NOTTINGHAM TRENT UNIVERSITY

Passive and Active Actuation of Droplet Motion

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Overview

1. Superhydrophobicity
2. Gradients in Superhydrophobicity

} Passive

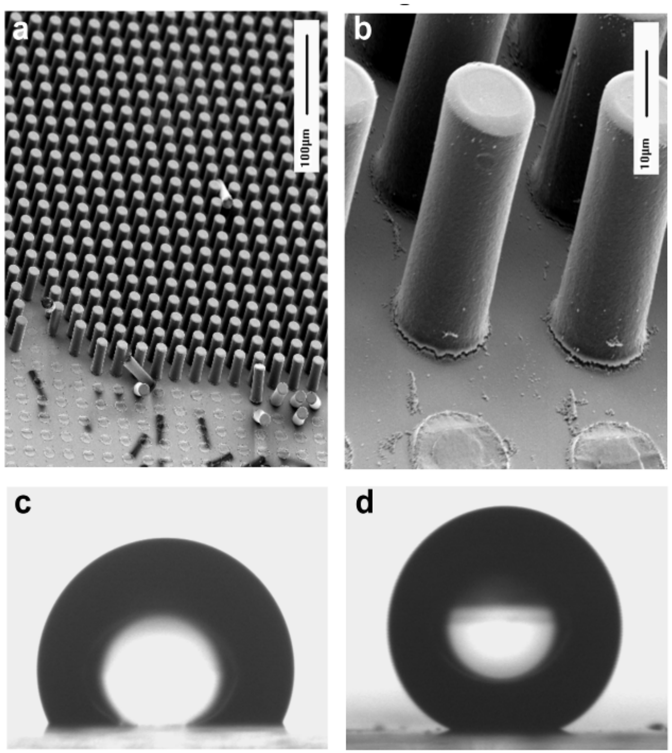
3. Electrowetting
4. Moving Liquid Marbles

} Active

Superhydrophobicity

Surface Structure

Effect on Water



a), b) Pillars *D*=15 μm, *L* = 2*D*

c) Flat and hydrophobic

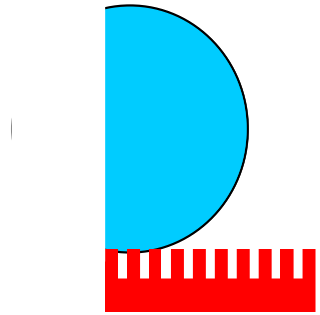
d) Tall and hydrophobic

"Skating" Droplets

Composite air-solid surface

(Cassie-Baxter)

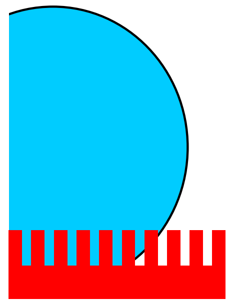
Low hysteresis: "Slippy" surface



"Penetrating" Droplets

Based on roughness (Wenzel)

Large hysteresis: "Sticky" surface

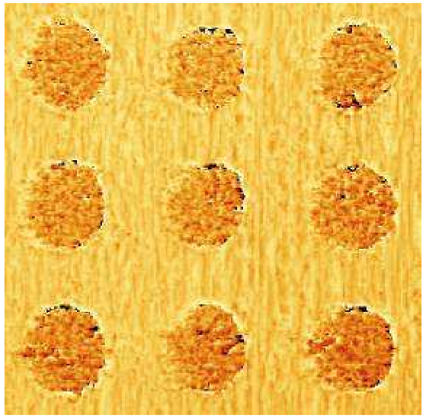


Reference Shirtcliffe *et al*, J. Micromech. Microeng. 14 (2004) 1384-1389.

