From Infiltrating Droplets to Rolling Balls

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Overview

1. Porous materials and wetting surfaces

    What is the critical contact angle for infiltration?

2. Hydrophobic soil with fixed grains

    Is hydrophobic soil a superhydrophobic surface?

3. Hydrophobic soil with non-fixed grains

    Do grains lift and coated droplets form naturally into liquid marbles?

4. Droplet evaporation and rolling “balls”

    Can grains self-sort and marbles cause soil erosion?

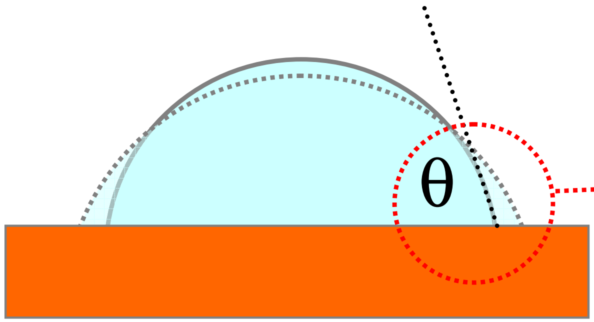
Porous Materials & Wetting Surfaces

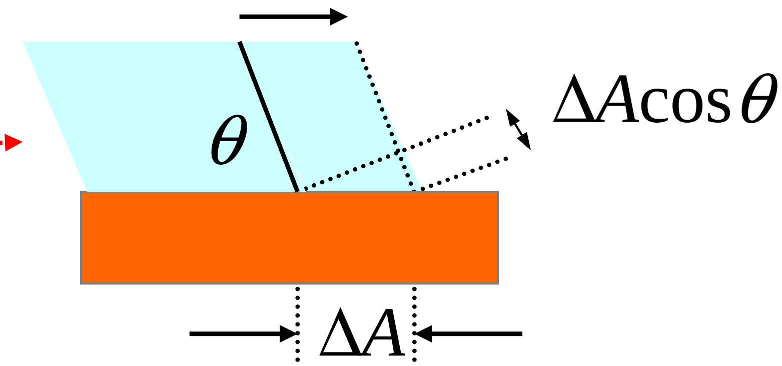
What is the critical contact angle for infiltration into bead packs and sand?

Minimum Surface Free Energy

Young's Law – The Chemistry

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





Change in surface free energy is

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

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

Equilibrium is when $\Delta F = 0$ $\Rightarrow$

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

Young's Law

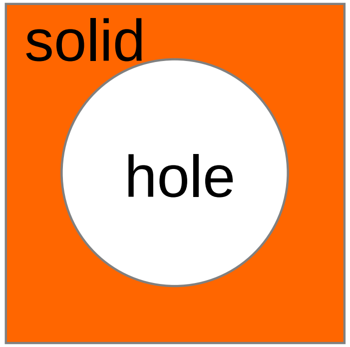
Cylindrical Model for Capillary Infiltration

Assumptions

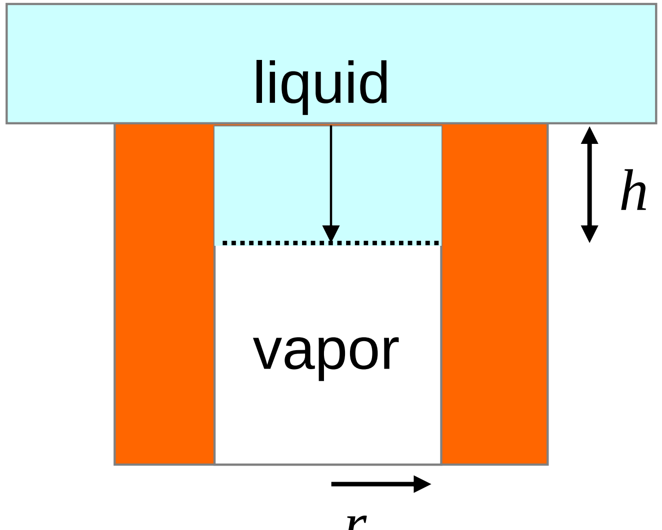
1. Fixed cylindrical pipe
2. Meniscus with Young's law

   contact angle, $\cos\theta_e = =(\gamma_{SV}-\gamma_{SL})/\gamma_{LV}$
3. Minimise surface free energy, F

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

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

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

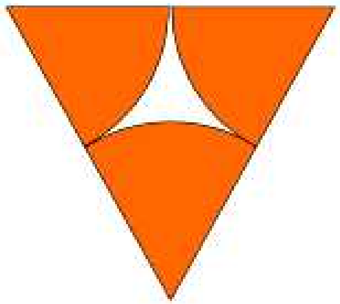
<u>But soil is not a set of parallel pipes</u>

Spherical Grain Model for Infiltration

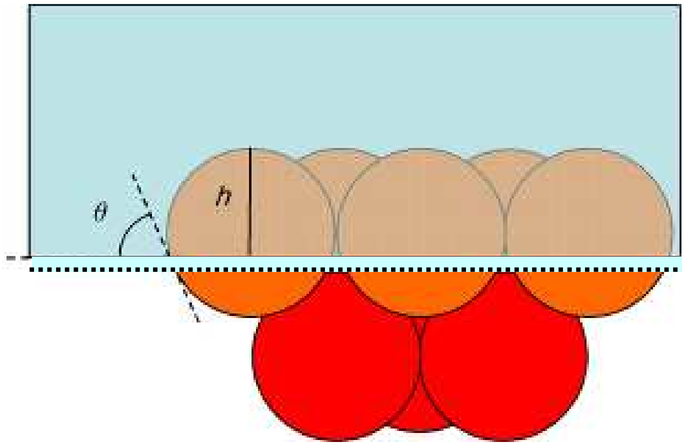
Assumptions

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 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

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

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

$\theta_c = 50.73^o$

*Consistent with experiments**

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

Infiltration into Bead Packs & Sand

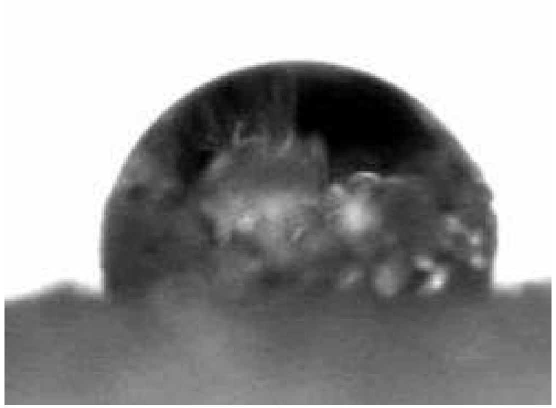
Fluorocarbon Bead Packs

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

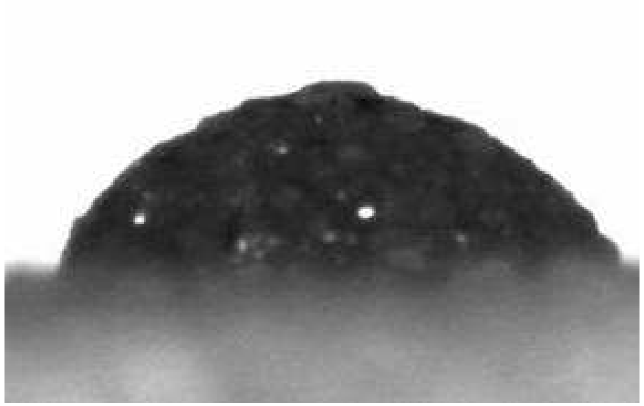
Liquid	***θ* on fluorocarbon coated glass slides / °±4**
Octane	72°
Heptane	65°
Hexane	61°
Pentane	52°

Fluorocarbon Coated Sand

Penetration occurs for hexane



Octane (72°)



Heptane (65°)

Hexane (61°)

Reference Shirtcliffe *et al*, Appl. Phys. Lett. 89 (2006) art 094101

<u>Answer to infiltration question</u>:

What is the critical contact angle for infiltration?

