NOTTINGHAM TRENT UNIVERSITY

The Absolute Hydrophilic Nature of All Solids (including Teflon®)

Glen McHale, Michael I. Newton and Neil J. Shirtcliffe

School of Science & Technology

International Workshop on Bubble & Drop Interfaces, Thessalonika, Greece

www.naturesraincoats.org 23-25 September 2009

Overview

1. Definitions of Hydrophilic and Hydrophobic
    - Origin of terminology of hydrophilic/hydrophobic
    - Wetting and non-wetting
2. Experiments on Adhesive "Hydrophobic" Surfaces
    - Hydrophobic grains and liquid marbles
    - Capillary Origami
    - Is Teflon® hydrophilic or hydrophobic?
3. Theory of Droplet Wrapping
    - Surface free energy
    - Wetting and adhesion

Definitions of Hydrophilic and Hydrophobic

The Language of Hydrophilic and Hydrophobic

Hydrophilic/Hydrophobic

These are words used extensively in science, but

- What are there origins?
- Do they always mean the same?
- Are they well-defined?
- Does a lack of understanding cause mis-conceptions?

Scientific Fields of Hydrophilic/Hydrophobic

Erwin A. Vogler identifies the origin of these words in several separate areas

- Colloid Science (e.g. hydrophilic colloids, J. Perrin 1905)
- Surface science (e.g. nature of molecular surfaces, I. Langmuir 1933)
- Biochemistry (e.g. hydrophobic effect/bond/scale)
- Surface Chemistry and Biomaterials (e.g. wetting related to solid surfaces)

Terminology originally related to the nature of chemical groups has come to have a meaning related to the nature of a solid surface and its interaction with water

Reference Vogler E.A. “*On the Origins of Water Wetting Terminology*”, pp. 149-182 in “*Water in Biomaterials Surface Science*”, ed. M. Morra, 2001 John Wiley & Sons.

Wetting/Non-Wetting v Hydrophilic/Hydrophobic

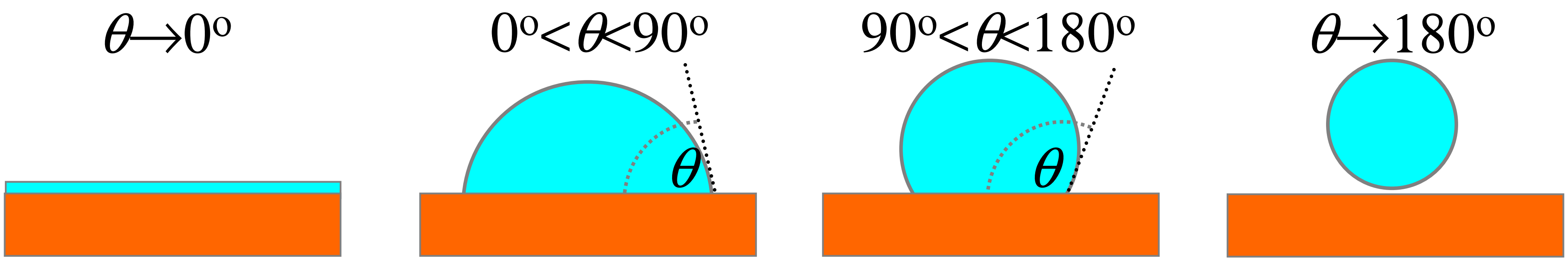
Hydrophilic/Hydrophobic

Harkins (1917) defined hydrophobic as any solid surface with a contact angle greater than 0°.

Langmuir (1938) defined hydrophilic as any solid surface on which complete wetting occurred and the contact angle went to 0°.

Many others regard 90° as the threshold between hydrophilic and hydrophobic

Are these reasonable definitions or do they have unreasonable implicit assumptions?