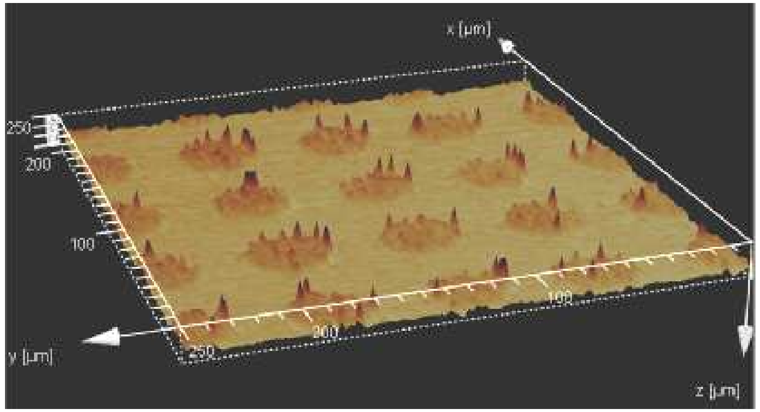
Electrodeposited Surfaces

Diffusion limited aggregation –copper acid bath, fractal roughness

Base Cu electroplated surface

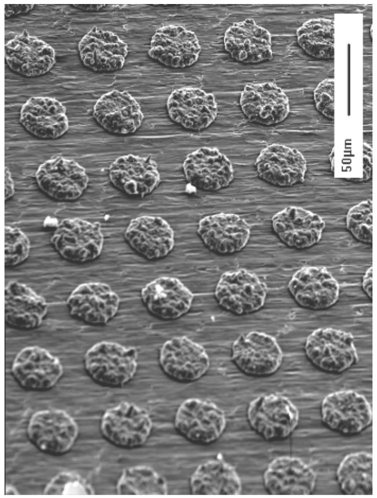


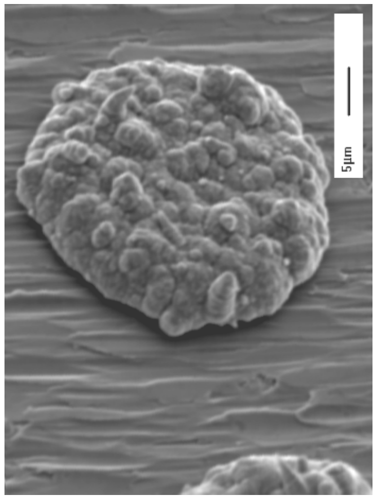
Confocal image of a 30μm textured electroplated Cu

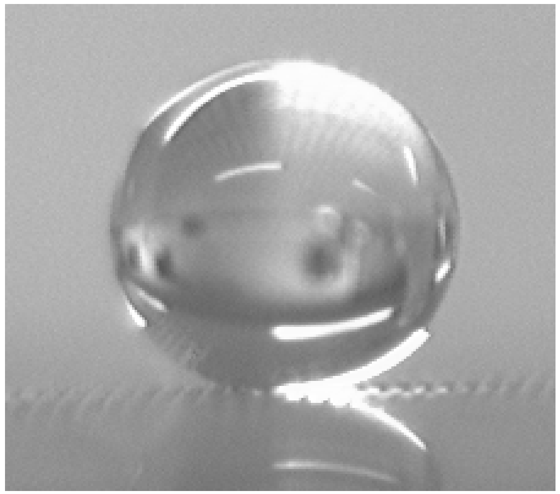


3D view of a electroplated copper sample

“Chocolate Chip Cookies” - Electroplating through a mask







Reference Shirtcliffe *et al*, Adv. Maters. 16 (2004) 1929-1932; Shirtcliffe *et al*, Langmuir 21 (2005) 937-943.

Gradients in Superhydrophobicity

Driving Force

Local Cassie-Baxter Contact Angle

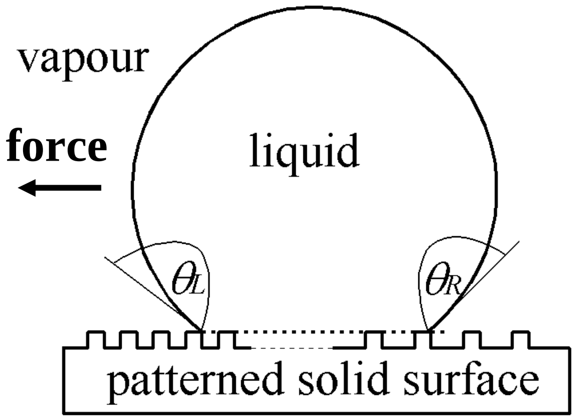
Make contact angle depend on position and surface chemistry $\theta(x, \theta_e^s)$