Depends on the soil structure,
but probably anything from 51^o to 62^o or higher

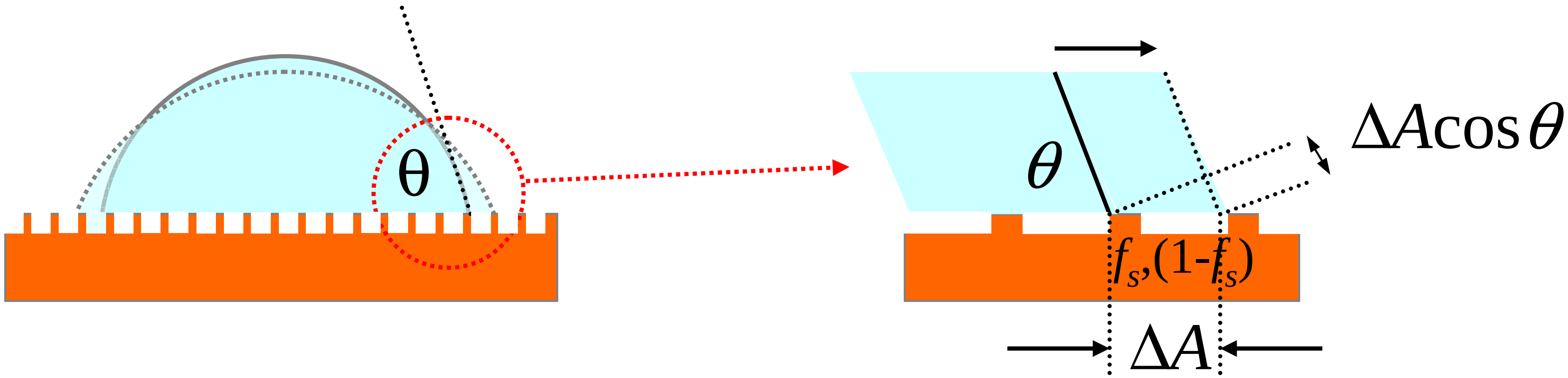
Hydrophobicity & Topography

Is hydrophobic soil with fixed grains a superhydrophobic surface?

Topography & Wetting

Droplets that Skate

What contact angle does a droplet adopt on a “rough” surface?



Change in surface free energy is

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

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

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

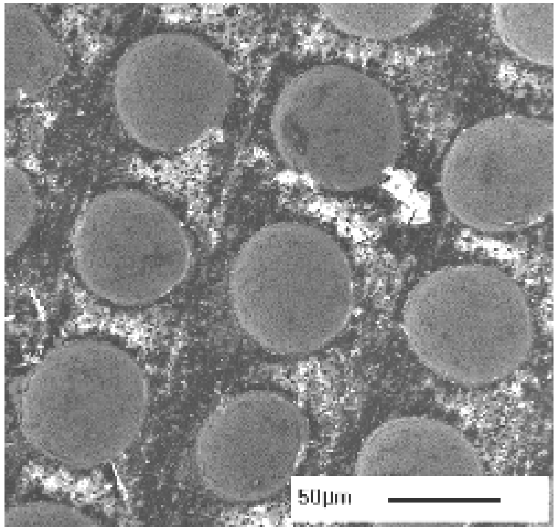
Cassie-Baxter Eq

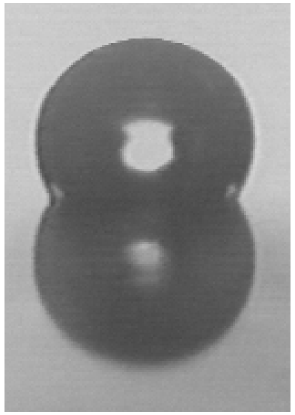
Topography $\Rightarrow$ f_s = solid surface fraction

