

# The Absolute Hydrophilic Nature of All Solids (including Teflon<sup>®</sup>)

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International Workshop on Bubble & Drop Interfaces, Thessalonika, Greece

[www.naturesraincoats.org](http://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<sup>®</sup> 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 their 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*

# Wetting/Non-Wetting v Hydrophilic/Hydrophobic

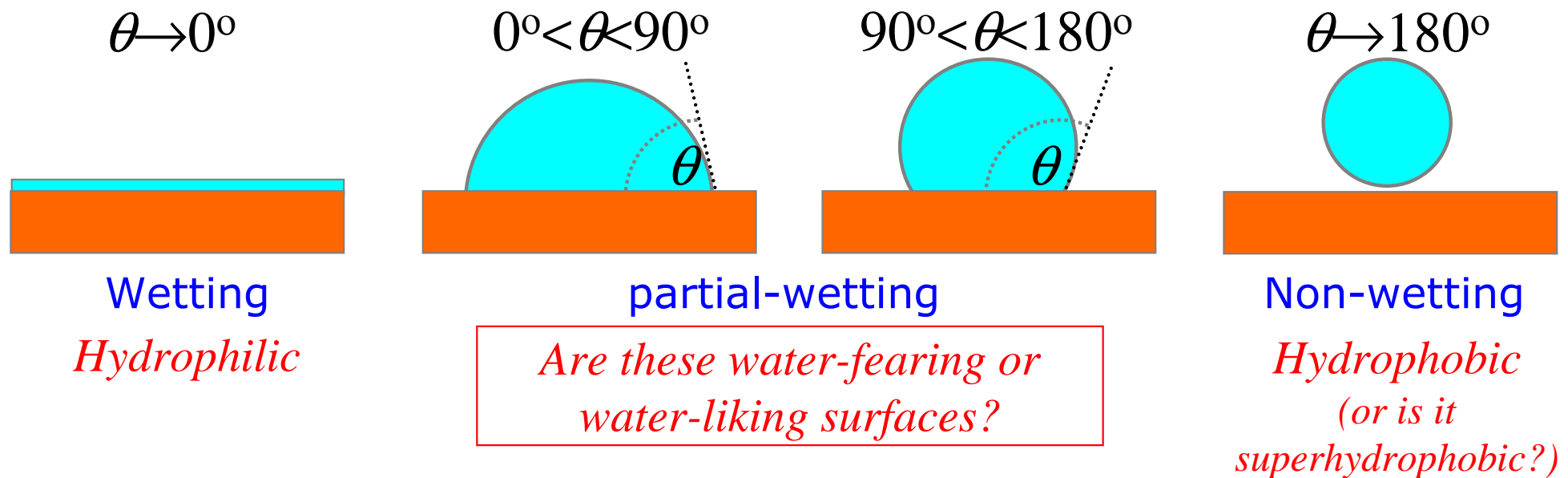
## Hydrophilic/Hydrophobic

Harkins (1917) defined hydrophobic as any solid surface with a contact angle greater than  $0^\circ$ .

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

Many others regard  $90^\circ$  as the threshold between hydrophilic and hydrophobic