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

Droplet experiences different contact angles ⇒ driving force



$$Force \propto \gamma_{LV}(\cos\theta_R - \cos\theta_L)$$

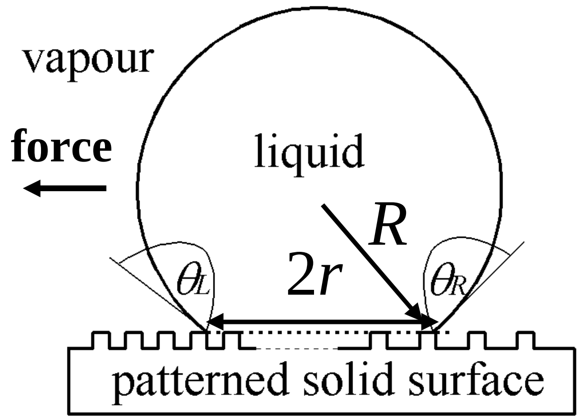
$$\propto \gamma_{LV}(f_R - f_L)(\cos\theta_e^s + 1)$$

Need to overcome contact angle hysteresis

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

Conditions for Motion

Spherical Cap



Assume small contact area:

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

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

$$= 2R\;\gamma_{LV}[2f_{ave}(x)]^{1/2}(1+\cos\theta_e^{\,s})]^{3/2}(\mathrm{d}f/\mathrm{d}x)$$

Defect Based Hysteresis Force

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

Drive Condition

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

More superhydrophobic | Larger droplets

Reference Joanny & de Gennes (1984) (cited by Quéré)

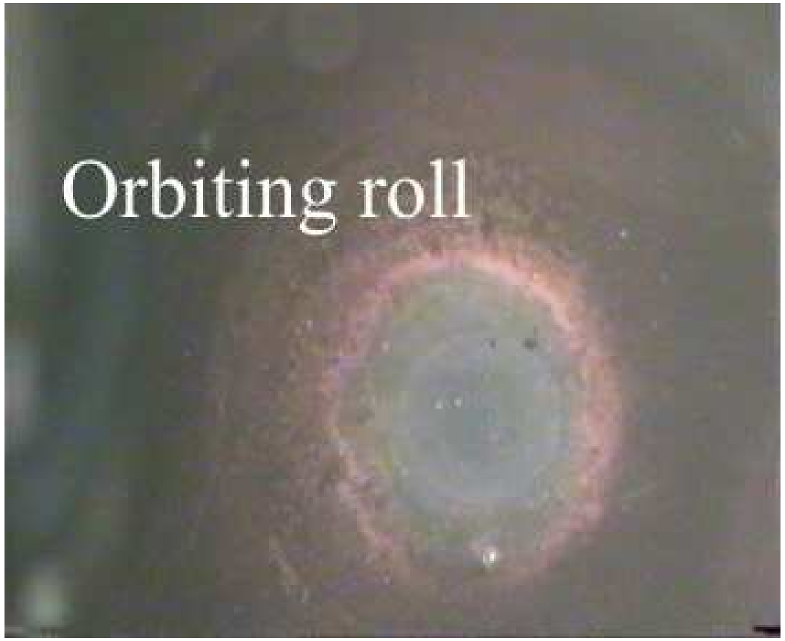
Self-Actuated Motion

Radial Gradient in Contact Angle

Electrodeposited copper – Diffusion limited aggregation

Fractal–like to overcome contact angle hysteresis

Radial gradient $\theta(r)$=110°$\rightarrow$ 160°



Reference McHale *et al*, to be submitted.