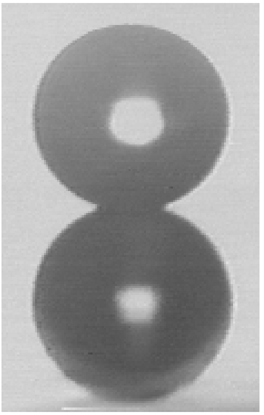
Chemistry $\Rightarrow$ Young’s Law θ_e

Topographic Enhancement of Water Repellence

Etched Metal



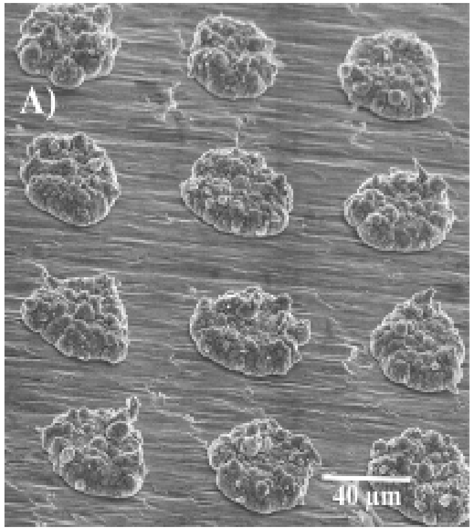


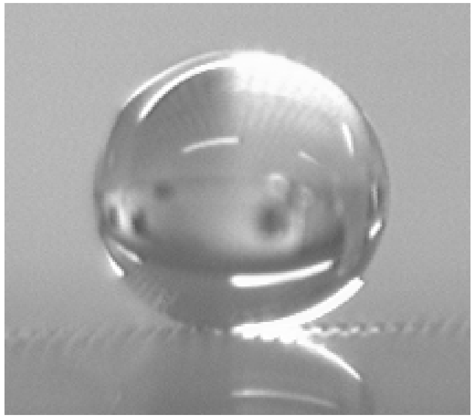


Flat & hydrophobic

Patterned & hydrophobic

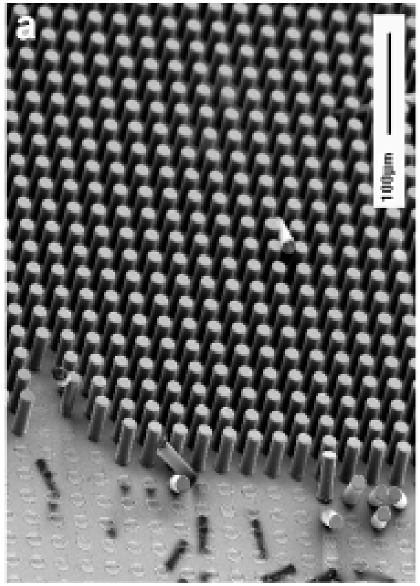
Deposited Metal

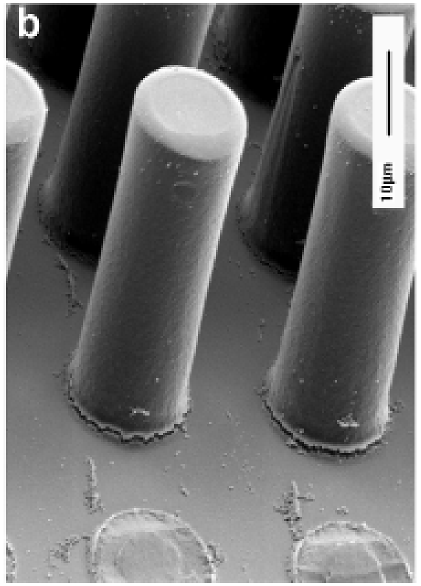


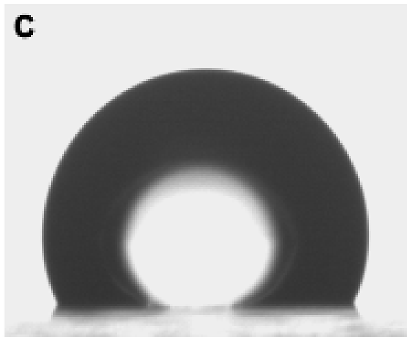


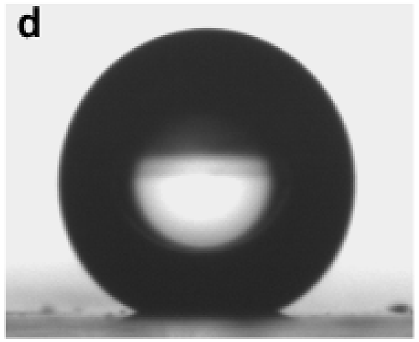
Patterned & hydrophobic

Polymer Microposts







