loose)

# Experiments on TMSCL Treated ($\theta$~108°) Glass Beads

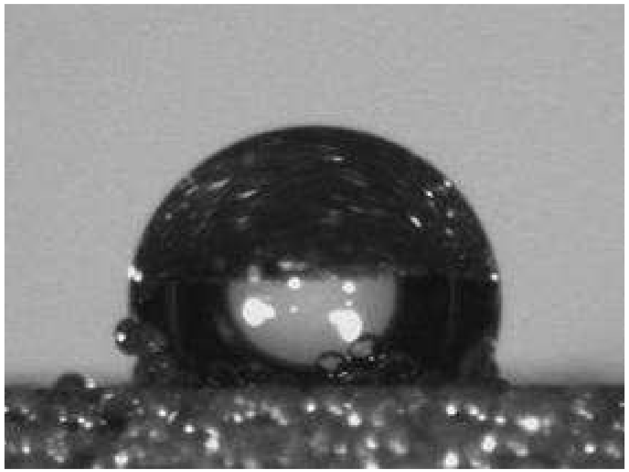
## 600 μm and 126°



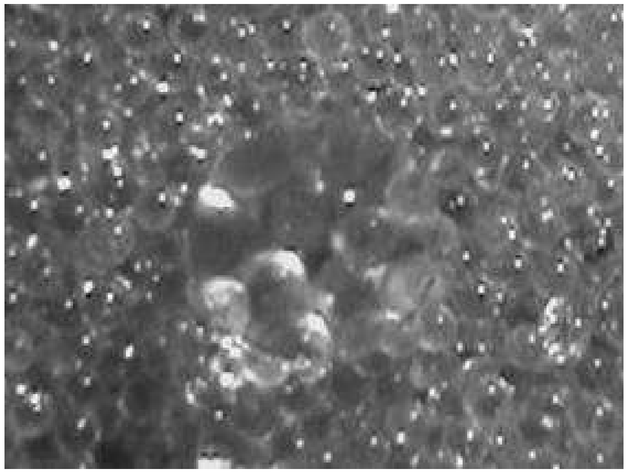
## 250 μm and 140°



## Forward Tilt View



## Top View



## Packing

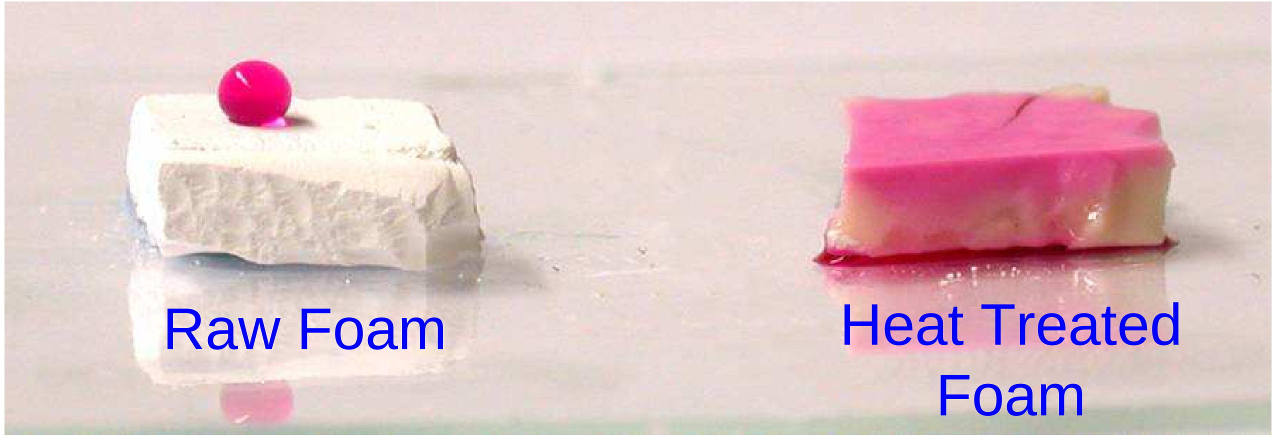
↔ 200 μm

# Wetting versus Porosity

# Switching of Super-hydrophobicity

## Super-hydrophobic to Super-slurp

1. Super-hydrophobic MTEOS sol-gel foam
2. Switched to porous foam by heat cycle to change to hydrophilic




## Imbibition into Soil

Switch to imbibition can be observed with change in liquid surface tension (rather than temperature)

