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Superhydrophobicity: Localized Parameters and Gradient Surfaces

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Contact Angle, Wettability & Adhesion

University of Maine 14th-16th July 2008

Overview

1. Theoretical Basis: Localized Cassie Fractions/Wenzel Roughness
    - Surface free energy derivation
    - Spatially varying Cassie fractions
    - 1-D v 2-D and random v non-random patterns
    - Dual length scales and re-entrant features
2. Experimental: Gradient Surfaces
    - Materials: Copper based radial gradient surface
    - Results
    - Forces due to Cassie-Baxter surface fraction gradients

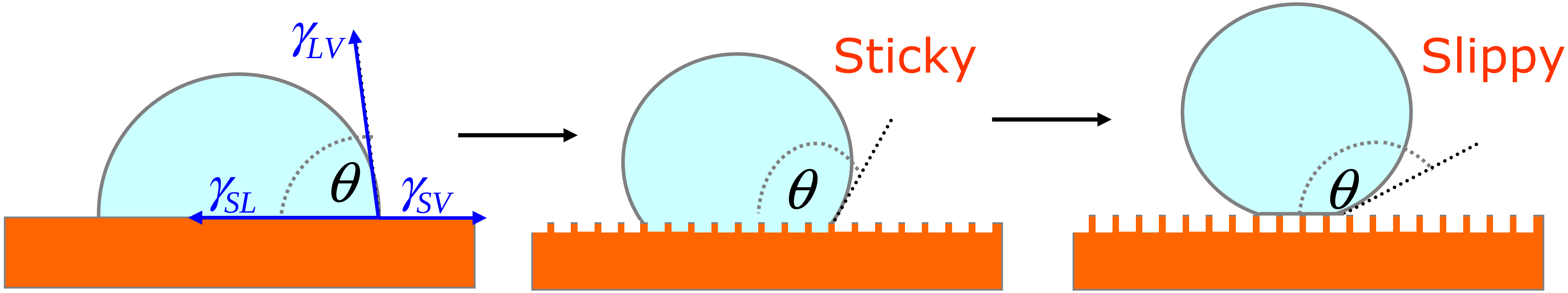
Theoretical Basis

Cassie Fractions and Wenzel Roughness

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. Coll. Chem. 53 (1949) 1466-1467.

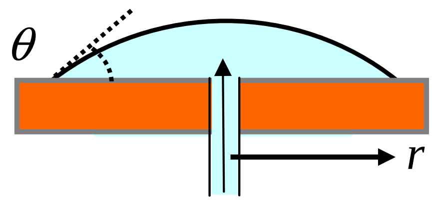
Surface Structure: Local not Global

Contact Angle

Usually have a syringe from above

Imagine measuring by filling from below[1,2]

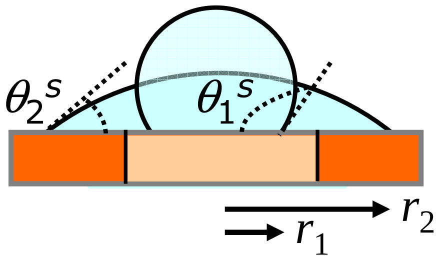
Does it effect the measurement of θ?

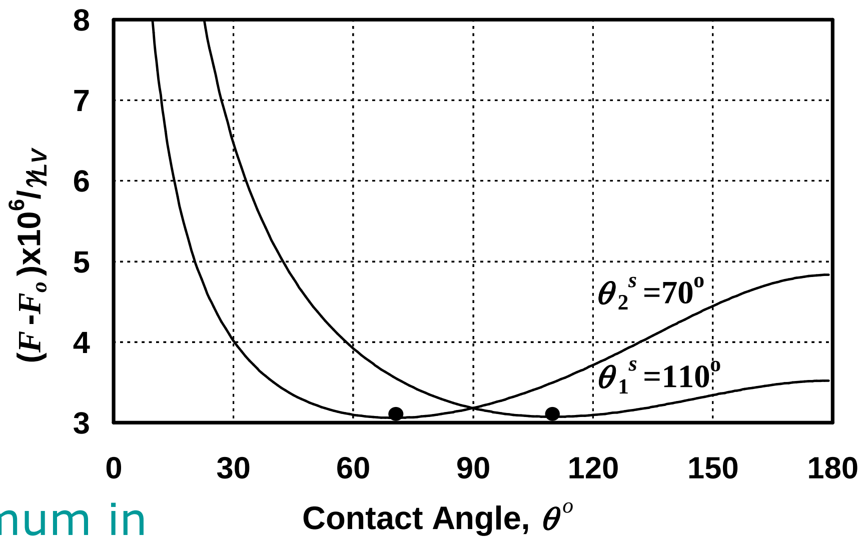


No – provided droplet contact area is wider than entry hole

Isolated Defect Surface

Surface has $\theta_1^s = 110^o$ and $\theta_2^s = 70^o$





Two droplet configurations exist with minimum in their local surface free energy for some droplets of fixed volume (see also ref 3)

The droplet state on initial deposition matters

References [1]Li, D. Colloids Surfaces A 116, (1996) 1-23; [2]Li, D.; Cheng, P. & Neumann, A.W. Adv. Colloid Interf. Sci. 39 (1992) 347-382. [3]Extrand, C. W. Langmuir 19 (2003) 3793-3796 (and 21 (2005) 11546-11546).