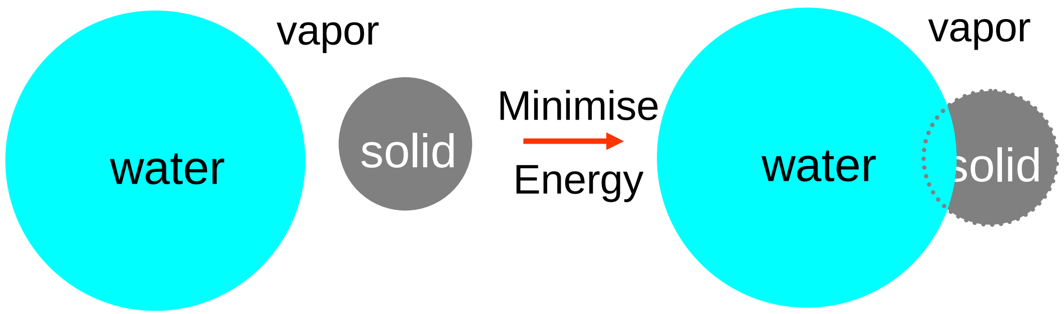
Wetting	partial-wetting	Non-wetting
Hydrophilic	*Are these water-fearing or water-liking surfaces?*	*Hydrophobic (or is it superhydrophobic?)*

Adhesive “Hydrophobic” Surfaces

Experiment 1: Liquid Marbles

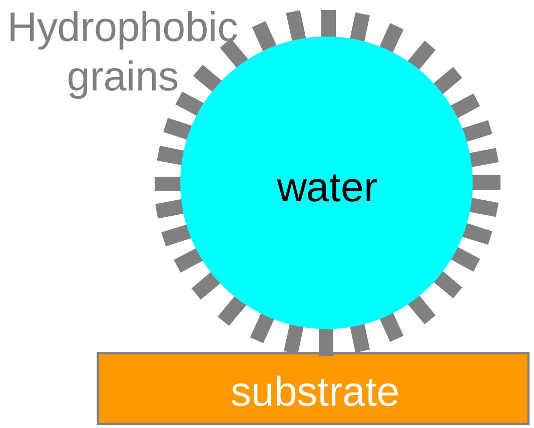
1. Loose surface: Grains are not fixed, but can be lifted by a liquid
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble (*hydrophobic means here: CF_3 surface chemistry with $\theta > 90^o$ when measured on a rigid flat substrate with same surface chemistry*)

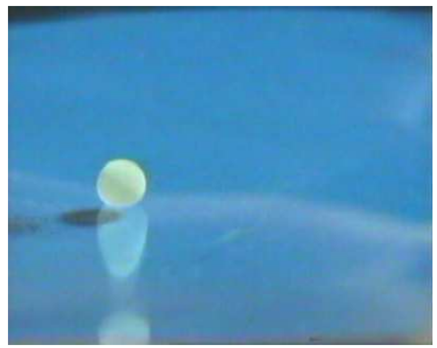
"Hydrophobic" Grains and Water



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

Energy is always reduced on grain attachment assuming grain is smooth (roughness, r=1)