Reference: Shirtcliffe *et al*, Chem. Comm. 25 (2005) 3135-3137 (also Nature News 20/7/05)

# Imbibition into Bead Packs & Sand

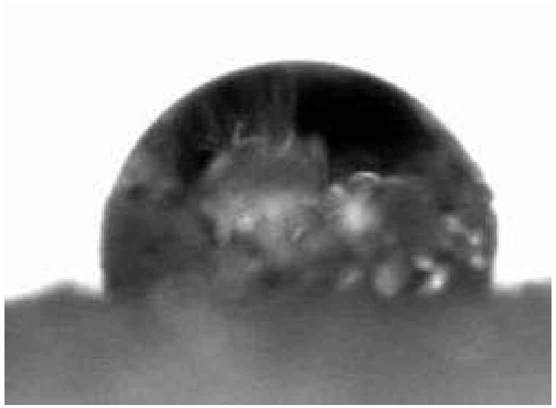
## Fluorocarbon Bead Packs

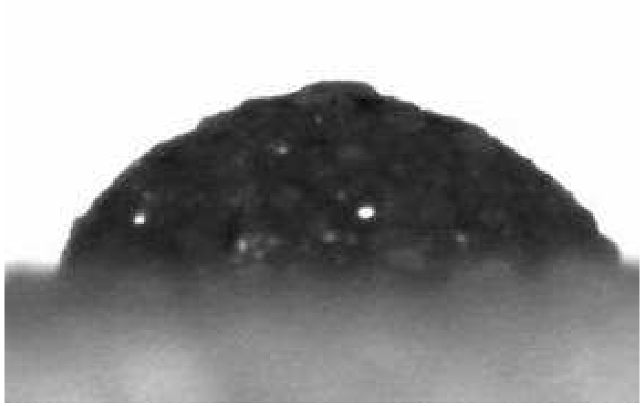
1. Fluorocarbon coated glass beads (size = 75 μm) on glass slides
2. Range of hydrocarbon liquids
3. Penetration occurs for pentane, but not for hexane

| **Liquid** | ***θ* on fluorocarbon coated glass slides / °±4** |
|---|---|
| Octane | 72$^o$ |
| Heptane | 65$^o$ |
| Hexane | 61$^o$ |
| Pentane | 52$^o$ |

## Fluorocarbon Coated Sand

Penetration occurs for hexane


Octane (72$^o$)


Heptane (65$^o$)


Hexane (61$^o$)

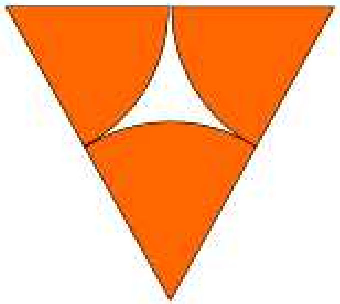
Reference: Shirtcliffe *et al*, Hydrological Processes (2006)

# Model for Capillary Imbibition

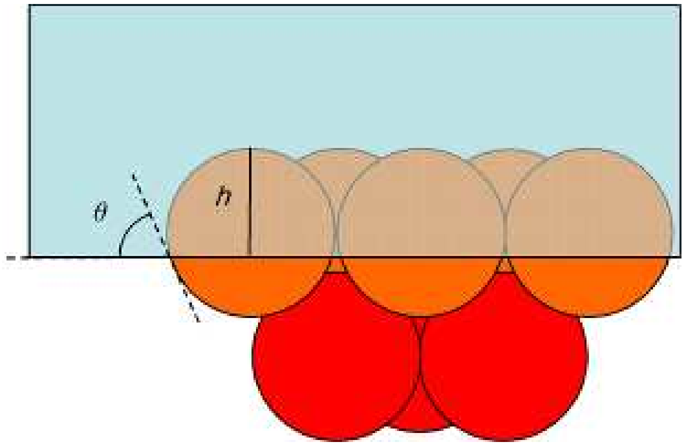
## Assumptions

1. Spherical particles
2. Fixed & hexagonally packed
3. Planar meniscus with Young's law contact angle, $\theta_e$
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 imbibition occurs
4. Critical contact angle, $\theta_c$, when $h_c$ reached