Local Roughness

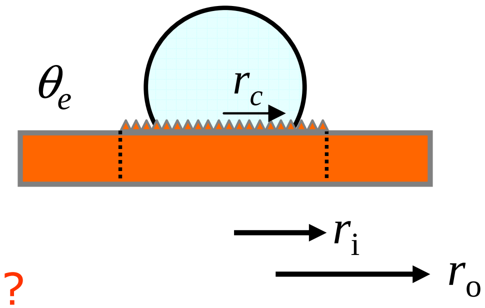
Wenzel Roughness Parameter, r

Is roughness, r=actual area/projected area?

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

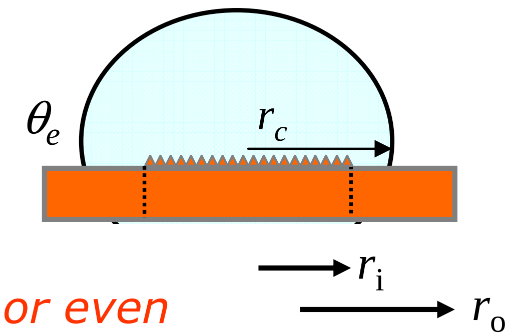
Is it a property of the substrate or of the substrate-droplet as a system?

Imagine a droplet on a rough patch surrounded by a smooth surface. All areas have same surface chemistry, i.e. θ_e



Is it $r = \dfrac{A_{wetted}}{\pi r_c^2}$ or $r = \dfrac{\Delta A_{wetted}}{\Delta A_{circle}} = \dfrac{\Delta A_{wetted}}{2\pi r_c \Delta r_c}$?

The first definition based on total areas would imply the centre of the drop mattered and contradict syringe (from below) experiments ...



Roughness is not an average property of the substrate or even of the substrate below the droplet – it is local to the three phase contact line(s) where changes can occur, ie. $r(x)$

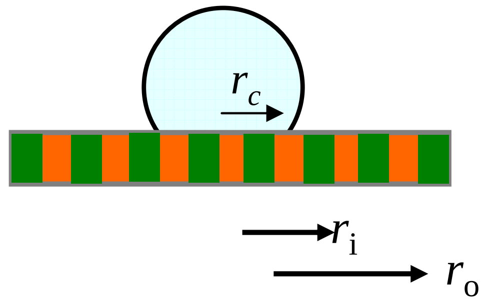
Local Cassie Fraction

Surface Fractions, f_i

Is the surface fraction, f_i=area of type i/total area? $\cos\theta_c = f_1 \cos\theta_1 + f_2 \cos\theta_2$

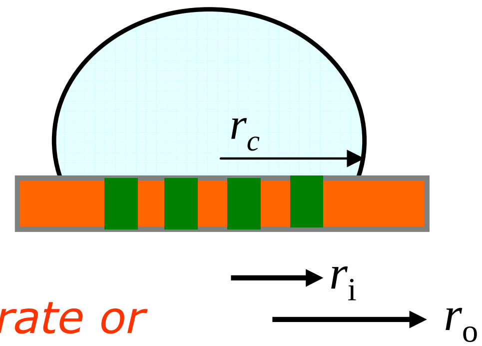
Is it a property of the substrate or of the substrate-droplet as a system?

Imagine a surface with patches of areas, A_1 and A_2, with two chemistries giving two contact angles, i.e. θ_1 and θ_2



Is it $f_i = \dfrac{A_i}{A_1 + A_2}$ or $f_i = \dfrac{\Delta A_i}{\Delta A_1 + \Delta A_2}$?

The first definition based on total areas would imply the centre of the drop mattered and contradict syringe experiments ...



Cassie fraction is not an average property of the substrate or even of the substrate below the droplet – it is local to the three phase contact line(s) where changes can occur, ie. $f_i(x)$

Cassie-Baxter and Wenzel Equations

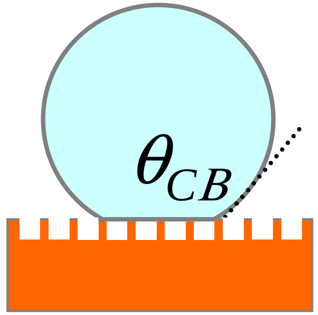
Cassie-Baxter

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 $\Rightarrow$

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

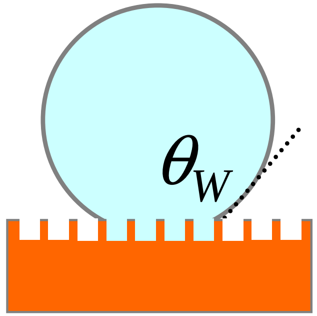


where $f_s(x)$ is the solid surface fraction and the x indicates values at the three-phase contact line (θ_e = $\theta_e(x)$ is also local to the three-phase contact line)