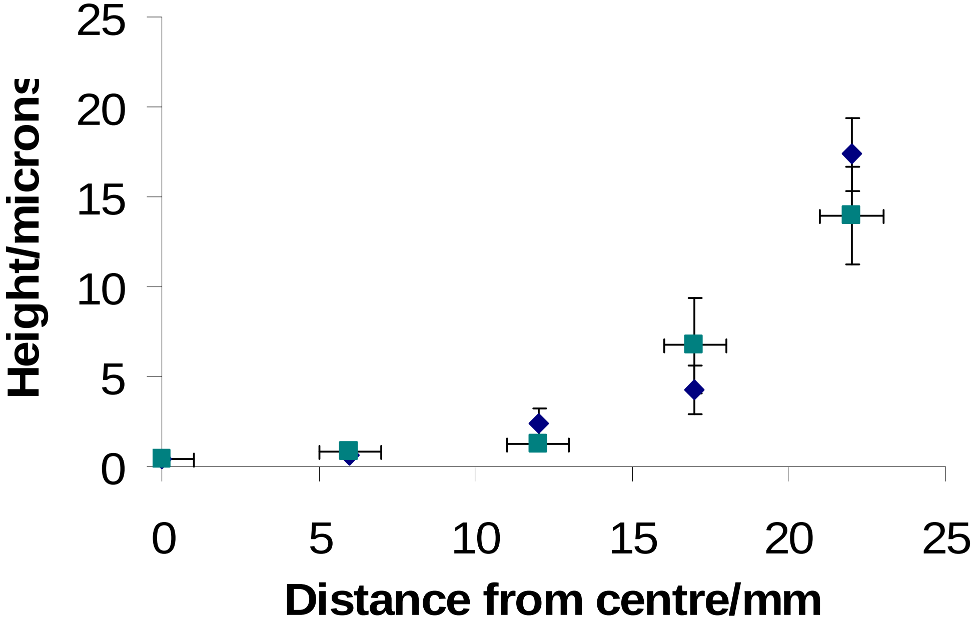
Surface Profile

Mechanism for Motion

Small slope on extremely low hysteresis surface?

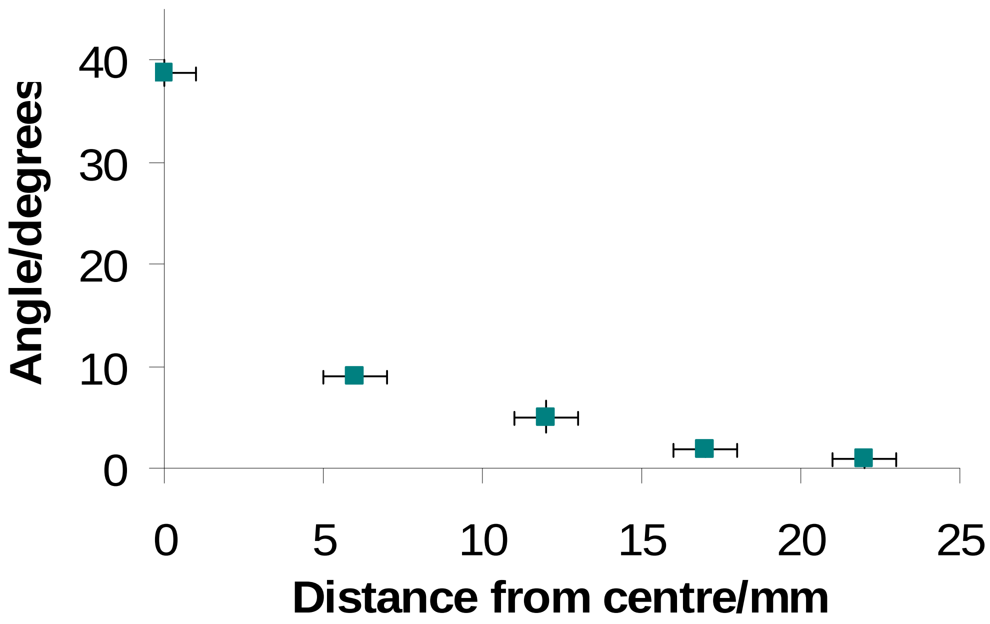
Truly contact angle driven?

Surface Profile



Multiple profiles have been taken along different radial lines

"Hysteresis"



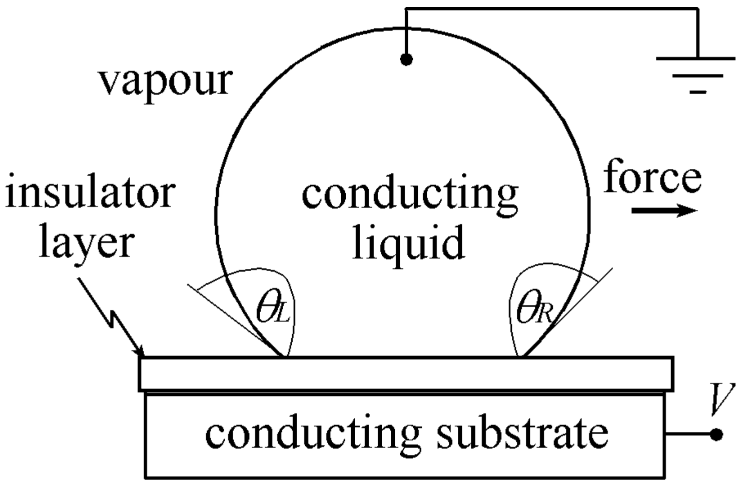
Using radial view and tilt table tangential to radius