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

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

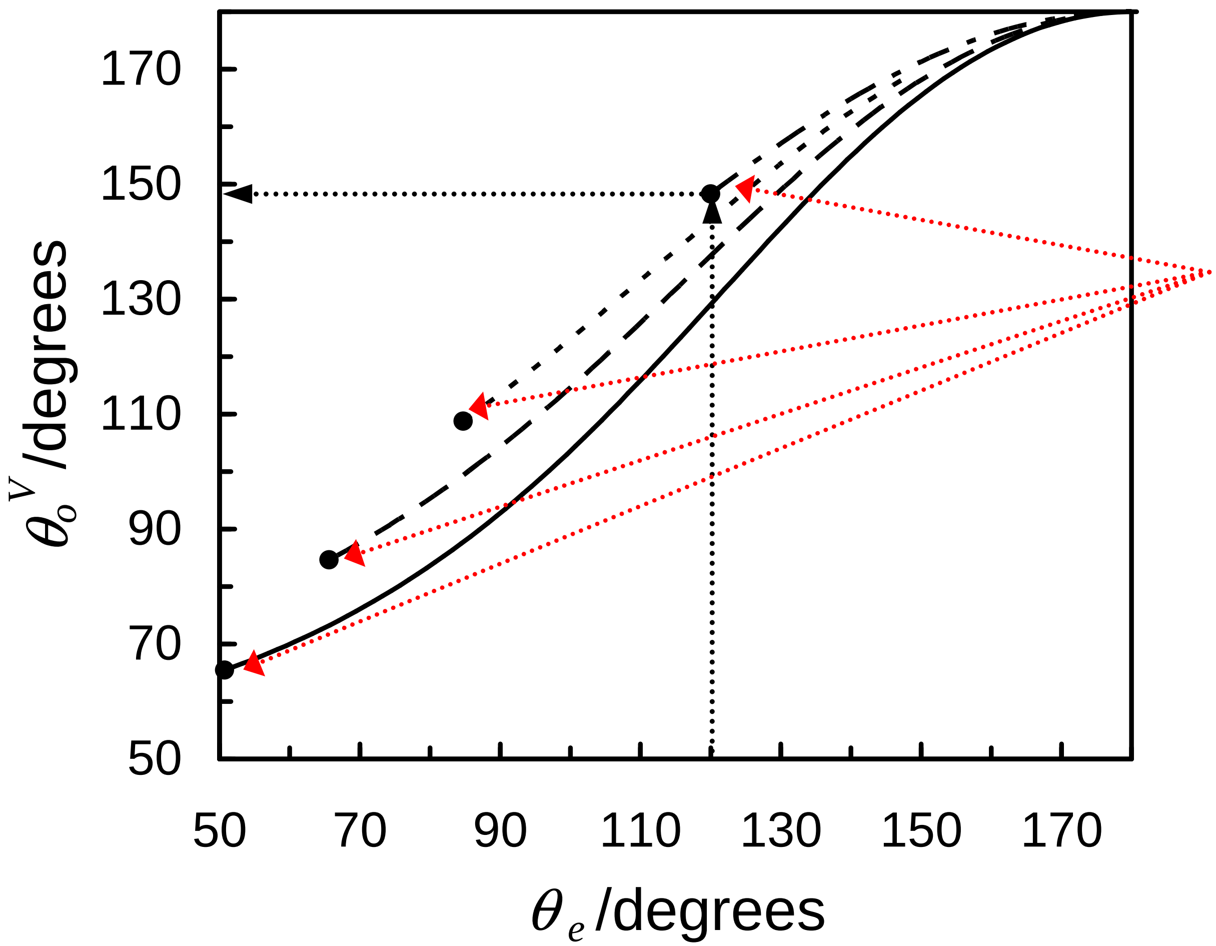
$\theta_c = 50.73^o$

*Consistent with experiments**

References: Shirtcliffe *et al*, Appl. Phys. Lett. 89 (2006) art 094101; *S. Bán, E. Wolfram, S. Rohrsetzher 22, (1987) 301-309.