Wenzel

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

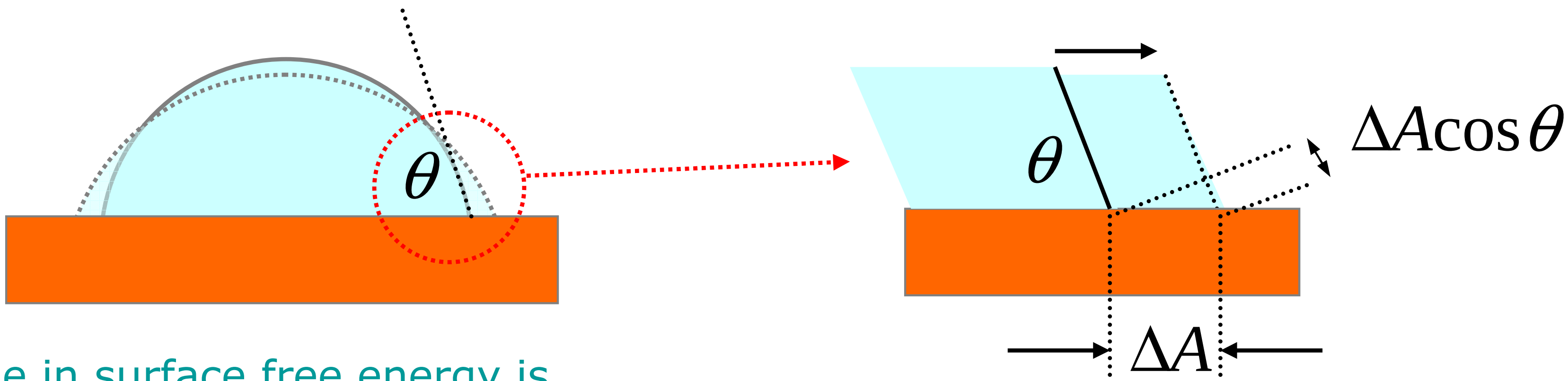
$$\cos\theta_W = r(x)\cos\theta_e$$



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

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

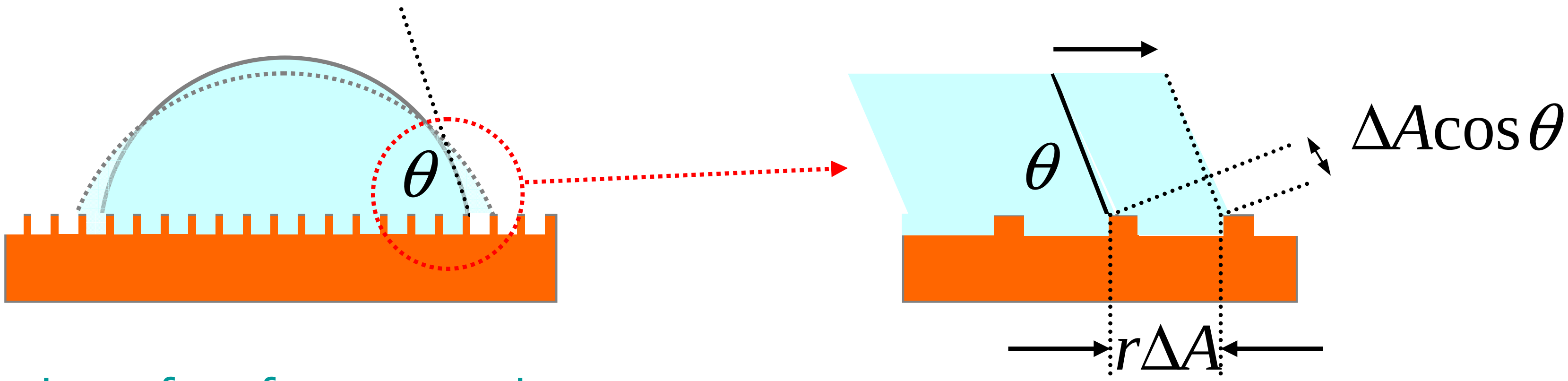
Equilibrium is when $\Delta F(x)=0$ $\Rightarrow$

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

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

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

Wenzel Eq

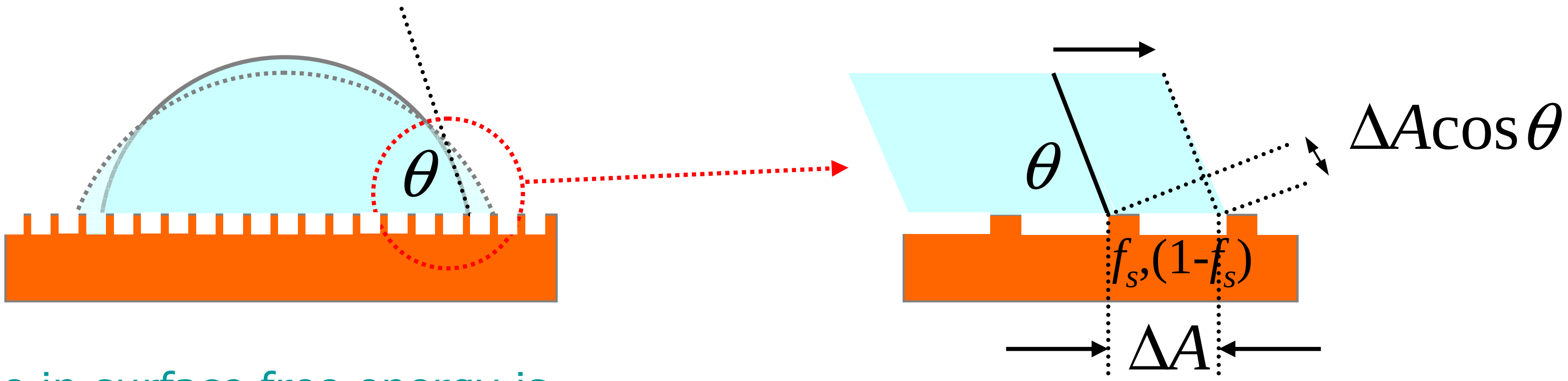
Topography $\Rightarrow$ $r(x)$ = roughness factor