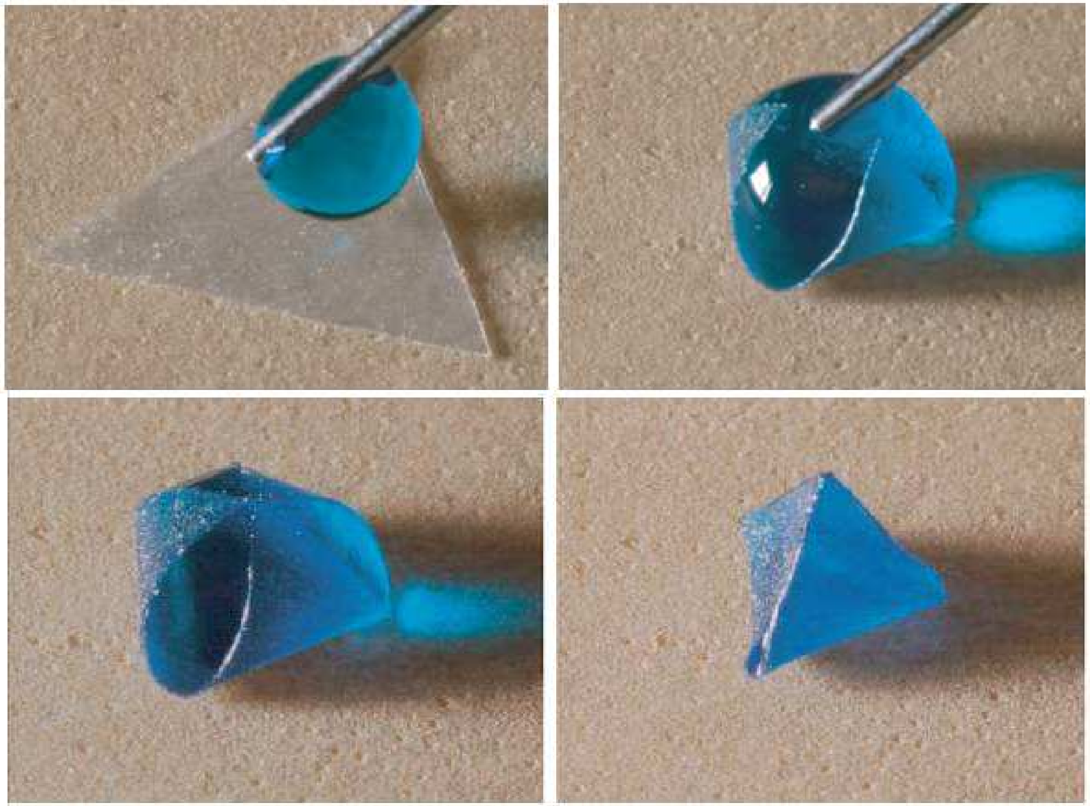




References: Aussillous, P.; Quéré, D. Nature 411 (2001) 924-927.; McHale, G. *et al*., Langmuir 23 (2007) 918-924; Newton M. I. *et al*., J. Phys. D. Appl. Phys. 40 (2007) 20-24.

Experiment 2: Py *et al*'s Capillary Origami

1. Consider a thin (40-80 μm) triangular sheet of PDMS
2. Consider contacting with a droplet of water and allow to evaporate



Acknowledgement: Py *et al.* Eur. Phys. J.

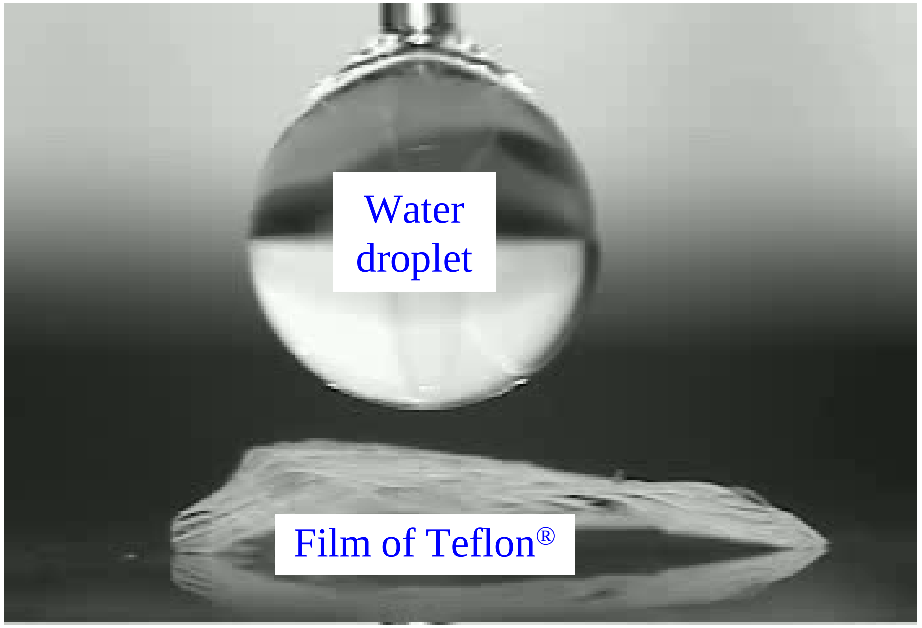
PDMS is normally considered hydrophobic (90°-120°), but water seems to like it

References Py, C. *et al*., Phys. Lett.. 98 (2007) art. 156103.
Py, C. *et al*., Eur. Phys. J. Special Topics, 166 (2009) 67-71.