# Minimum Hydrophobicity to Support Liquid when Grains are Loose Packed

## Recall Soil Graph




## Minimum Hydrophobicity

$$\cos\theta_e^{\min} = -1 + 2\sqrt{\frac{2 - 2\varepsilon - \varepsilon^2}{3}}$$

i.e. Solid point at start of each curve

Separation when bead pushes up through hole is $\varepsilon_{max} = \sqrt{3} - 1 = 0.732$

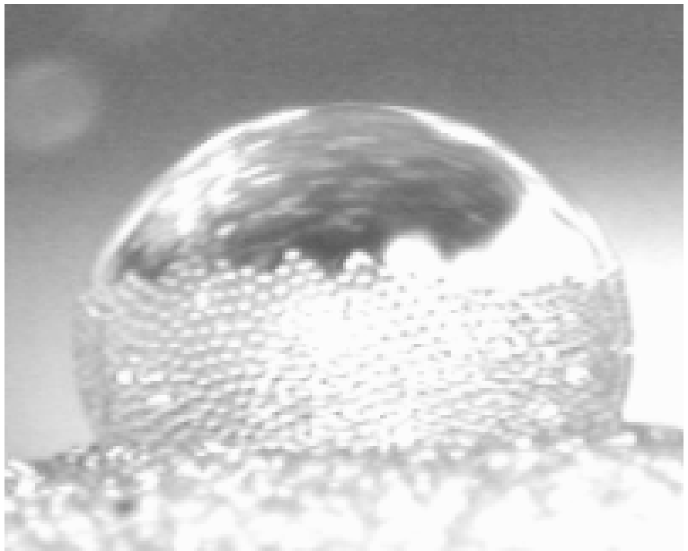
# Droplet Self-Coating

# Liquid Marbles

## Loose Surfaces

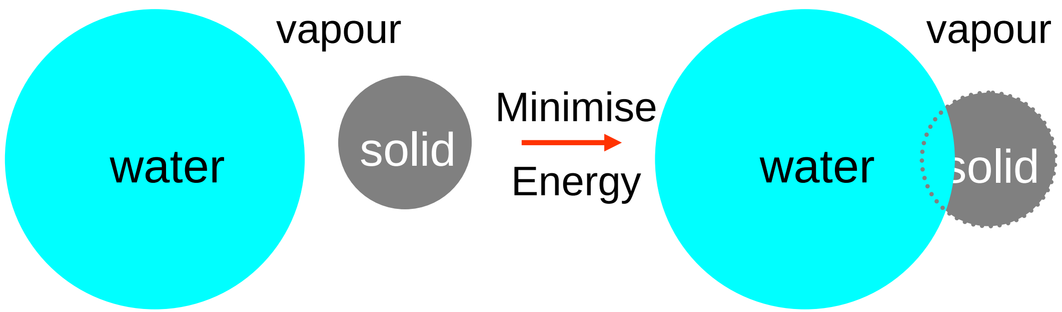
1. Loose sandy soil – grains are not fixed, but can be lifted
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic sandy surface becomes coated and forms a liquid marble