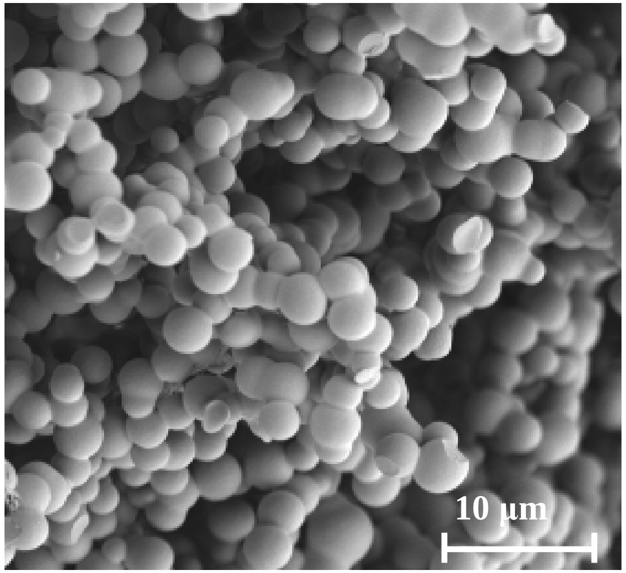


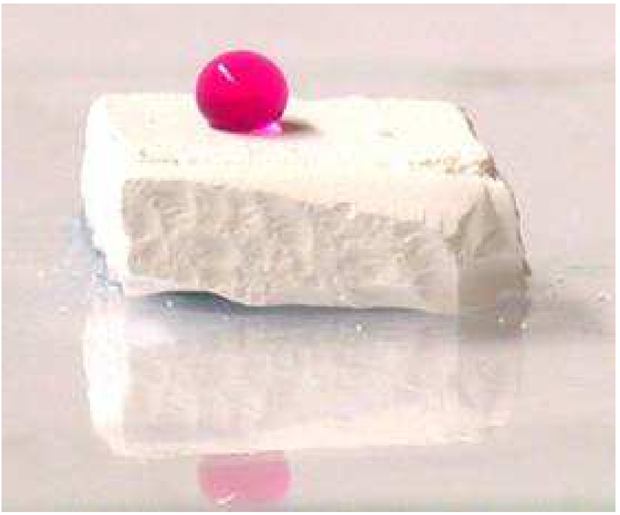
Flat & hydrophobic

Patterned & hydrophobic

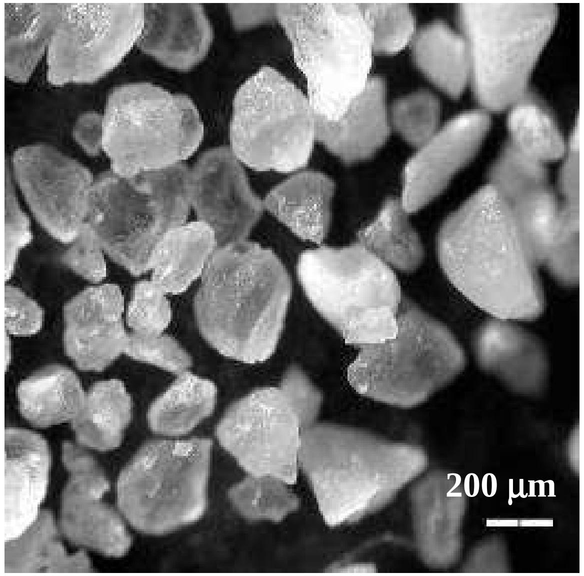
Hydrophobic Foam & Sand

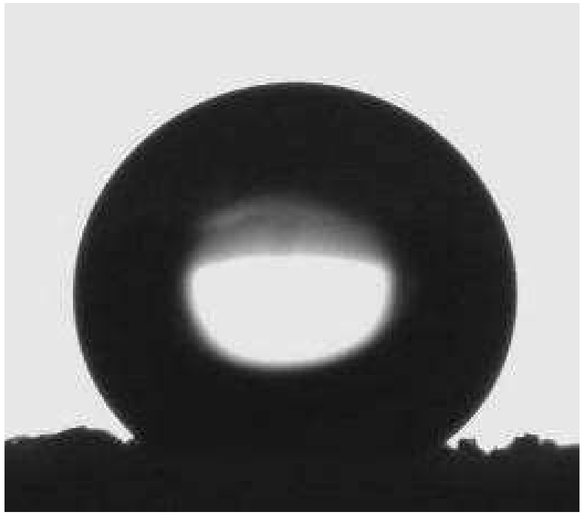
Foam



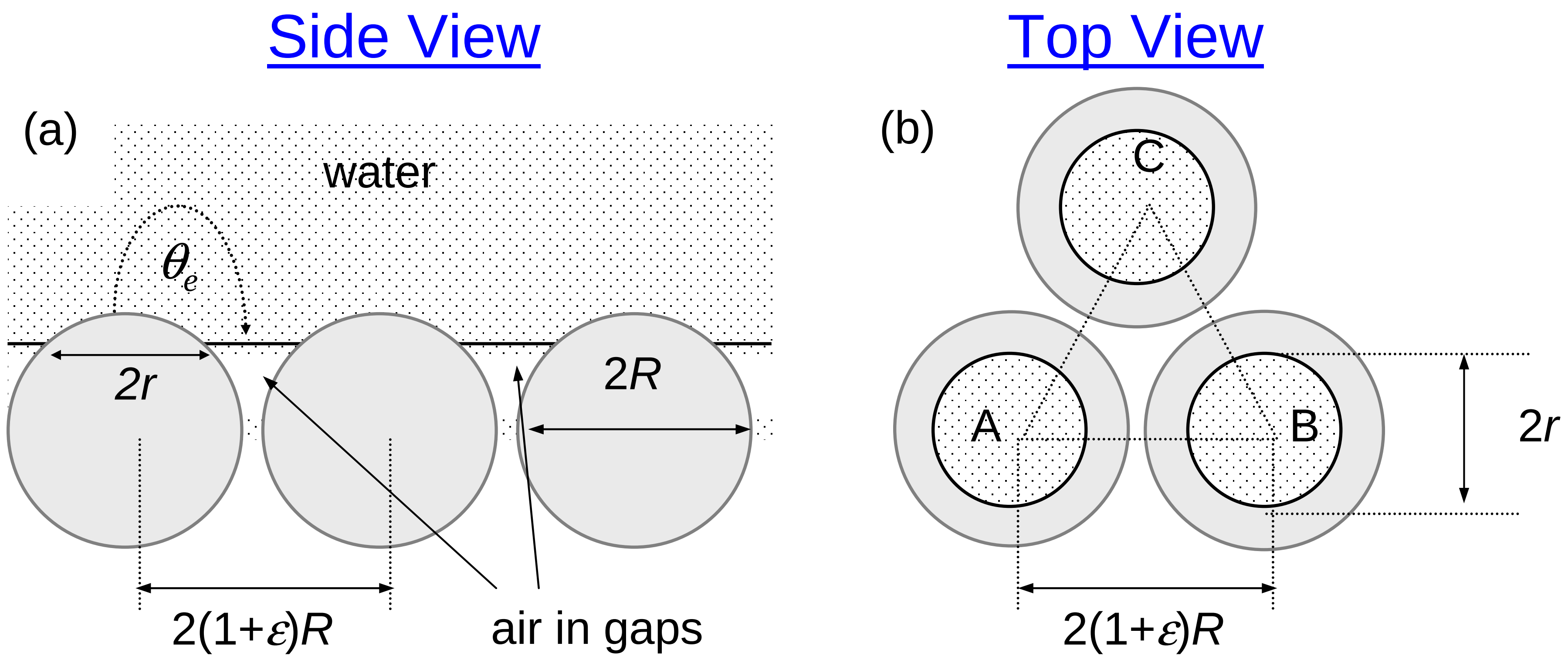


Fixed Sand





Simple Model of Soil

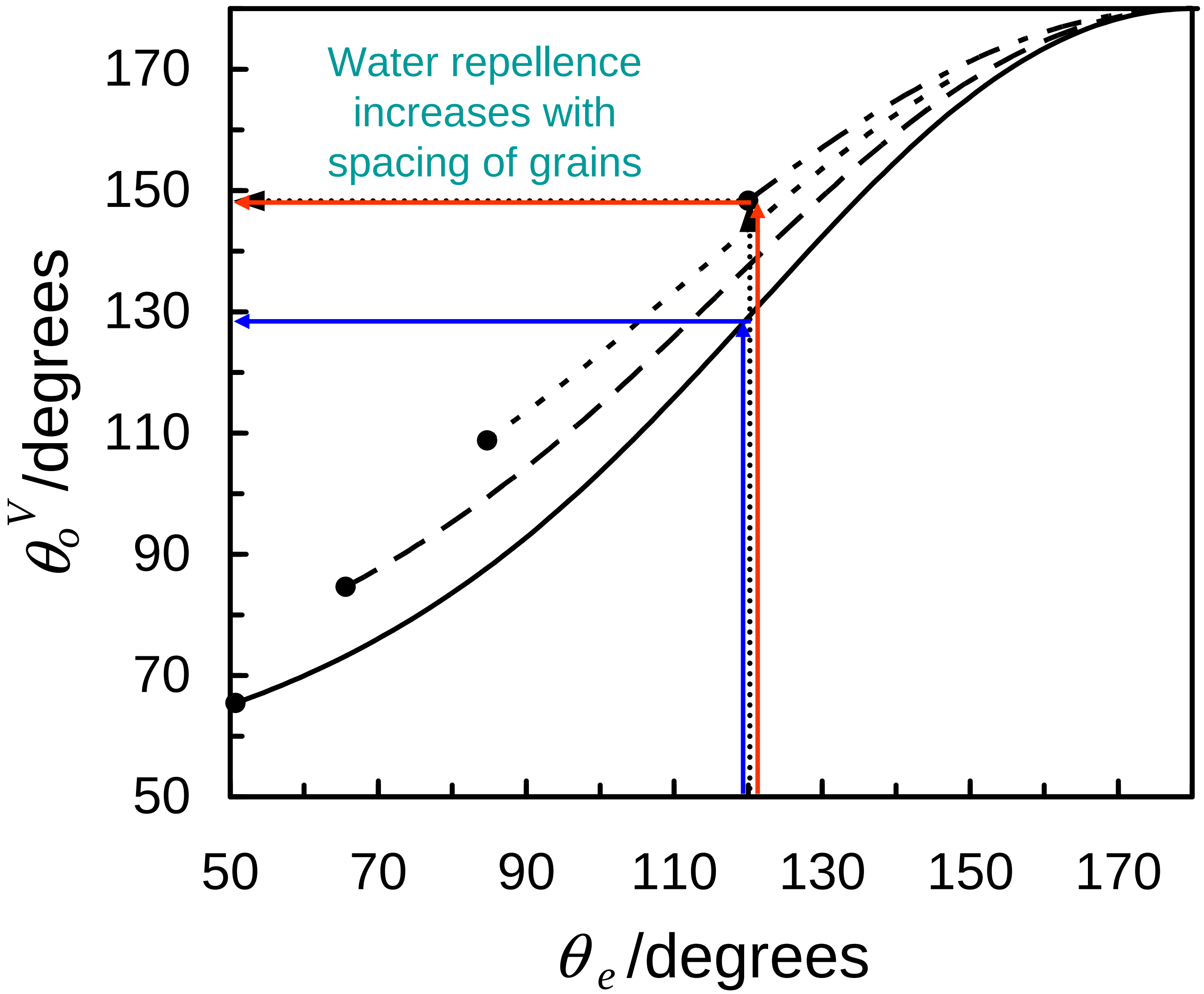


Assumptions

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}=2.7 mm

Reference McHale *et al*, Eur. J. Soil. Sci. 56 (2005) 445-452.