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

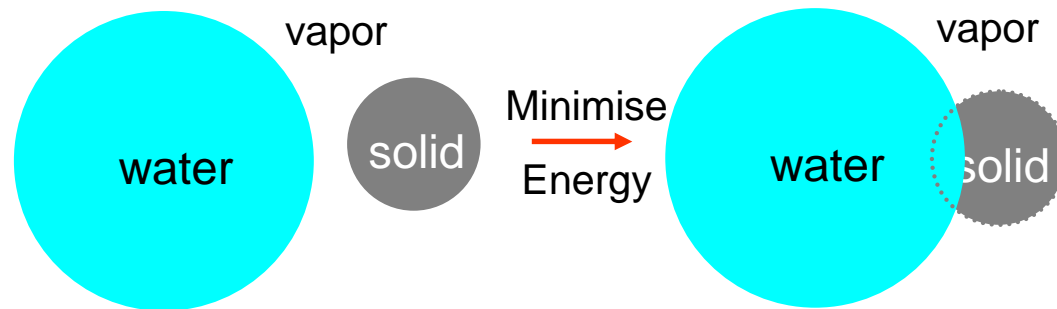


# Adhesive “Hydrophobic” Surfaces

# Experiment 1: Liquid Marbles

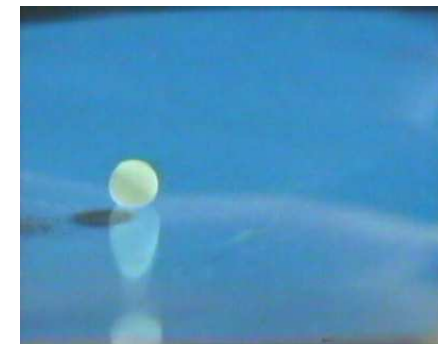
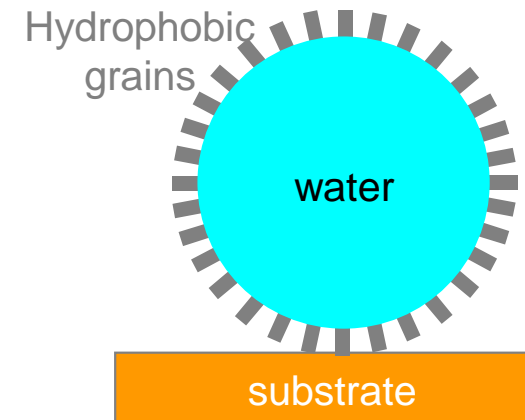
1. Loose surface: Grains are not fixed, but can be lifted by a liquid
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble (*hydrophobic means here:  $CF_3$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

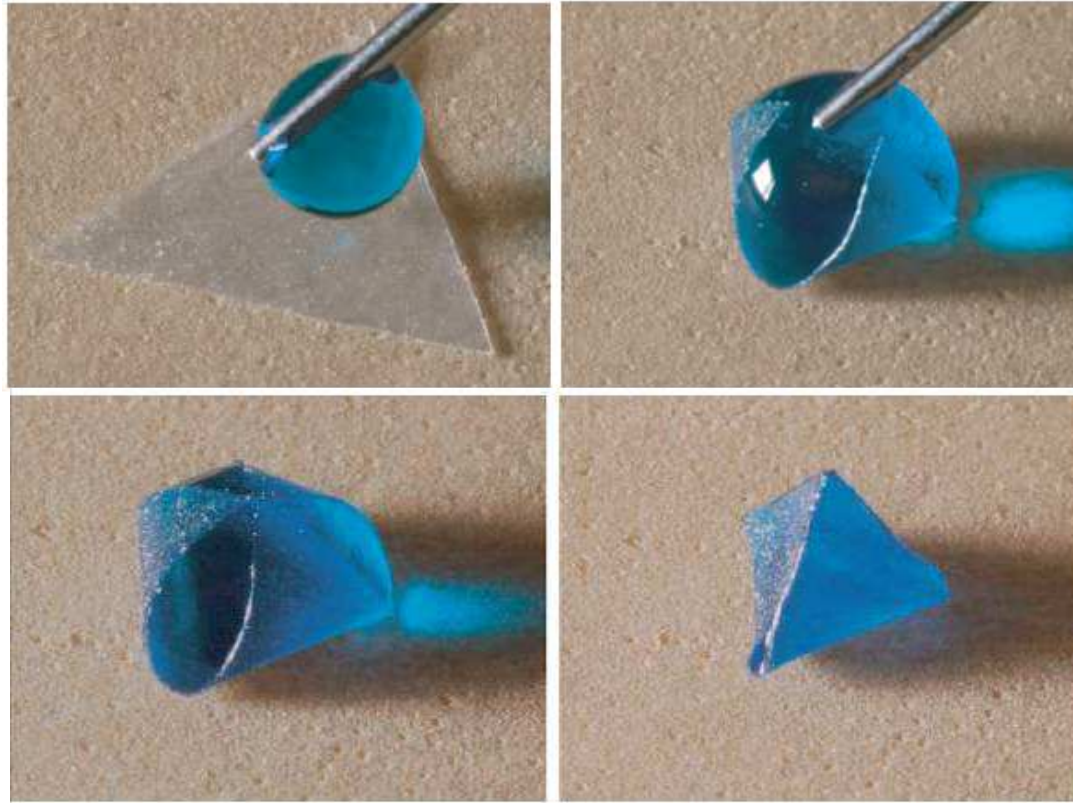


References: Aussillous, P.; Quéré, D. Nature **411** (2001) 924-927.; McHale, G. et al., Langmuir

06 September 2002 **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  $\mu\text{m}$ ) 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 ( $90^\circ$ - $120^\circ$ ), but water seems to like it*