## Particle Lifting



75 µm silica spheres and hexane

## Surface Free Energy



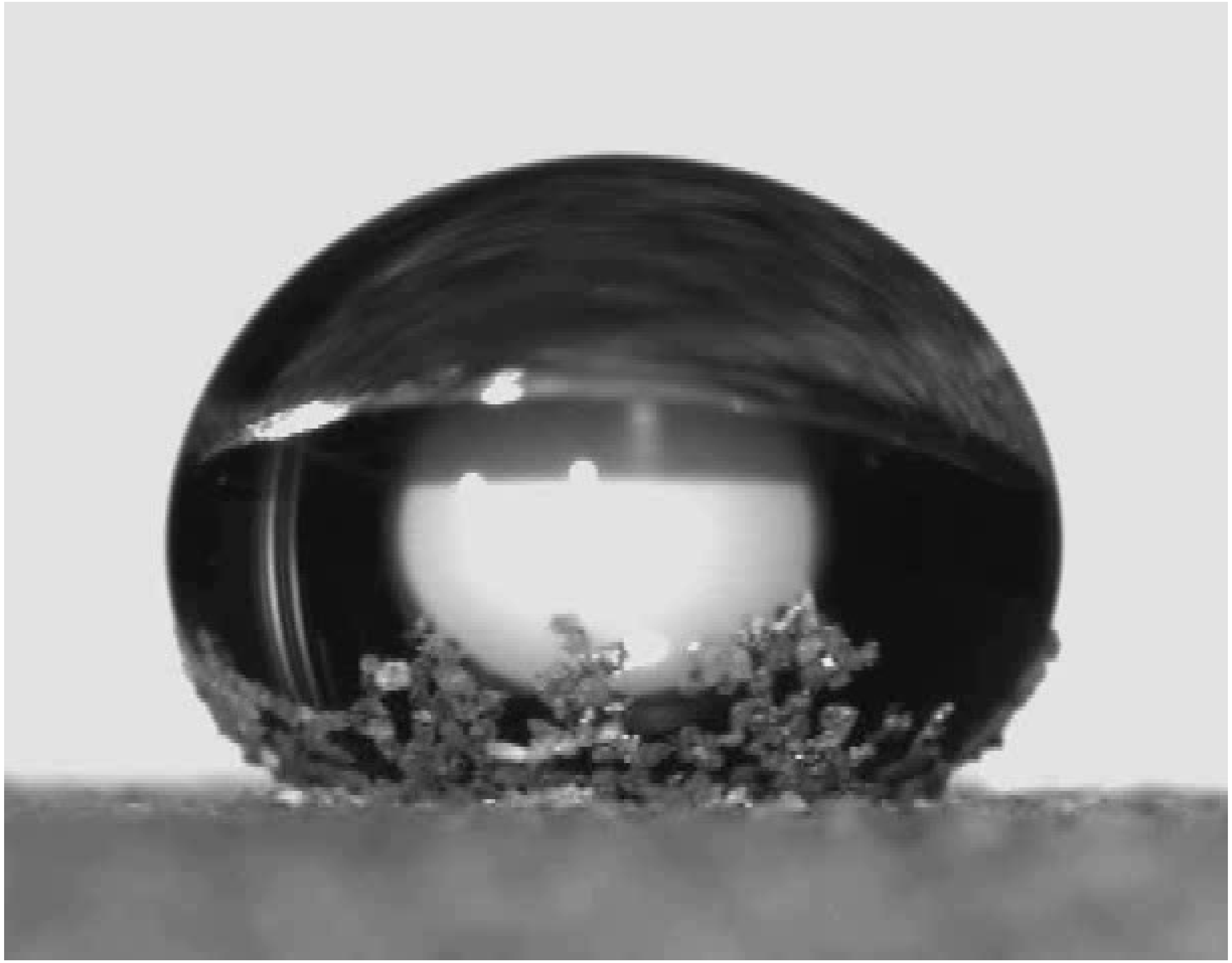

$$\Delta F = -\pi R^2 \gamma_{LV} (1 + \cos\theta_e)^2$$

Energy is always reduced on grain attachment

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

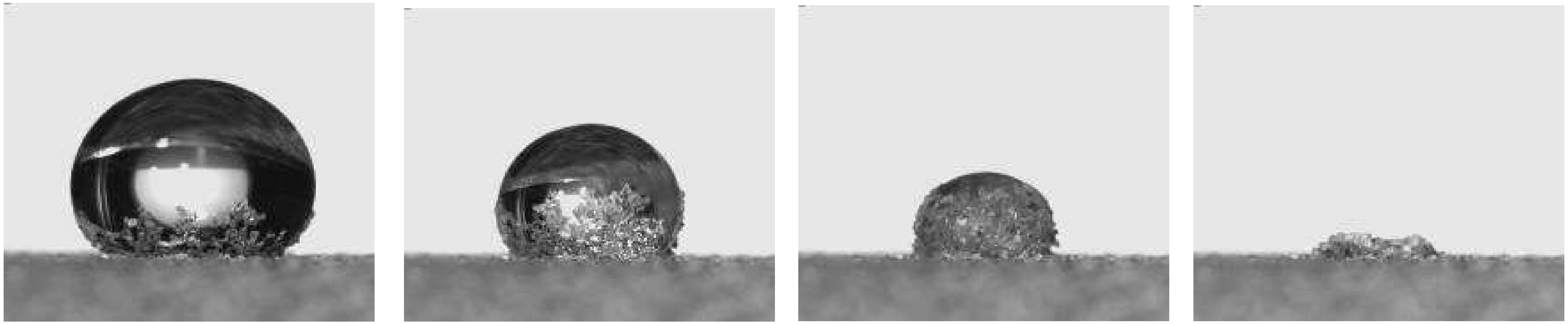
Acknowledgement: David Quéré

# Water Droplet Evaporation on Hydrophobic Sand

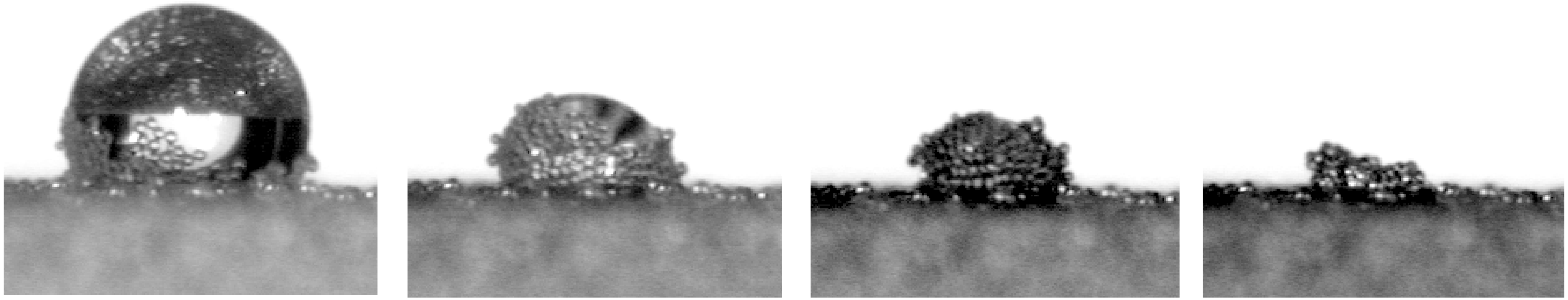


# Evaporatively Driven Coating

## Water on Hydrophobic Sand



## Water on Hydrophobic 75 μm Silica Beads



Reference Shirtcliffe *et al.*, to be submitted to APL (2006). See also reports on drying and buckling: Tsapis, *et al.,* Phys. Rev. Lett. 94, 018302-1 (2005); Schnall-Levin, *et al.,* Langmuir 22, 4547-4551, (2006);.

# Evaporatively Driven Sorting

## Surface Free Energies

When two particles of the same size, but different wettabilities, compete for a reducing air-water interface the one with its contact angle $\theta_e$ closest to 90$^o$ should win and remain at the interface

Ejection: Surface–into-Air