Electrowetting on a Superhydrophobic Surface

Electrowetting-on-Dielectric (EWOD)

Electrowetting Principle

- Conducting liquid on electrical insulator on conducting substrate

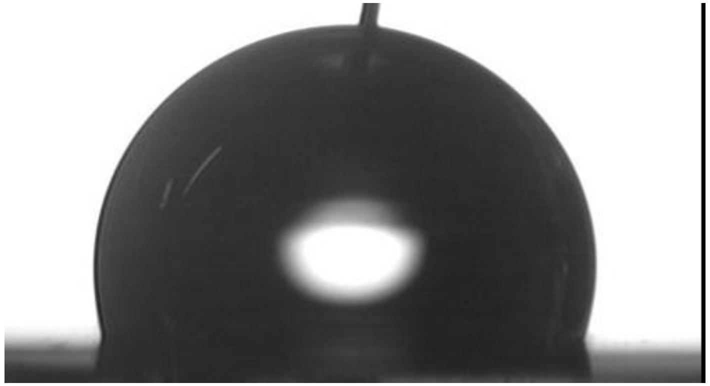


- Applying voltage electrically charges solid-liquid interface (i.e. a Capacitive effect)

- Droplet spreads and contact angle reduces

$$\cos\theta_e(V) = \cos\theta_e(0) + CV^2/2\gamma_{LV}$$

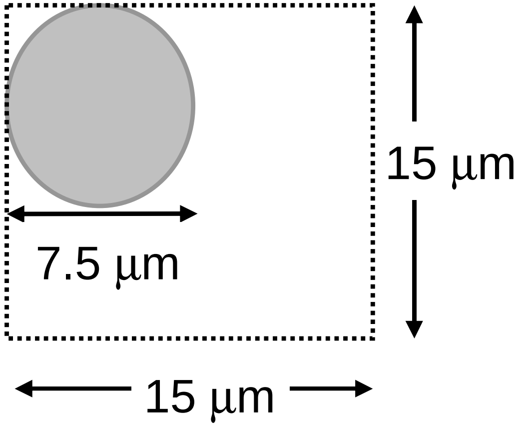
- Difference in angles at edge of droplet reflects an actuating force

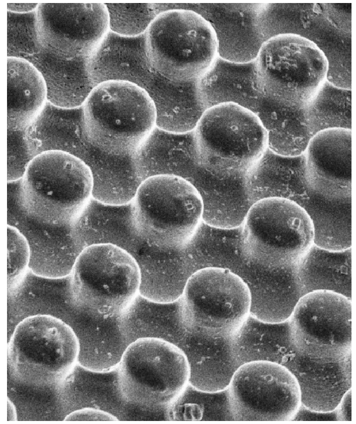


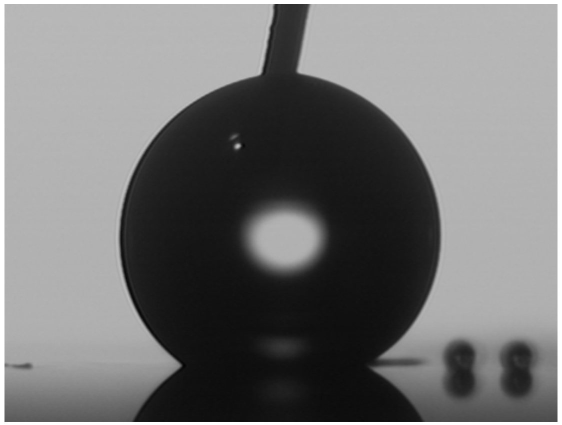
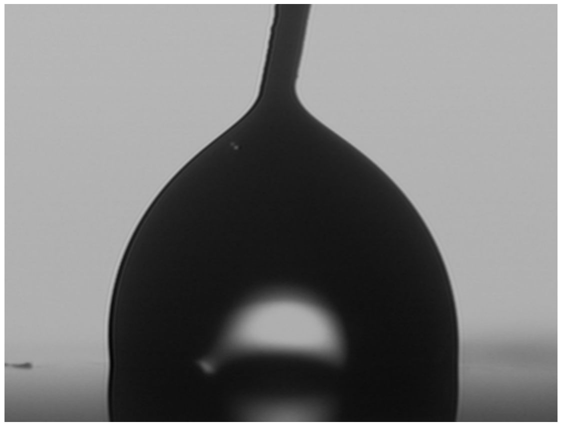
Irreversible Electrowetting on S/H Surface