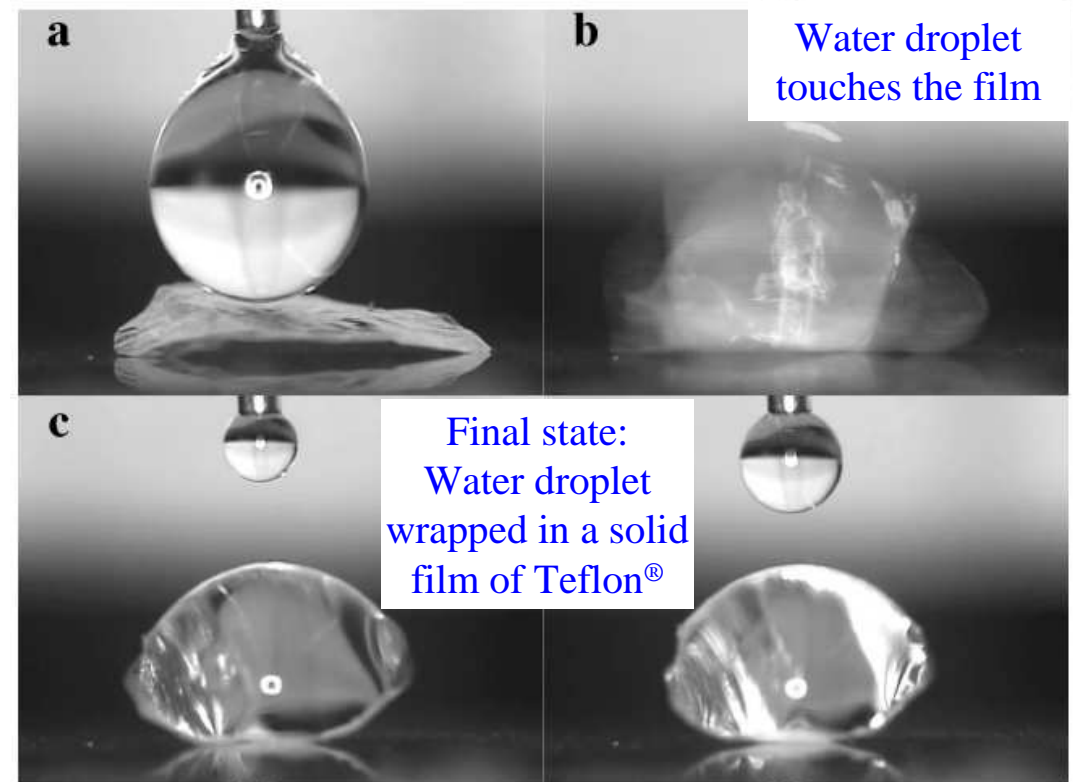
# Experiment 3: Droplet Wrapping with Teflon®

1. We all know Teflon® is a hydrophobic solid and gives a non-stick surface .....
2. Consider a thin, 3.7  $\mu\text{m}$ , film of Teflon® AF2400 contacted by a droplet of water
3. Droplet wraps itself up in the Teflon® ... is this consistent with being hydrophobic?

## Droplet Wrapping Video



## Stills from Video



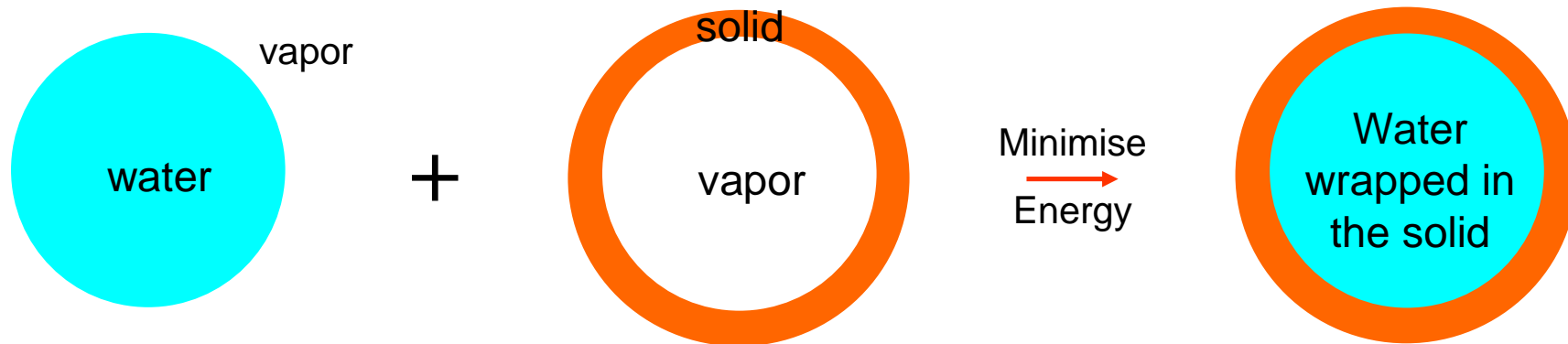
Courtesy: Prof. Tom McCarthy (UMass, Amherst)