Dry Soil - Water Repellence Enhancement



Curves for packings:

ε= 0.677 (loose)

ε = 0.452

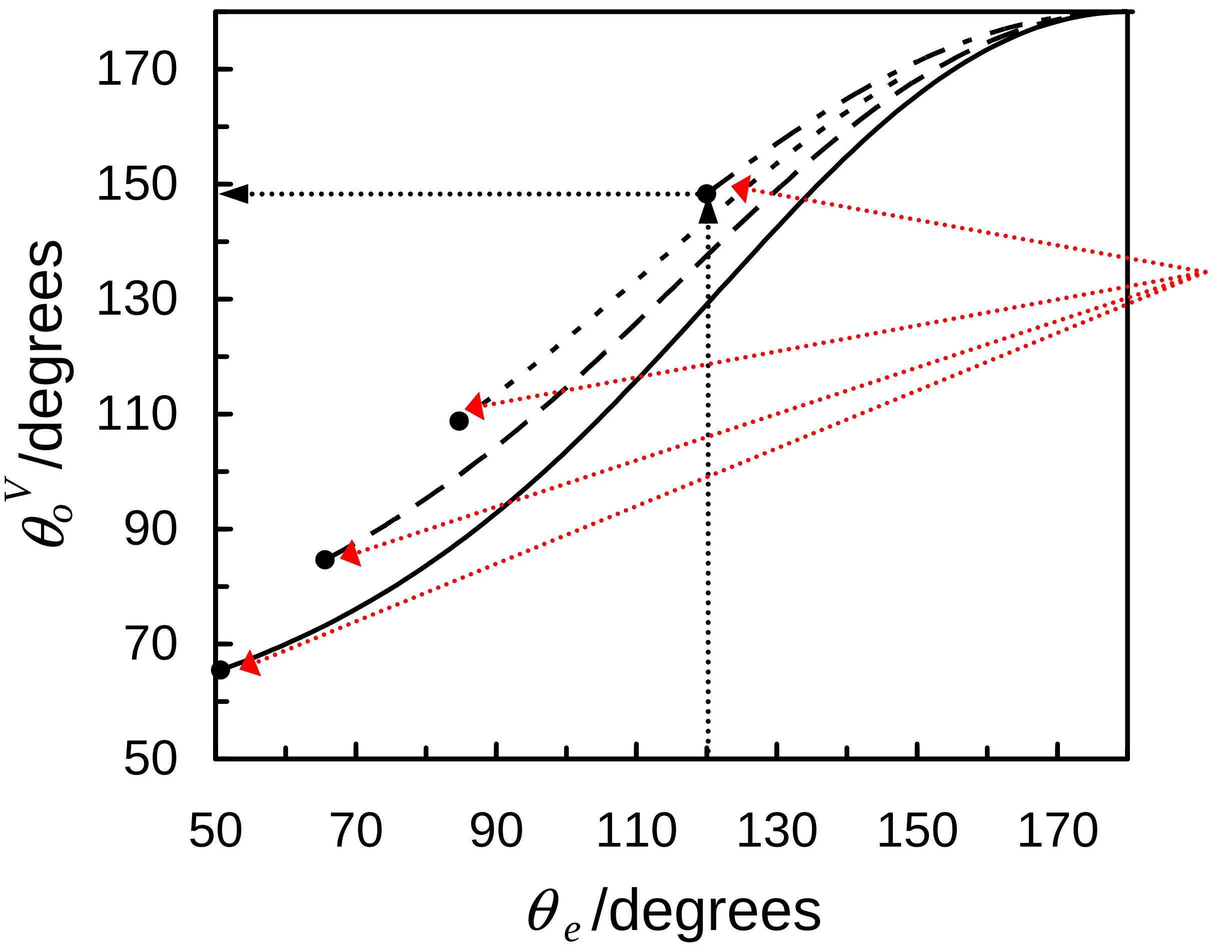
ε = 0.226

ε = 0.0 (close)

