NOTTINGHAM TRENT UNIVERSITY

Definitions of Hydrophobic and Hydrophilic: Adhesive Interactions On Flexible "Hydrophobic" Substrates

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Overview

1. Definitions of Hydrophilic and Hydrophobic
   - Origin of terminology of hydrophilic/hydrophobic
   - Wetting, non-wetting and partial wetting states
   - Immersion, wetted, chemistry and topography
2. Experiments on Adhesive "Hydrophobic" Surfaces
   - Hydrophobic grains and liquid marbles
   - Capillary Origami
   - Adhesive hydrophobic surfaces
3. Theory of Droplet Wrapping
   - Surface free energy
   - Wetting and adhesion
   - Flexible substrates and Cassie-Baxter and Wenzel effects

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

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

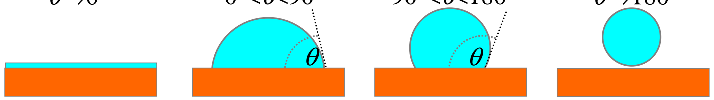
Hydrophilic/Hydrophobic

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

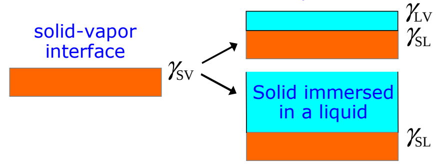
Are these reasonable definitions or do they have unreasonable implicit assumptions?



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

Is Hydrophobicity at a 0° or 90° Threshold?

Initial State | Final State | Surface Free Energy



$\Delta f = (\gamma_{SL}+\gamma_{LV}) - \gamma_{SV} = \gamma_{LV}(1-\cos\theta_e)$

$\Delta f = \gamma_{SL}-\gamma_{SV} = -\gamma_{LV}\cos\theta_e$

Define hydrophobic as when a dry surface is preferred (i.e. $\Delta f>0$)

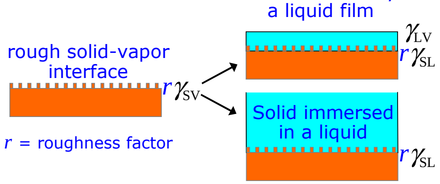
⇒ *Film (wetted) state definition gives $\theta_e > 0^\circ$*

⇒ *Immersed state definition gives $\theta_e > 90^\circ$*

Same chemistry, but different threshold?

Is Hydrophobicity Chemistry or Topography?

Initial State | Final State | Surface Free Energy



r = roughness factor

$\Delta f = (r\gamma_{SL}+\gamma_{LV}) - r\gamma_{SV} = \gamma_{LV}(1-r\cos\theta_e)$

$\Delta f = r(\gamma_{SL}-\gamma_{SV}) = -r\gamma_{LV}\cos\theta_e$

Define hydrophobic as when a dry state is preferred (i.e. $\Delta f>0$)

⇒ *Film (wetted) state definition changes to $\theta_e > \cos^{-1}(1/r) \to 90^\circ$* for large r

⇒ *Immersed state definition still gives $\theta_e > 90^\circ$*

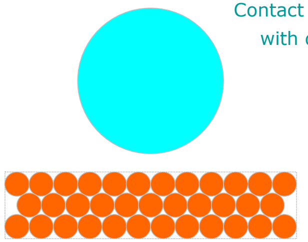
common 90° threshold

Even more complex when final state is a hemi-wicking state

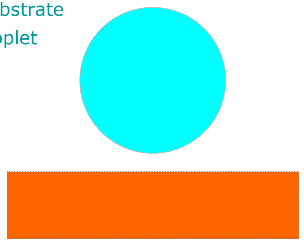
⇒ *Hemi-wicked state definition gives $\theta_e > \cos^{-1}((1-\varphi_s)/(r-\varphi_s)) \to 90^\circ$* for large r

Not just chemistry- Are there other assumptions?

What about substrate rigidity?



Contact substrate with droplet



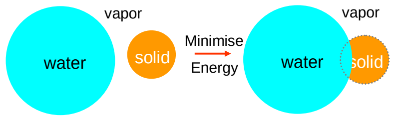
particles in substrate are loose	substrate is flexible and can bend
Interfacial energies determine outcome	Additional effect from bending energy of substrate

Adhesive “Hydrophobic” Surfaces

Experiment 1: Liquid Marbles

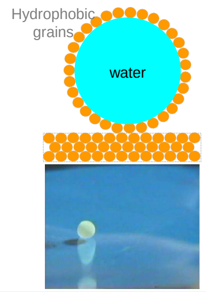
1. Loose surface: Grains are not fixed, but can be lifted by a liquid
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble (*hydrophobic means here:* CF_3 *surface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

“Hydrophobic” Grains and Water



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

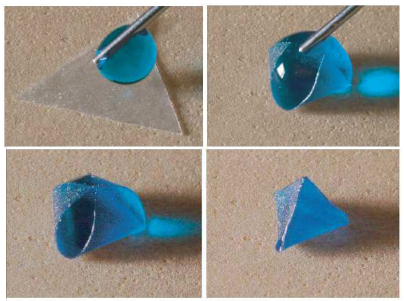
Energy is always reduced on grain attachment assuming grain is smooth (roughness, r=1)



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.

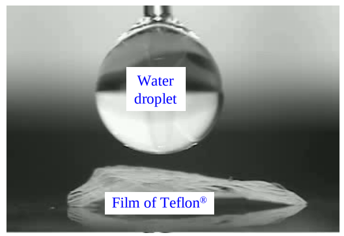
PDMS is normally considered hydrophobic (90^o-120^o), but water seems to like it

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

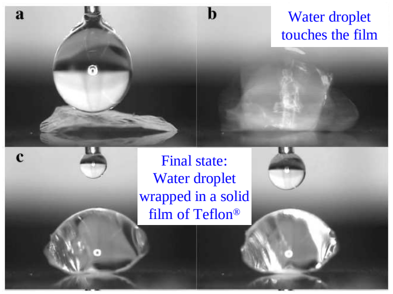
Experiment 3: Droplet Wrapping with Teflon®

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?