Lithographic System

- Ti/Au on glass, SU-8 microposts, Teflon AF1600 capped
- Droplets of deionised water with 0.01M KCl and AC or DC





Initial Shape	Applied Voltage	Voltage Removed
		

152° ⟶ 114°

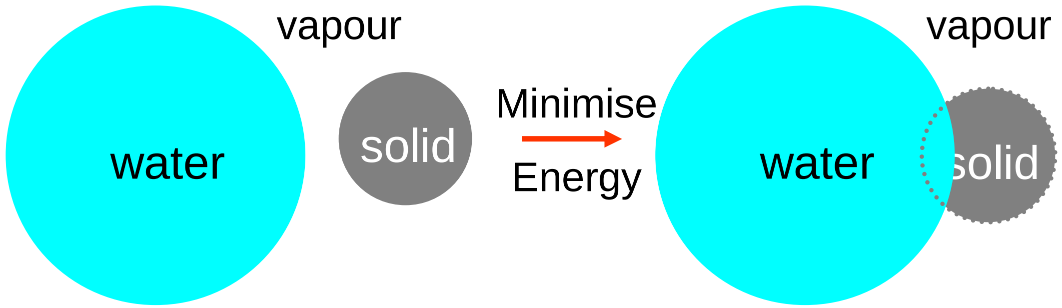
Irreversible and so difficult for actuating motion

Reference   Herbertson *et al*, Sens. Act. A. 130 (2006) 189-193.