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

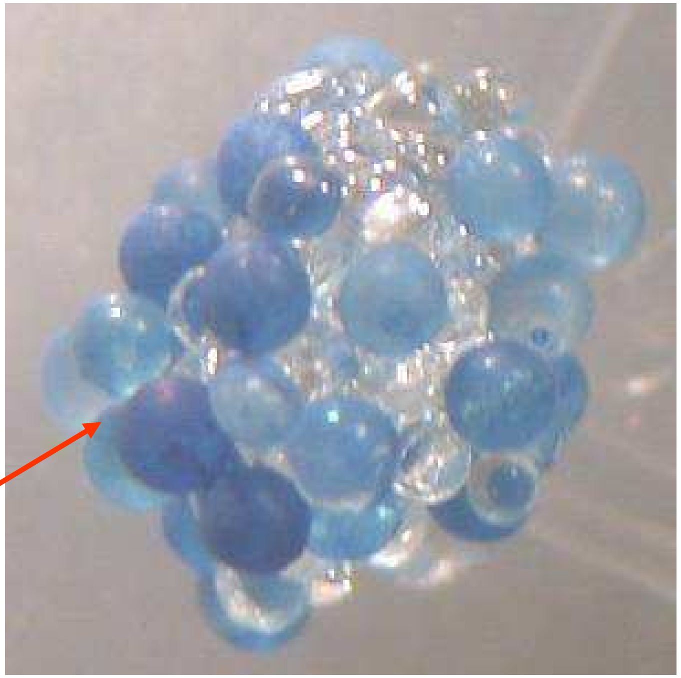
Ejection: Surface–into-Liquid

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

## Experimental Test

1. Bed of blue hydrophobic (115$^o$) spheres of diameter 500 μm and transparent hydrophilic (17$^o$) spheres of diameter 700 μm
2. Allow droplet to evaporate and clump to form

After evaporation blue particles are on outside of clump



# Conclusions

1. Porous Material versus Super-hydrophobic Surface

   S/H predicts hydrophobicity enhancements on sand/beads

   Extreme soil water repellence is an example

2. Imbibition of Liquids

   Critical contact angle is 50.73º on hexagonal bead packs

   For hydrophobic sand this increases to 61º-65º

3. Droplet Self Coating

   Substrate features may not be fixed

   Grains can re-arrange – droplets become liquid marbles

   Evaporation drives self-coating and grain sorting

## The End

# Acknowledgements


Funding Bodies

EPSRC GR/R02184/01

*Super-hydrophobic & super-hydrophilic surfaces* (GM, MIN, NJS)