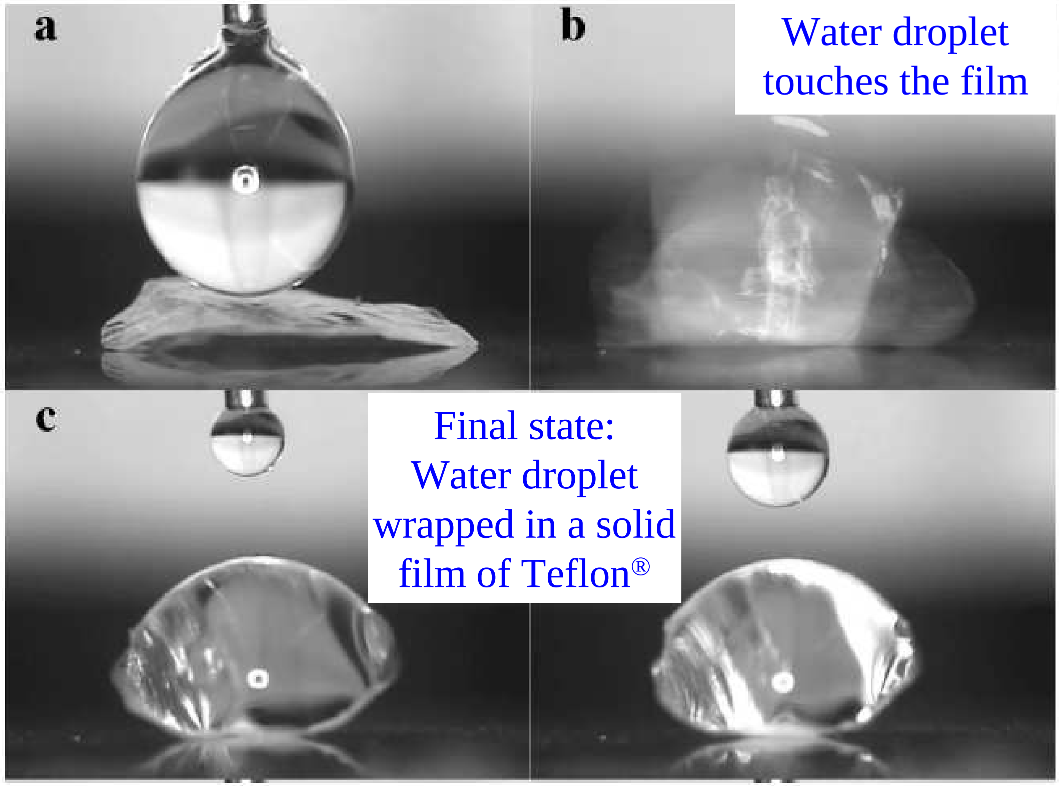
Experiment 3: Droplet Wrapping with Teflon®

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
3. Droplet wraps itself up in the Teflon® … is this consistent with being hydrophobic?

<u>Droplet Wrapping Video</u>



<u>Stills from Video</u>



<u>Courtesy</u>: Prof. Tom McCarthy (UMass, Amherst)

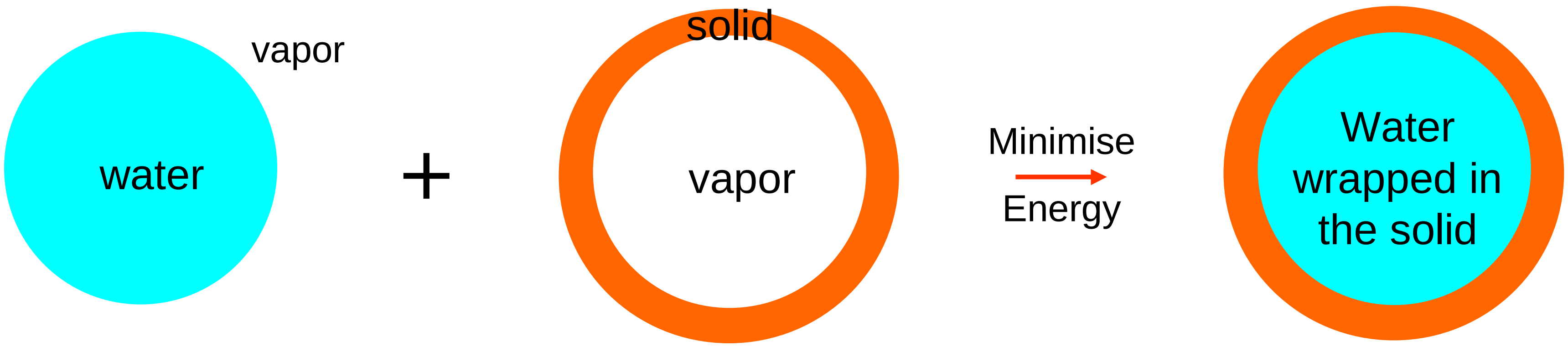
<u>References</u> Gao, L.; McCarthy, T.J. Langmuir <u>24</u> (2008) 9183-9188.