Angular sand grains, will give much higher enhancements

Minimum Hydrophobicity to Support Water when Grains are not Close-Packed

Recall Soil Graph



Minimum Hydrophobicity

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

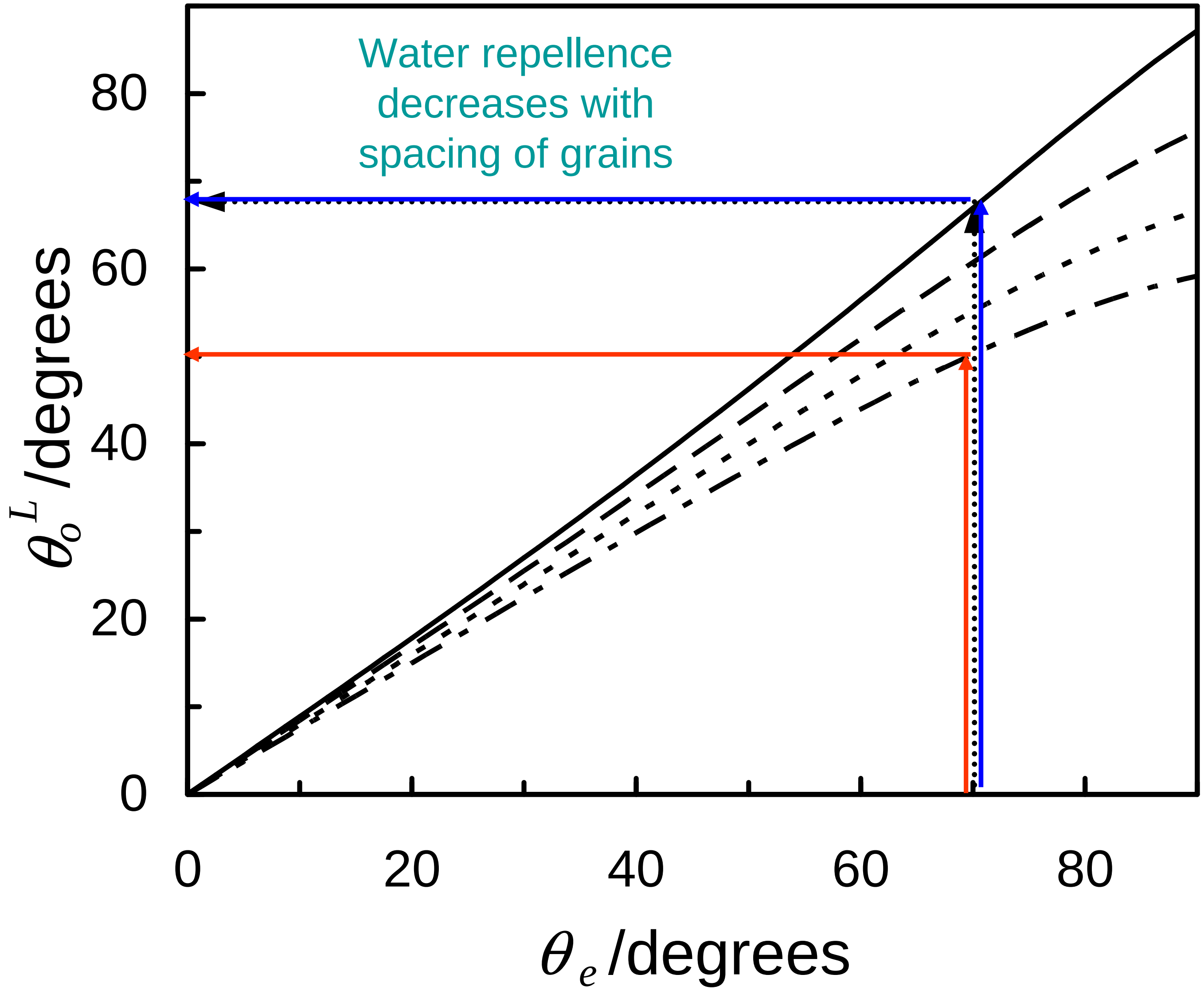
i.e. Solid point at start of each curve

Separation when bead pushes up through hole is

$\varepsilon_{max} = \sqrt{3} - 1 = 0.732$

Reference McHale *et al*, Hydrological Processes (2007).

Wet Soil - Water Repellence Reduction



Curves for packings:

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

Answer to superhydrophobic question:

Is hydrophobic soil (with fixed grains) a superhydrophobic surface?

Most likely – yes in some situations

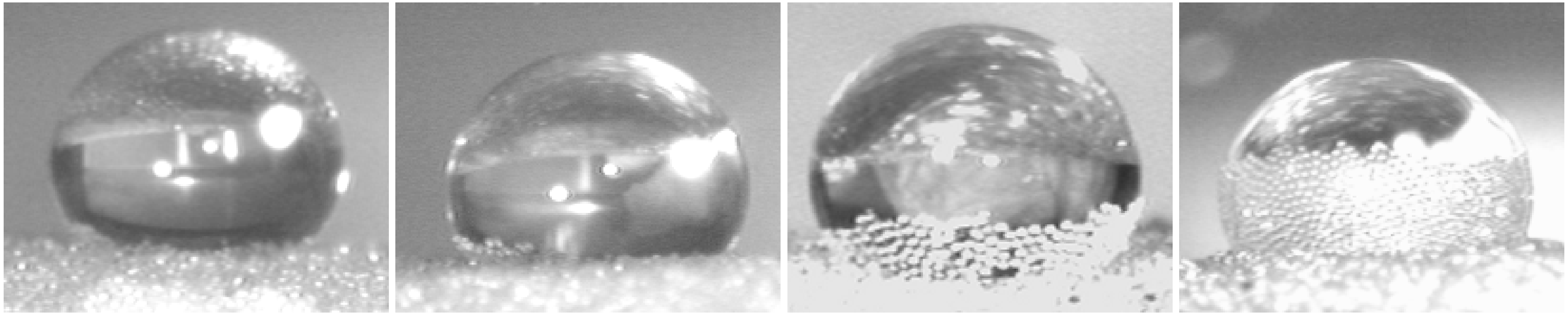
Fixed versus Loose Grains

Do grains lift and coated droplets form naturally into liquid marbles?