Chemistry $\Rightarrow$ Young's Law θ_e

The derivation is based on contact line changes[2], 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 $\Delta F(x)=0$ $\Rightarrow$ $\cos\theta_{CB}(x) = f_s(x)(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} - (1-f_s(x))$

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

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 $f_s(x)$ and $(1-f_s(x))$

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

2-D Cartoons to 3-D Droplets

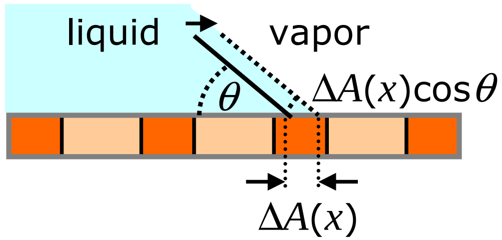
Radial Symmetry

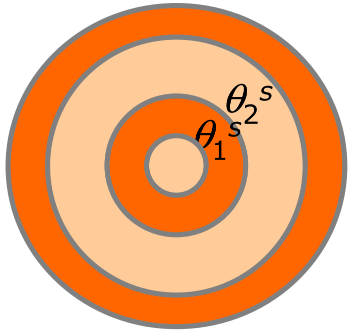
1-D surface becomes concentric circles ….. two cases

Case 1: $\Delta A(x)$<<pattern period

Adopts the appropriate

Young's Law θ_i^s angle





Case 2: $\Delta A(x)$=pattern period (*unlikely*)

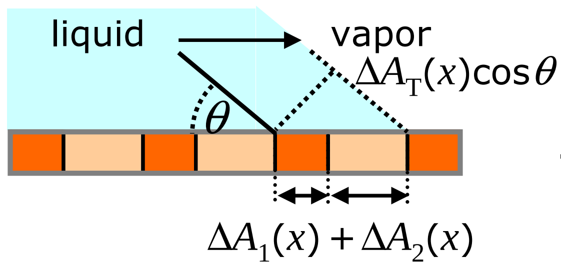
Adopts Cassie angle using the two Young's law angles θ_1^s and θ_2^s

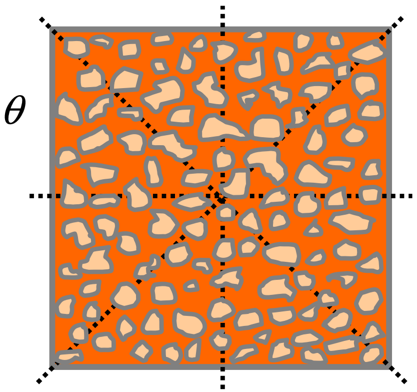
Random Surface

Cassie-Baxter requires:

$\Delta A(x)$=pattern period

Taken in random directions, may be true on average



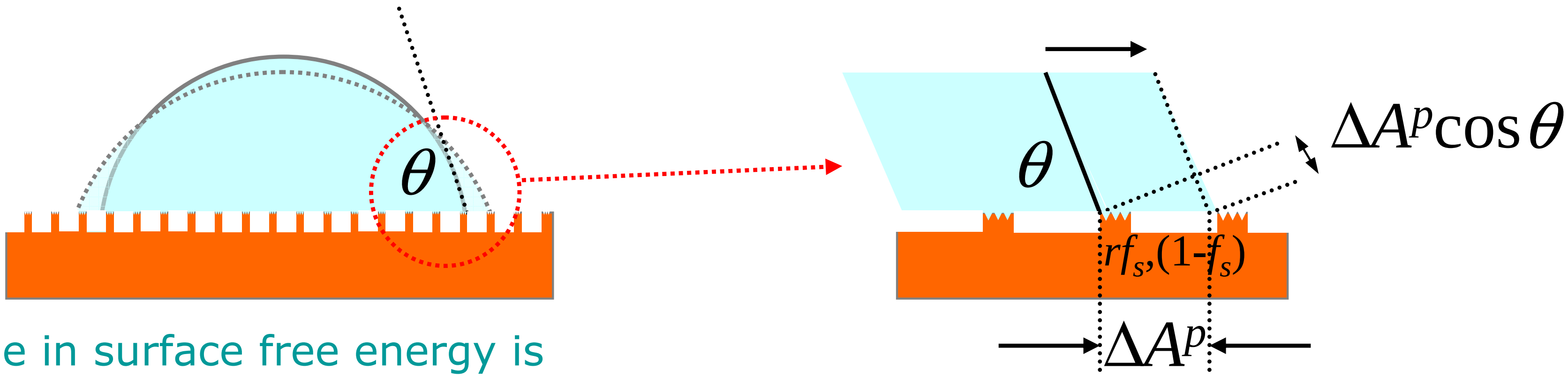


Drop size compared to patch size may matter - drop contact area must look circular on average

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

Dual Length Scales
&
Re-entrant Features

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

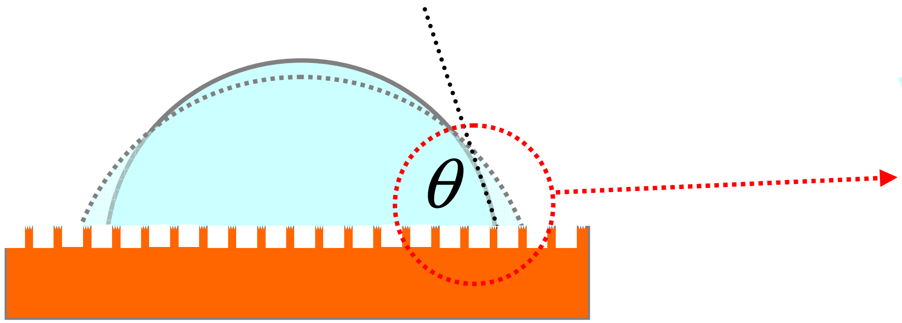
$r= \Delta A_{SL}/\Delta A_{SL}^{P}$ = roughness of "tops" of features