Theory of Droplet Wrapping

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

1. Assume energy in deforming/bending solid is zero
2. Assume solid is smooth and droplet is small
3. Under these conditions surface free energy always favors solid wrapping up a droplet providing the Young's eq. contact angle (defined by combination of surface tensions or by measurement on a rigid substrate) is less than 180º

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



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

gives $\Delta F/4\pi R^2 = \gamma_{SL} - \gamma_{LV} - \gamma_{SV}$ Use Young's eq. $\Rightarrow \Delta F = -(1 + \cos\theta_e) < 0 \Rightarrow \theta_e < 180^o$

All smooth solids with Young's eq. θ_e<180º , incl. Teflon, are absolutely hydrophilic

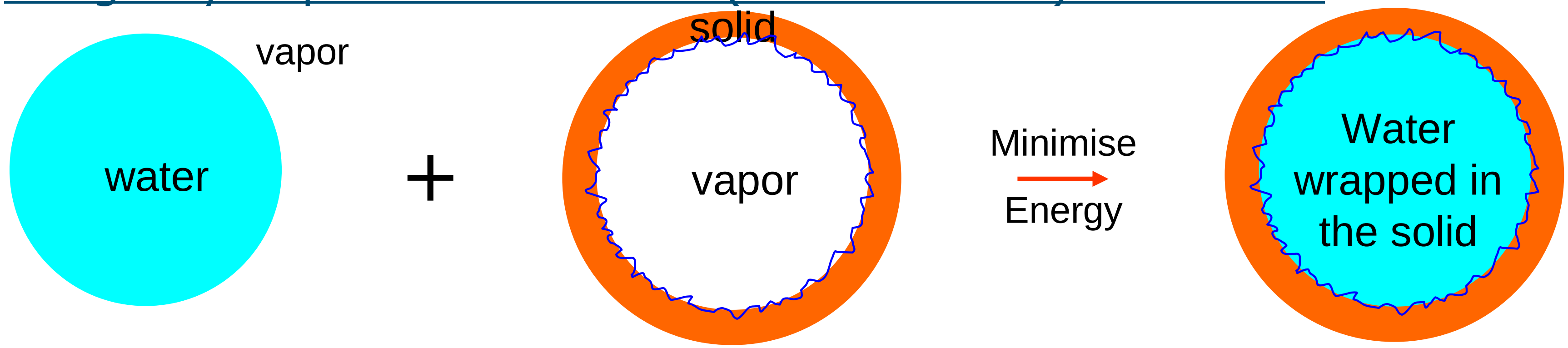
i.e. the solid film wrapping the droplet lowers the surface free energy

<u>Reference</u> McHale, G. Langmuir <u>25</u> (2009) 7185-7187.

Roughness induced Hydrophobic Tendencies

1. Assume energy in deforming/bending solid is zero
2. Assume solid surface is rough and droplet is small
3. Assume liquid penetrates features (Wenzel roughness, r)

Rough Hydrophobic Solid Shell (of thickness ε) and Water



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

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

Rough solids with $r>1/|\cos\theta_e|$ and Young's eq. $\theta_e>90^o$ do not reduce surface free energy by the solid film wrapping the droplet

i.e. surfaces with $\theta_e > 90^o$ have a tendency to hydrophobicity (in a Wenzel sense) as $r \rightarrow \infty$

Reference McHale, G. Langmuir 25 (2009) 7185-7187.

Bending Stiffness and Droplet Size

1. Assumption of zero energy in deforming/bending solid is zero can be relaxed. Energy stored in bending is:

$$E_{\text{sphere}} = 4\pi(2\kappa_{\text{b}} + \kappa_{\text{G}})$$

2. Droplet wrapping is still favoured, but droplet must be above a critical radius

$$R_{\text{c}} = \sqrt{\frac{2L_{\text{EC}}^2 + L_{\text{GC}}^2}{1 + \cos\theta_W}}$$

3. Characteristic *elasto-capillary* and *Gaussian-capillar*y bending lengths, $L_b = (\kappa_b/\gamma_{\text{LV}})^{1/2}$ and $L_G = (\kappa_G/\gamma_{\text{LV}})^{1/2}$, become important