EPSRC EP/C509161/1

*Extreme soil water repellence* (GM, FBP, MIN, NJS)

NERC NER/J/S/2002/00662

Advanced Fellowship for Dr Stefan Doerr (SD)

NERC NEC003985/1

*Fundamental controls on soil hydrophobic behaviour* (SD)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EPSRC Engineering and Physical Sciences Research Council

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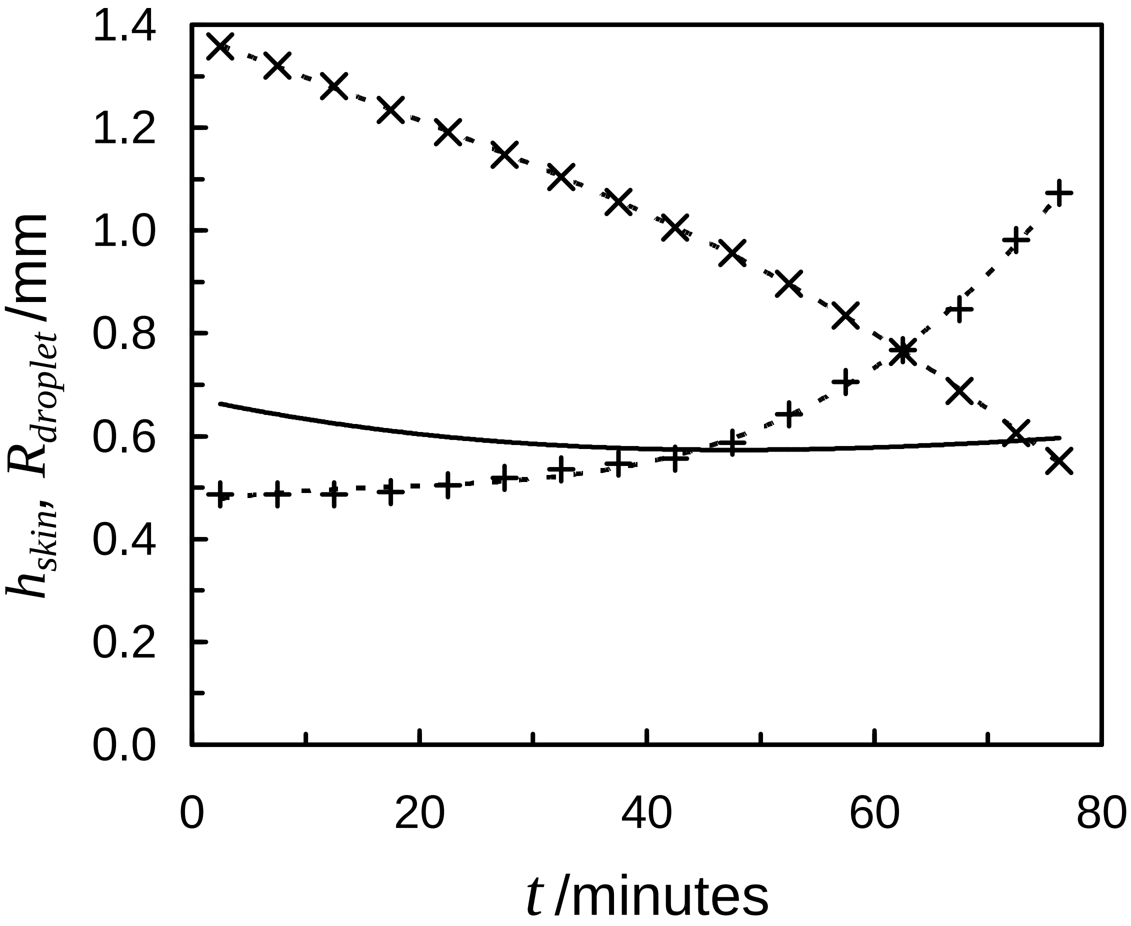
# Particle Lifting Data

1. Evaporation of water droplet on 75 µm diameter silica bead "free" pack
2. Droplet spherical radius (xxx) and height of a skin of silica beads (+++)

*If skin is constant in area then product of these should tend to a constant*




Solid line is product $h_{skin}R_{droplet}$

Reference Shirtcliffe *et al.*, to be submitted to APL (2006).