Loose v Fixed Hydrophobic Grains

Loose Hydrophobic Silica Particles

Initial coverage effect of different liquids on 75 μm silica spheres

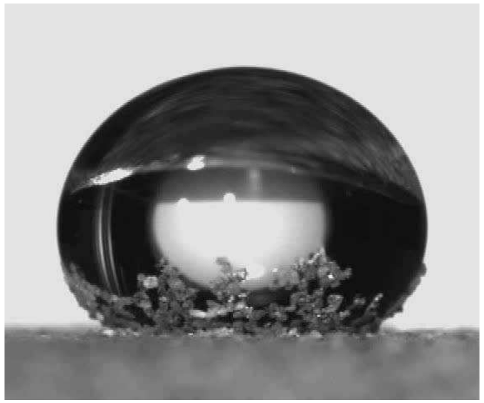


hexane

Hydrophobic Sand

Water contact angle on fixed hydrophobic sand $\theta = (155 \pm 2)^o$

Water contact angle on loose hydrophobic sand $\theta = (166 \pm 4)^o$



Attachment of grains ⇒ higher contact angle

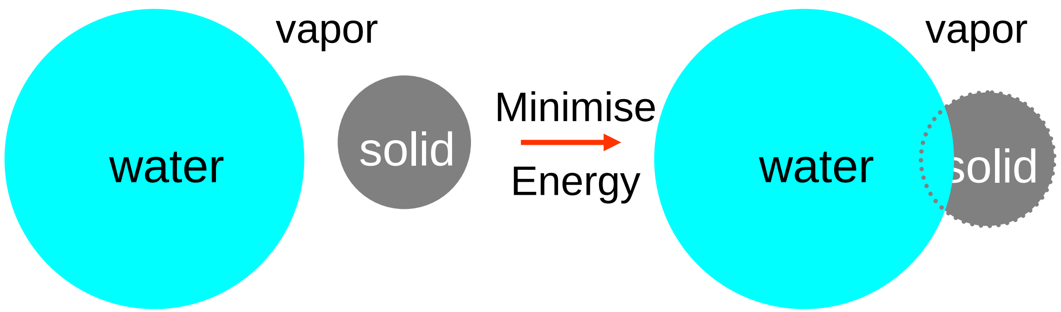
Acknowledgement Maxine Pugh

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

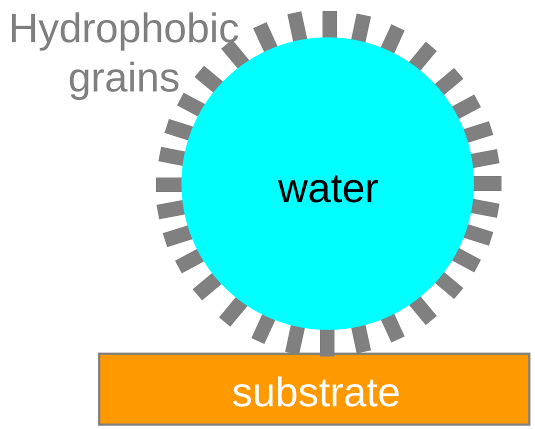
Hydrophobic Grains and Water



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

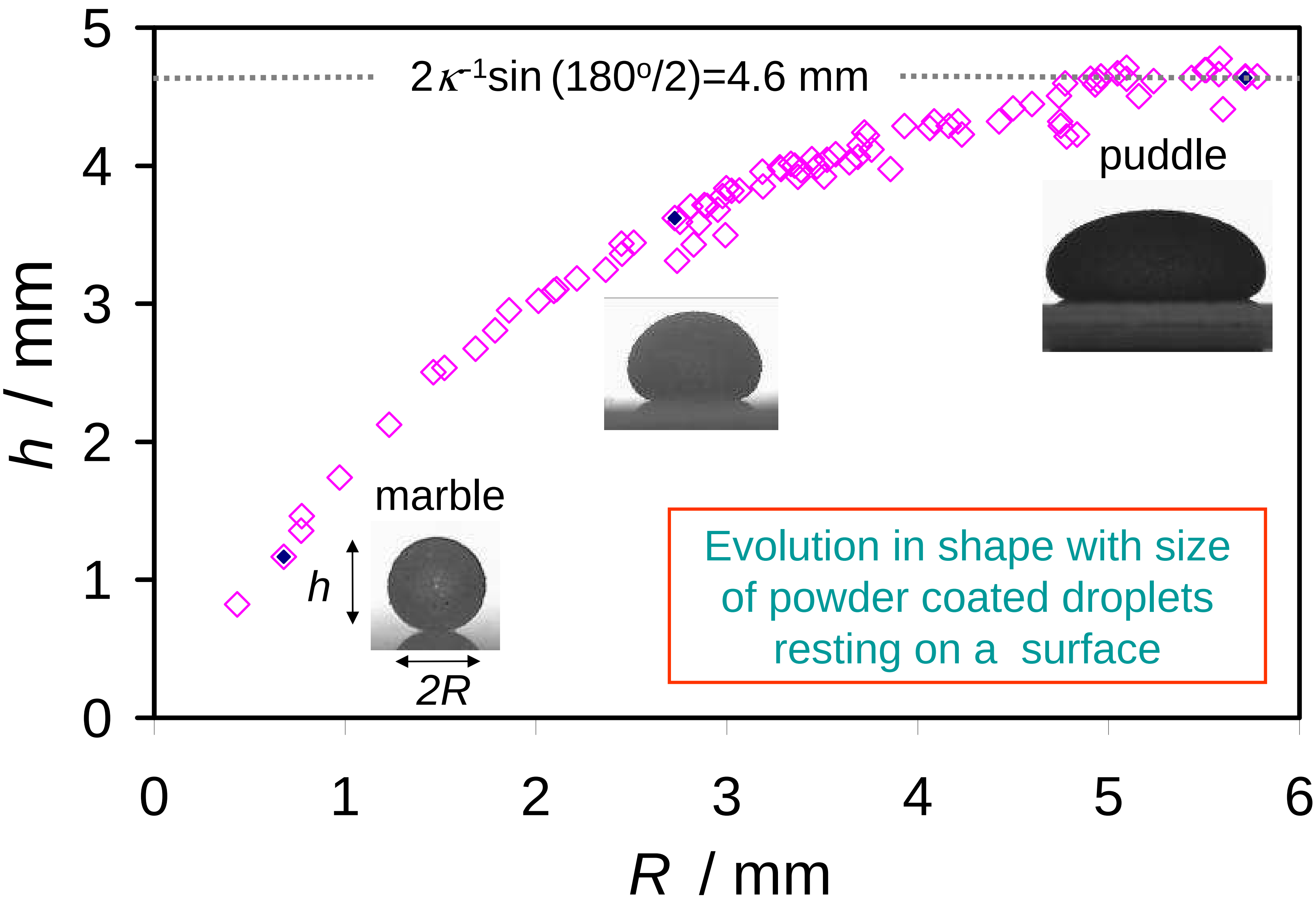
Energy is always reduced on grain attachment

Lycopodium grains are 15-19 µm



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

Size Data for Liquid Marbles



<u>Answer to grain lifting & liquid marble question</u>:

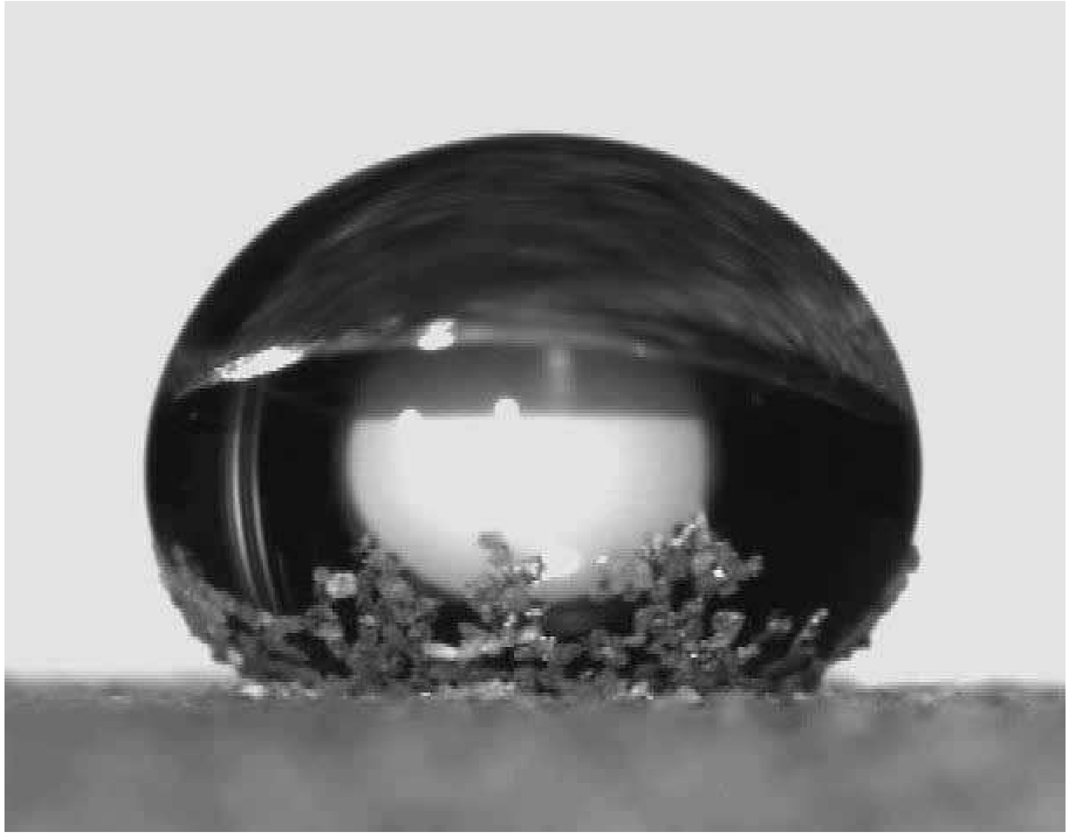
Do grains lift and coated droplets form naturally into liquid marbles?

Yes grains appear to lift (if small enough) and, if droplets roll, liquid marbles can form

Droplet Evaporation & Rolling "Balls"

Can grains self-sort and marbles cause soil erosion?