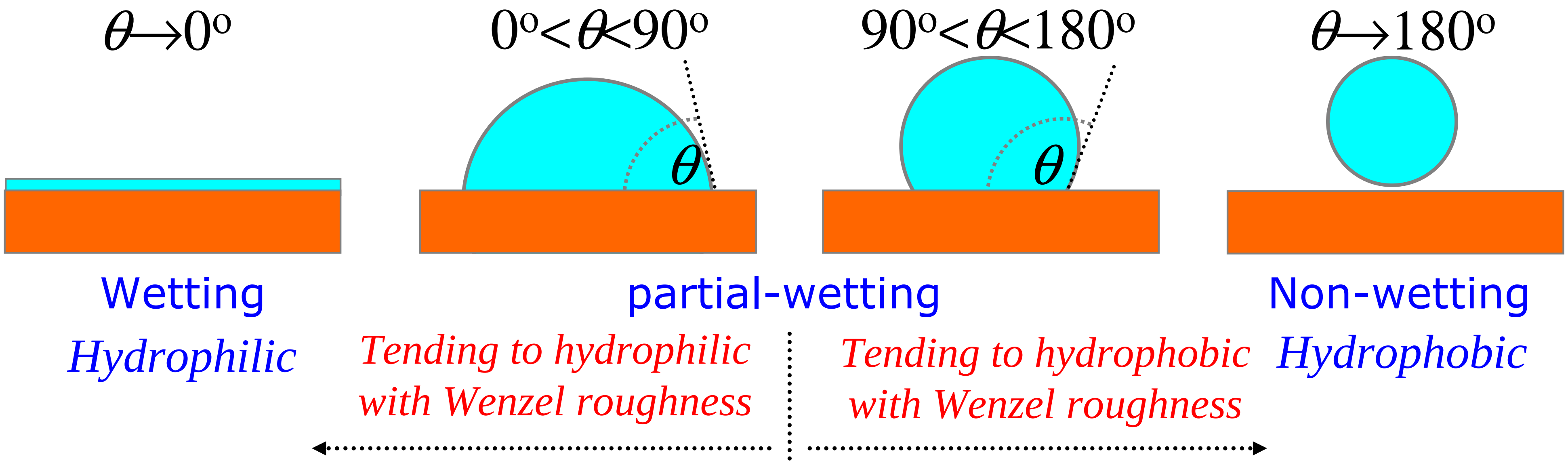
4. The critical radius also depends on the Wenzel roughness of the film ($\cos\theta_W = r\cos\theta_e$)

5. A granular surface is conceptually "a solid film with no bending energy". Droplet wrapping becomes the formation of a liquid marble

Reference: McHale, G. Langmuir 25 (2009) 7185-7187.

Hydrophobicity and Adhesion

1. Do we implicitly assume hydrophilic/hydrophobic terminology should only describe the surface chemistry?
2. Why should a surface that water attracts be called hydrophobic?
3. Why should the substrate rigidity be an implicit part of the definition of a hydrophobic surface?
4. Penetration into capillary tubes is not an argument for using $\theta_e=90^o$ as the definition of hydrophobic – non-parallel walls have penetration at other contact angles
5. All partial-wetting surfaces are hydrophilic ("water-liking") in an absolute (adhesive) sense, even if they have hydrophobic tendencies with Wenzel-like roughness



Conclusions and Future Work

Hydrophilic/Hydrophobic Terminology

1. Meaning varies from one scientific area to another
2. “Hydrophobic” surfaces can be adhesive surfaces (between solid and water)
3. Usual definition of hydrophobicity implicitly assumes non-surface chemistry property of substrate (flat and rigidity and/or parallel walled capillaries)
4. Surfaces can be completely wetting (“hydrophilic”) or (theoretically) non-wetting (“hydrophobic”)
5. Partial-wetting surfaces, including Teflon®, “like” water and are, in an adhesive sense, absolutely hydrophilic, but can have wetting and non-wetting tendencies according to the effect of Wenzel roughness

Future Work

1. Theory for Cassie-Baxter droplet wrapping surfaces
2. Experiments on smooth/rough films - “Superhydrophobicity in droplet wrapping?

The End

Acknowledgements

Prof. Tom McCarthy, Univ. Mass. (at Amherst)

Dr Dale Herbertson, Mr Steve Elliott

EPSRC Engineering and Physical Sciences Research Council

COST