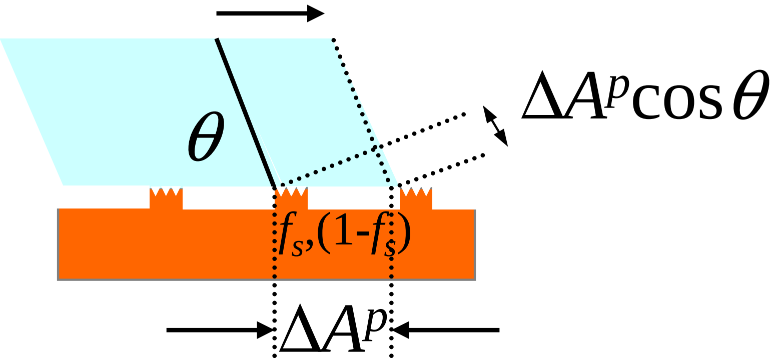
Transformation via Wenzel law and then by Cassie-Baxter equation

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

References Shirtcliffe, N.J. *et al.*, Adv. Maters. 16 (2004) 1929-1932; Bachmann, J.; McHale, G. accepted for publication Eur. J. Soil Sci. (2008).

Topography 5: Top-Empty Dual Scale Surfaces





Change in surface free energy is

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

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

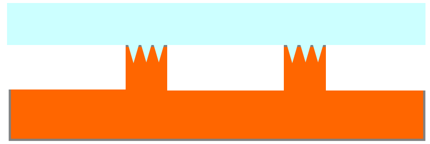
Transformation via Cassie-Baxter and then by Cassie-Baxter again

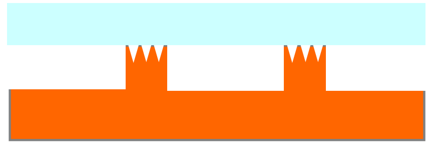
$\theta_e \rightarrow \theta_{CB}\,(\theta_e) \rightarrow \theta_{CB}\,(\theta_{CB})$

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

Complex Topography

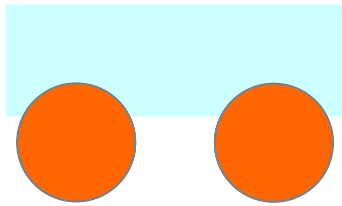
Roughness on Top of Features

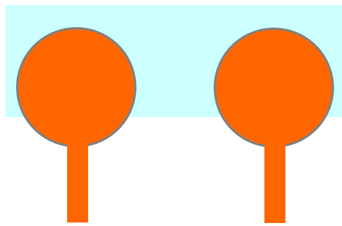




- Liquid filled case: Create Wenzel angle and use in Cassie-Baxter equation
- Non-filled case: Create Cassie-Baxter angle for top and use in Cassie-Baxter for large scale structure

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 (*i.e. may depend on the liquid*)
- Surfaces can support droplets even when θ_e is substantially below 90^o[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.

Experimental Consequences

Gradient Surfaces

Driving Force

Gradients in Cassie-Baxter Contact Angle

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

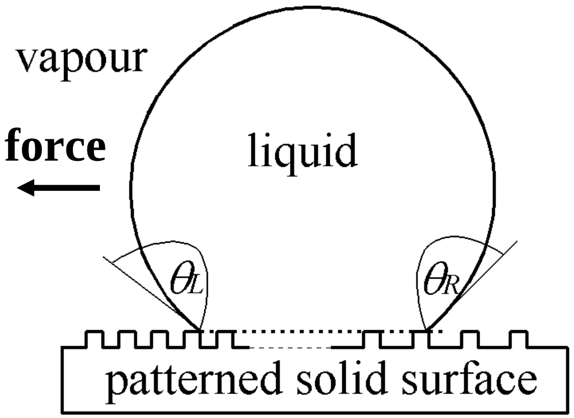
Same surface chemistry, but vary Cassie-Baxter fraction across surface

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

Driving Force

Idea: Alter topography so that droplet experiences different contact angles on the two sides

Consequence: Driving force generated to move droplet

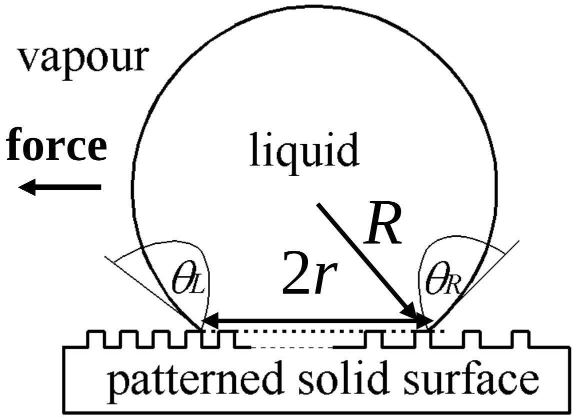


$$Force \propto \gamma_{LV}(\cos\theta_R - \cos\theta_L)$$
$$\propto \gamma_{LV}(f_R - f_L)(\cos\theta_e^s + 1)$$

Need to overcome contact angle hysteresis

References Quéré *et al* (unpublished); McHale *et al*, Analyst 129 (2004) 284-287.