Droplet Wrapping Video



Stills from Video



Courtesy: Prof. Tom McCarthy (UMass, Amherst)

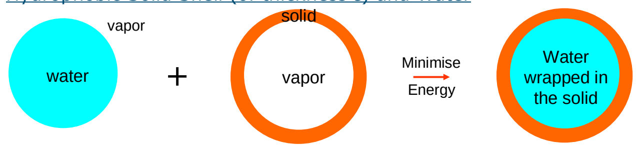
References Gao, L.; McCarthy, T.J. Langmuir 24 (2008) 9183-9188.

Theory of Droplet Wrapping

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

1. Assume energy in deforming/bending solid is zero – solid is deformed by liquid
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

Hydrophobic Solid Shell (of thickness ε) 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. $\Rightarrow \Delta F=-(1+\cos\theta_e)<0 \Rightarrow \theta_e<180^\circ$

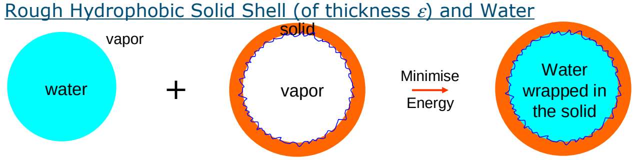
All smooth solids with Young's eq. θ_e<180º , incl. Teflon, are absolutely hydrophilic in an adhesive sense *i.e. a solid film wrapping the droplet lowers the surface free energy*

 Reference McHale, G. Langmuir 25 (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



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

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. θ_e>90º do not reduce surface free energy by the solid film wrapping the droplet

i.e. surfaces with θ_e >90º 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 (using elastic and Gaussian bending energies) is:

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

2. Assuming Wenzel-like liquid penetration droplet wrapping is still favoured (with $\cos\theta_W = r\cos\theta_e$), but droplet size must be above a critical radius:

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

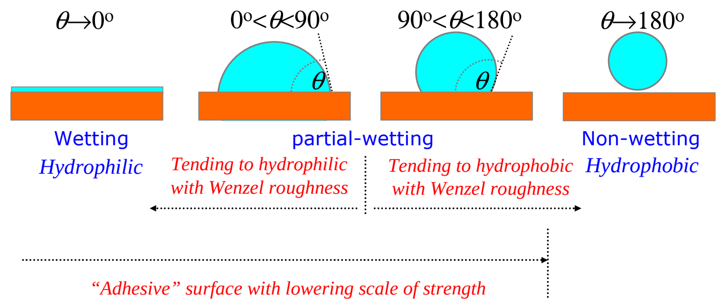
3. Characteristic *elasto-capillary* and *Gaussian-capillary* bending lengths, $L_b = (\kappa_b/\gamma_{LV})^{1/2}$ and $L_G = (\kappa_G/\gamma_{LV})^{1/2}$, become important
4. If the liquid does not penetrate between surface features, the critical radius involves the Cassie-Baxter contact angle rather than the Wenzel contact angle
5. A granular surface is conceptually "a solid film with no bending energy". Droplet wrapping becomes the formation of a liquid marble ($R_c\rightarrow 0$)

 References: McHale, G. Langmuir 25 (2009) 7185-7187 and Proceeding paper.

Concerns - Hydrophobicity and Adhesion?

1. Do we implicitly assume hydrophilic/hydrophobic terminology should only describe the surface chemistry?
2. Why should a solid surface to which water adheres be called hydrophobic ("water fearing")?
3. Why should the substrate rigidity be an implicit part of the definition of a hydrophobic surface?
4. Can penetration into capillary tubes give an argument for using $\theta_e=90^o$ as the definition of hydrophobic, despite non-parallel walls have penetration at other contact angles?
5. Aren't all partial-wetting surfaces "water-liking" (hydrophilic) in an absolute (adhesive) sense, even if they have hydrophobic ("water-fearing") hydrophobic tendencies with Wenzel-like roughness?

A Picture - Hydrophobicity and Adhesion



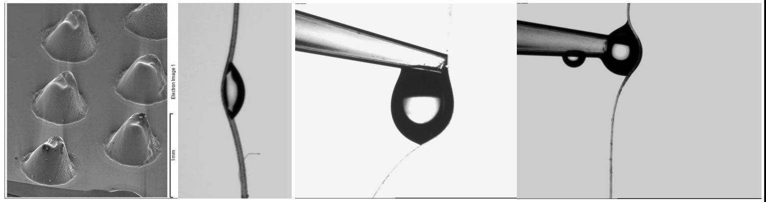
Conclusions and Future Work

Conclusions: Hydrophobic/Hydrophilic Terminology

1. Meaning varies from one scientific area to another
2. "Hydrophobic" surfaces can be adhesive surfaces (between solid and water/liquid)
3. Usual definition of hydrophobicity implicitly assumes non-surface chemistry properties of substrate (smoothness, rigidity and/or parallel walled capillaries)
4. Surfaces can be completely wetting ("hydrophilic") or (theoretically) completely non-wetting ("hydrophobic"/"super-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

Conclusions: Future Work

- Experiments on smooth/rough films – "Superhydrophobicity" in droplet wrapping?
- Microtape lens substrate – evaporation sequence (frame rate has been increased)
- Wrapping induced by droplet evaporation and sliding (frame rate has been increased)



The End

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