# Theory of Droplet Wrapping

# Aren't all Solids with $\theta_e < 180^\circ$ 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  $180^\circ$

## Hydrophobic Solid Shell (of thickness $\varepsilon$ ) and Water



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

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

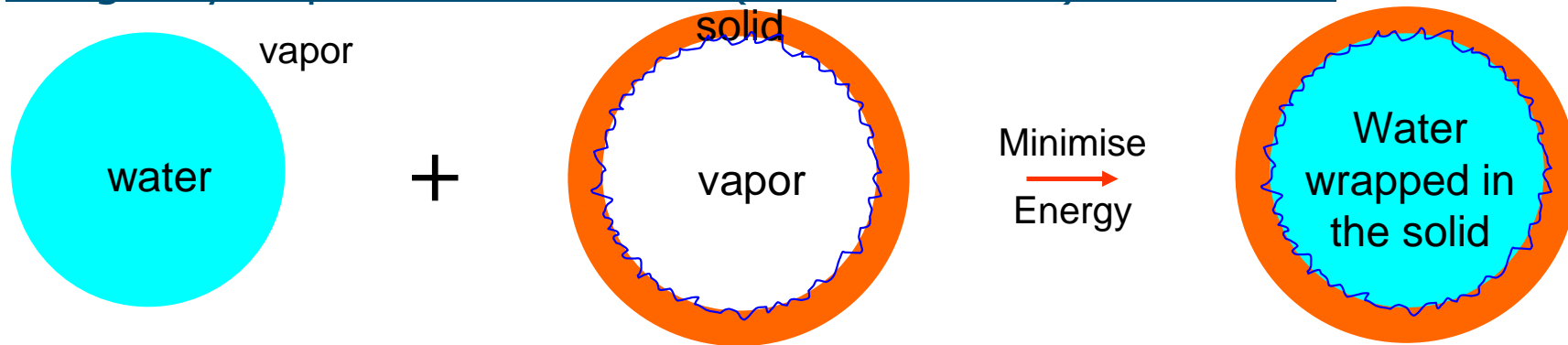
All smooth solids with Young's eq.  $\theta_e < 180^\circ$ , incl. Teflon, are absolutely hydrophilic

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

# 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 $\epsilon$ ) and Water



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

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

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

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

# Bending Stiffness and Droplet Size

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

$$E_{\text{sphere}} = 4\pi(2\kappa_b + \kappa_G)$$

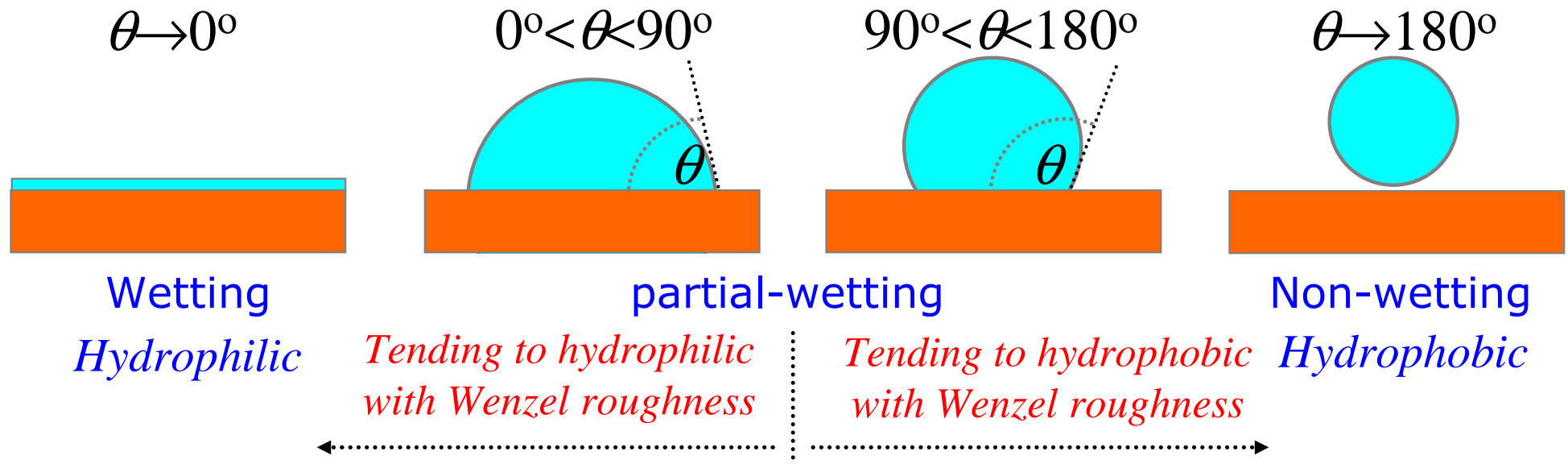
2. Droplet wrapping is still favoured, but droplet must be above a critical radius

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

3. Characteristic *elasto-capillary* and *Gaussian-capillary* 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

# 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  $\theta_c=90^\circ$  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<sup>®</sup>, "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?"

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The End

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## Acknowledgements

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

Dr Dale Herbertson, Mr Steve Elliott

**EPSRC**

Engineering and Physical Sciences  
Research Council