Conditions for Motion



Spherical Cap

Assume small contact area:

$$2r \approx 2R\ [2f_{ave}(x)(1+\cos\theta_e^s)]^{1/2}$$

$$Force/length = \gamma_{LV}(f_R - f_L)(\cos\theta_e^s + 1)$$

$$= 2R\ \gamma_{LV}[2f_{ave}(x)]^{1/2}(1+\cos\theta_e^s)]^{3/2}(df/dx)$$

Defect Based Hysteresis Force

$$Force/length = \gamma_{LV}\Delta(\cos\theta) \approx \gamma_{LV} f(x)\log f(x)$$

Drive Condition

$$(df/dx) > constant \times f_{ave}(x)^{1/2}\log f_{ave}(x)/[R(1+\cos\theta_e^s)^{3/2}]$$

More superhydrophobic

Larger droplets

Reference Joanny, J. F. & de Gennes, P. G. (1984) J. Chem. Phys. 81 (1984) 552-562; C. R. Acad. Sci. Paris Ser. II 299 (1984) 279-283 (cited by Quéré).

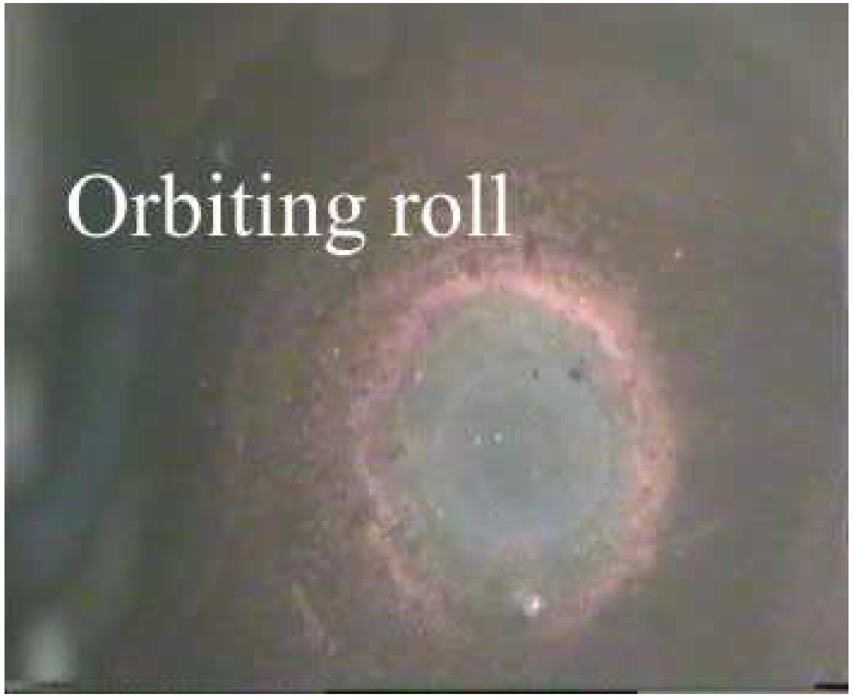
Self-Actuated Motion

Radial Gradient in Contact Angle

Electrodeposited copper – Diffusion limited aggregation

Fractal–like to overcome contact angle hysteresis

Radial gradient $\theta(r)$=110º→ 160º



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

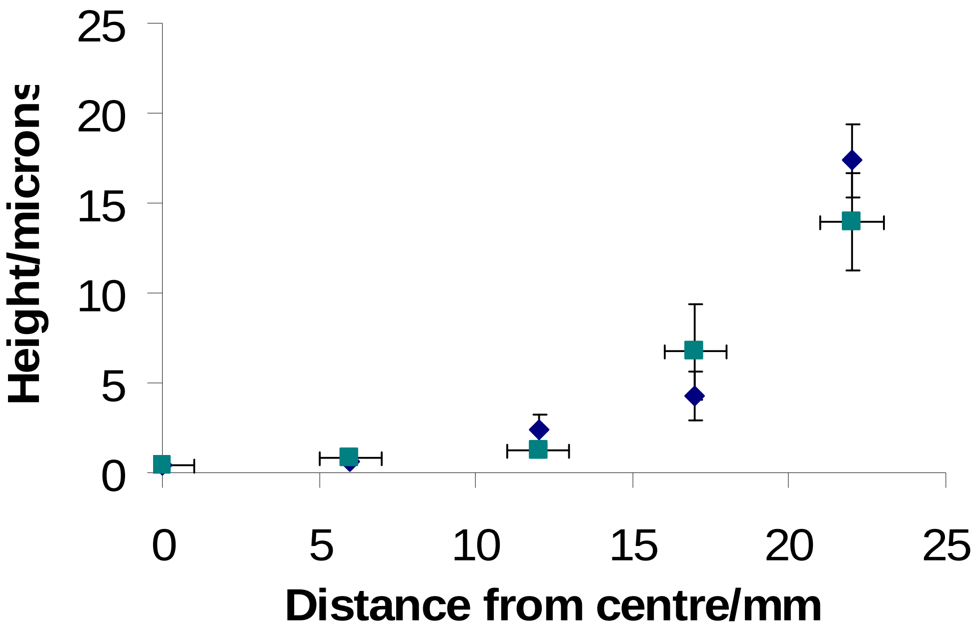
Surface Profile

Mechanism for Motion

Small slope on extremely low hysteresis surface?