Liquid Marbles

Liquid Marbles

- Hydrophobic Grains Adhere to the Water-Air Interface

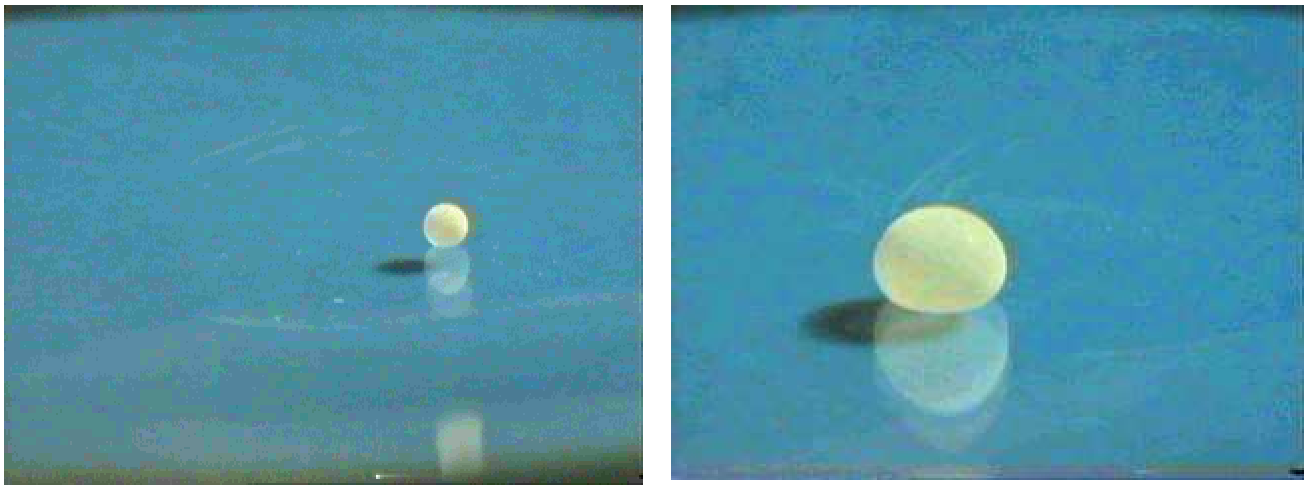


$$\Delta F = -\pi R_g^{\,2} \gamma_{LV} (1 + \cos\theta_e)^2$$

Lycopodium

Lycopodium grains are 15-19 μm, but monolayers can be achieved

Mobility



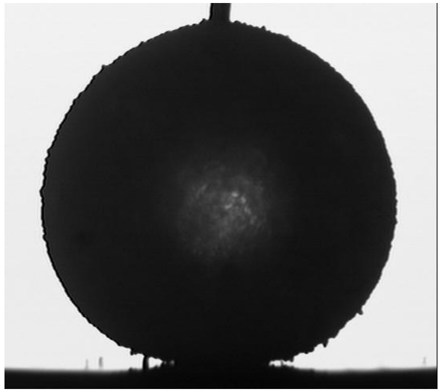
Perfect non-wetting system with zero hysteresis
Gravity flattens shape as volume increases

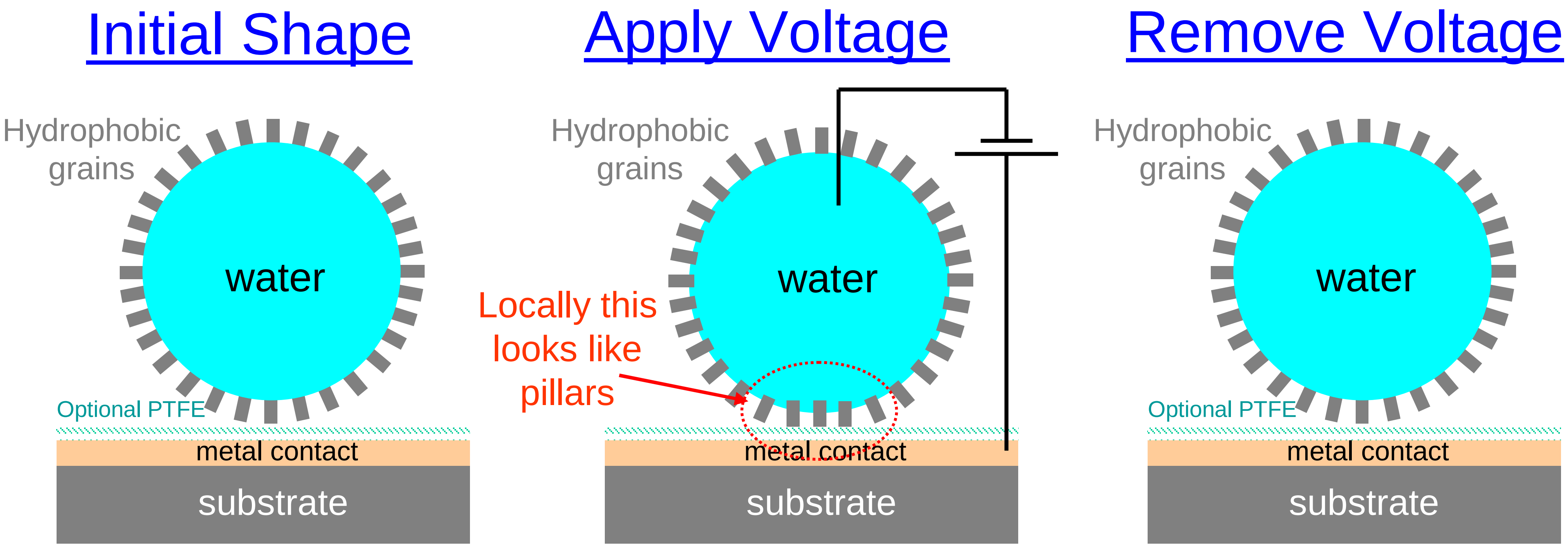
Acknowledgement David Quéré, College de France, Paris.

Active Actuation of Marble Motion

"Electrowetting" of Liquid Marbles

- Reversibility Idea
  - Make the solid "pillars" adhere more to the liquid than to the substrate
  - Provides insulating "pillars" conformal to the liquid shape
  - More hydrophobic grains "stick out" further (i.e. taller pillars)





Reference Newton *et al*, J. Phys. D: Appl. Phys. 40 (2007); McHale *et al*, 20-24; Langmuir 23 (2007) 918-924.