Water Droplet Evaporation on Hydrophobic Sand

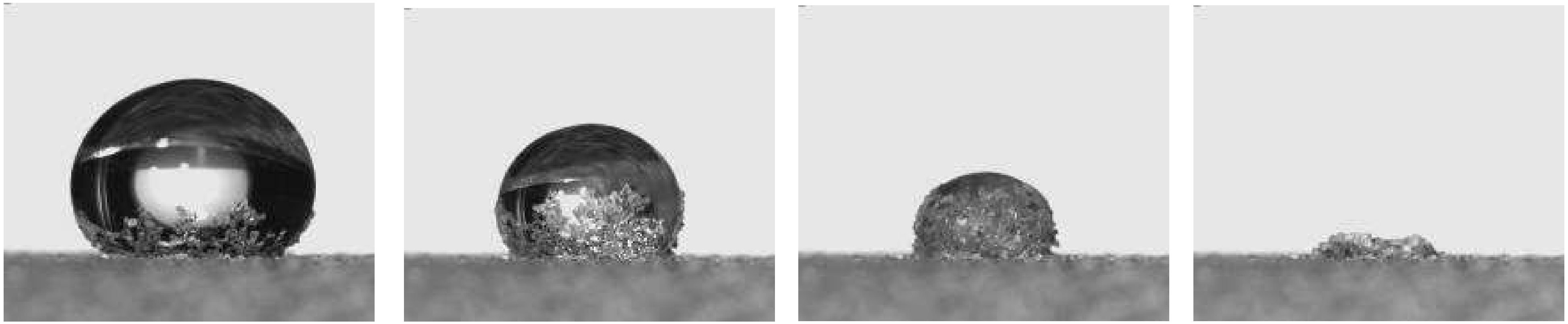


Video in original presentation shows particles climbing, closing and crumpling. See next slide for stills.

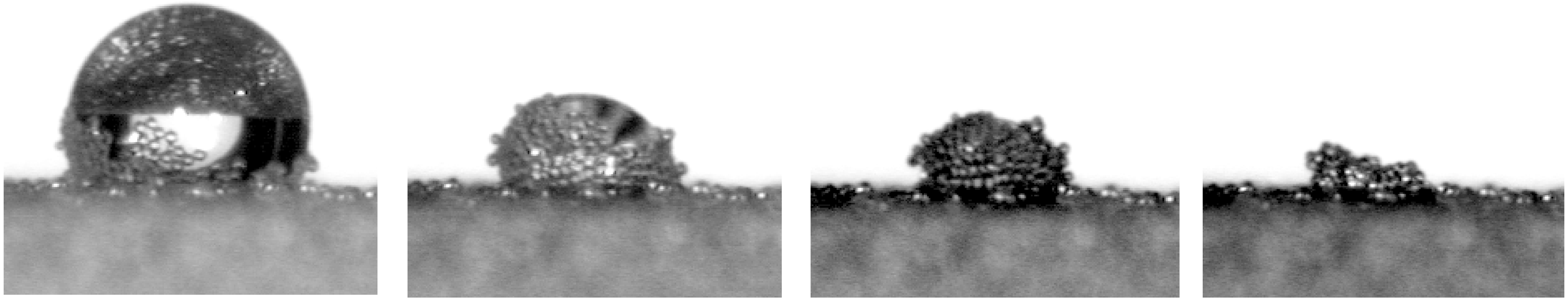
Reference Shirtcliffe *et al.*, APL 90 (2007) art. 054110.

Evaporatively Driven Coating

Water on Hydrophobic Sand



Water on Hydrophobic 75 μm Silica Beads



Reference Shirtcliffe *et al.*, APL 90 (2007) art. 054110. See also reports on drying and buckling: Tsapis, *et al.,* Phys. Rev. Lett. 94 (2005) 018302-1; Schnall-Levin, *et al.,* Langmuir 22 (2006) 4547-4551

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 θ_e closest to 90° should win and remain at the interface

Ejection: Surface–into-Air

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

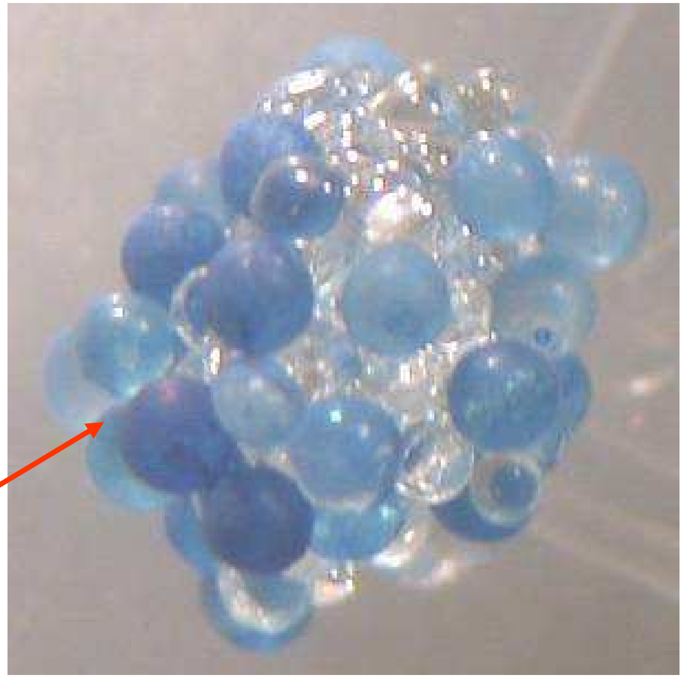
Ejection: Surface–into-Liquid

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

Experimental Test

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

After evaporation blue particles are on outside of clump



Droplet Mobility and Erosion

Liquid Marbles

1. Perfect non-wetting droplets
2. Zero contact angle hysteresis, so highly mobile

Videos in original presentation show complete mobility of the liquid marbles. The larger one moves more slowly than the smaller one.

Soil Erosion?

1. Some preliminary experiments performed
2. Droplets dripped onto a loose hydrophobic sandy slope
3. Liquid marbles formed, ran down slope (in some size ranges) and transported sand grains

Answer to self-sorting and erosion question:

Can grains self-sort and marbles cause soil erosion?

Grains can self-sort by size and by hydrophobicity. Rolling droplets can become liquid marbles, and strip away hydrophobic grains.

Not sure if these mechanisms occur strongly with hydrophobic soil

Conclusions

1. Capillary infiltration

   Occurs for θ_e substantially less than 90º (e.g. 51º-65º)

2. Hydrophobic sand

   Can act as a superhydrophobic surface in some situations

3. Droplet self-coating

   Grains can re-arrange – droplets become liquid marbles

   Evaporation drives self-coating and grain sorting

4. Erosion?

   Rolling droplets can become liquid marbles/puddles

   Liquid marbles/puddles transport hydrophobic sand grains

   - Is the transport selective when grains are mixed hydrophobic/hydrophilic?

The End

Acknowledgements

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

EPSRC EP/C509161/1

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NERC NEC003985/1

Fundamental controls on soil hydrophobic behaviour (SD)

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NOTTINGHAM TRENT UNIVERSITY

EPSRC Engineering and Physical Sciences Research Council

NATURAL ENVIRONMENT RESEARCH COUNCIL