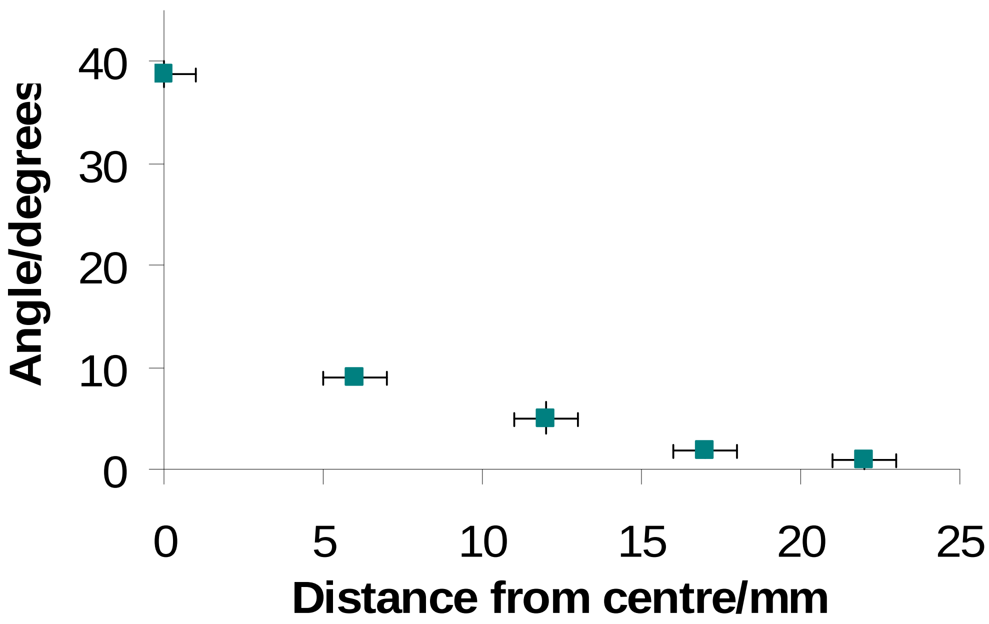
Truly contact angle driven?

Surface Profile



Multiple profiles have been taken along different radial lines

“Hysteresis”



Using radial view and tilt table tangential to radius

Summary

1. Cassie-Baxter and Wenzel Equations
   - Often over-simplified use of Cassie-Baxter and Wenzel equations
   - Roughness factor and Cassie fractions are defined by surface sampled by droplet at three-phase contact lines, i.e. local values
   - Can design applications to take advantage of the effects

2. Spatial Variations in Topography
   - Gradients in topography define driving forces
   - Paths can be defined on surface
   - Droplets can enter into self-actuated motion

The End

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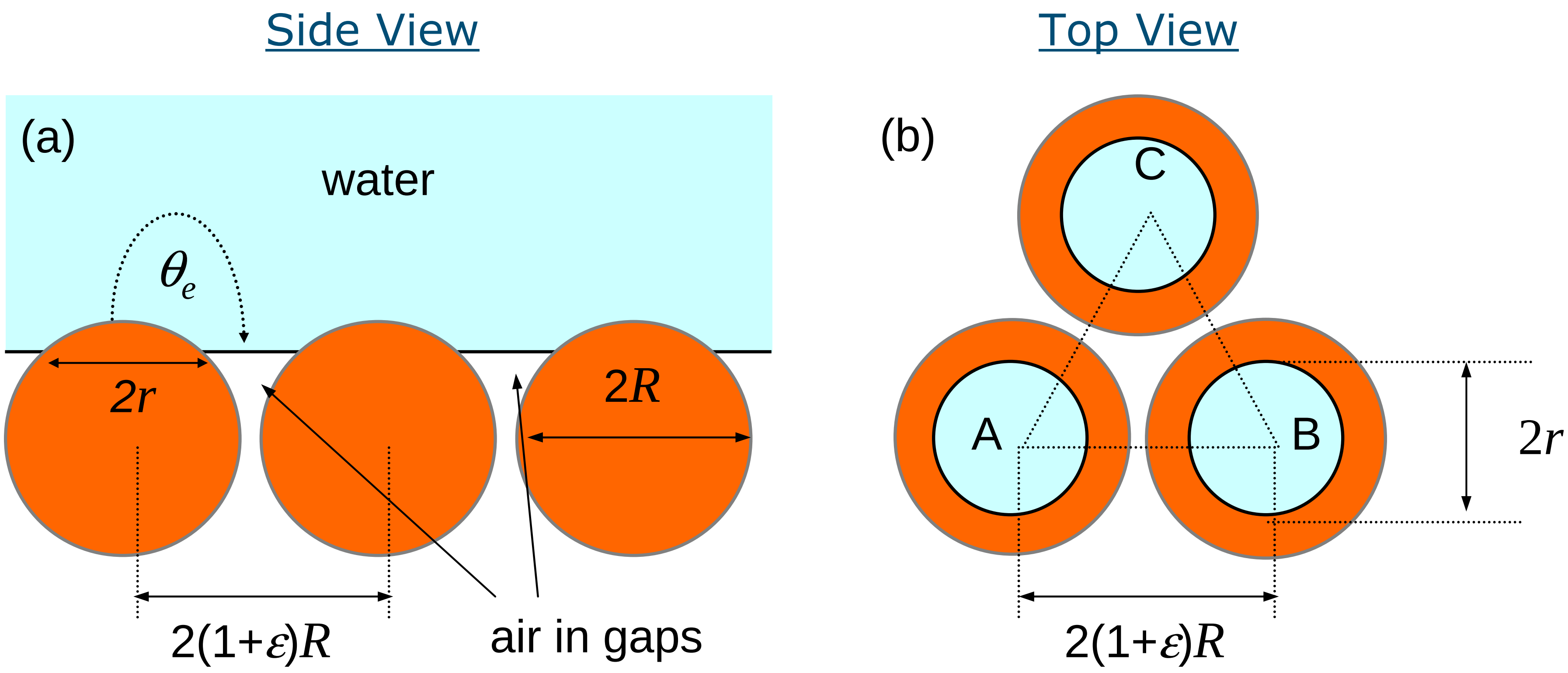
Appendices

Model of Bead Pack/Soil



Assumptions

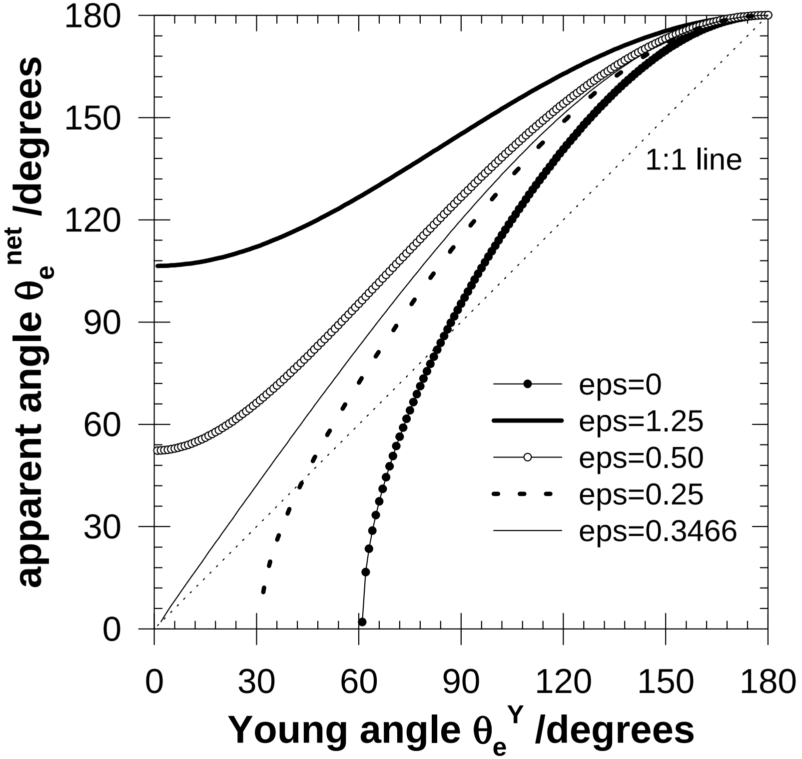
1. Uniform size, smooth spheres in a hexagonal arrangement
2. Water bridges air gaps horizontally between spheres
3. Capillary (surface tension) dominated size regime of gaps<< κ^{-1}=2.73 mm

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

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

$$\cos\theta_e^{net} = f_S r_s \cos\theta_e - (1 - f_S)$$

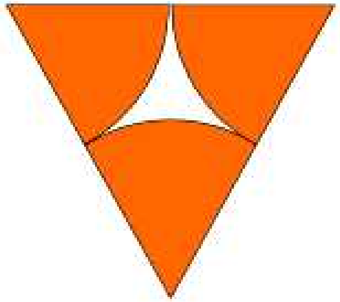
$$f_s = \frac{\pi \sin^2\theta_e}{2\sqrt{3}(1+\varepsilon)^2} \qquad r_s = \frac{2(1+\cos\theta_e)}{\sin^2\theta_e}$$

References McHale, G. *et al.*, Eur. J. Soil. Sci. 56 (2005) 445-452. Bachmann, J.; McHale, G. submitted to EJSS (2008).

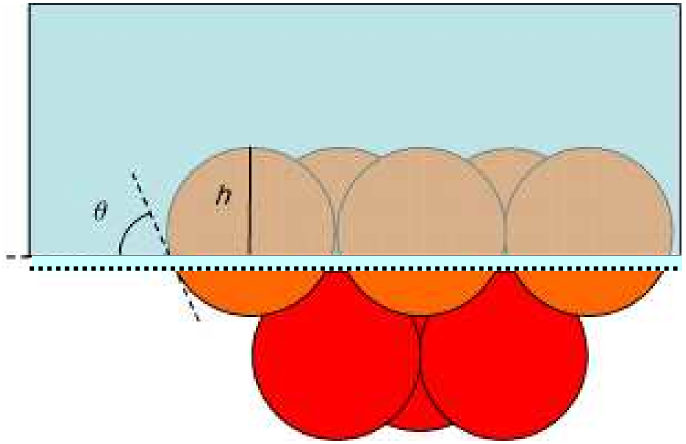
Transition from Wetting to Porosity

Assumptions

Top View



Side View



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

Results for Close Packing

1. Change in surface free energy with penetration depth, h, into first layer of particles

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

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

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

4. Critical contact angle, θ_c, when h_c reached[1,2]

$\theta_c = 50.73^o$

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.

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