Model for Liquid Marbles

Minimise total energy of a spherical cap

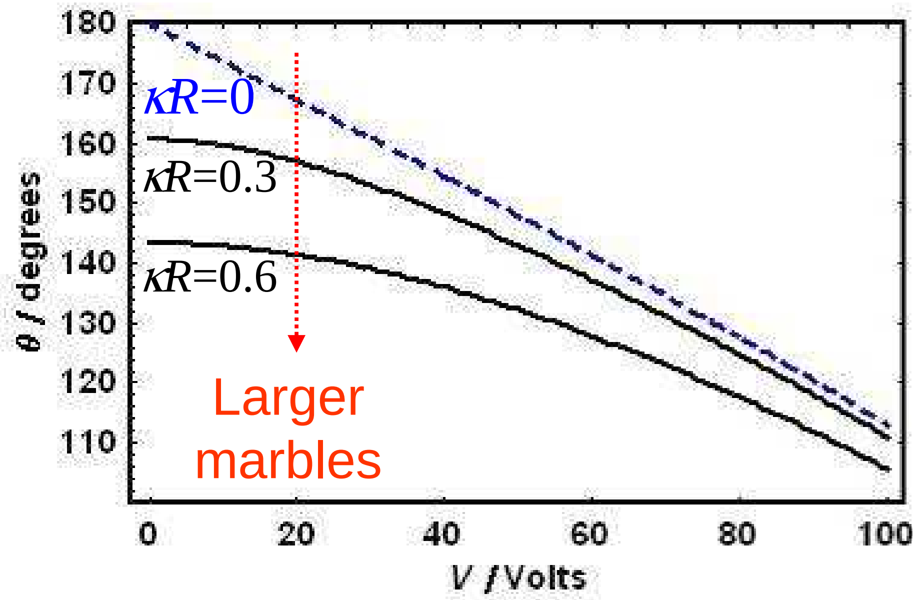
$$\cos\theta = \cos\theta_e + (\kappa h)^2/6 + CV^2/2\gamma_{LV}$$

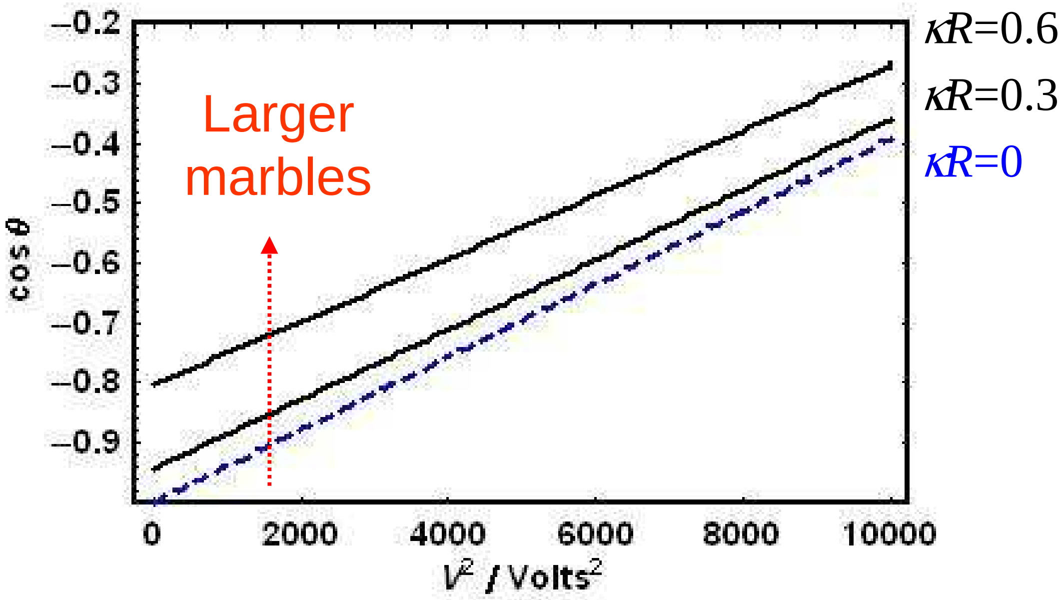
From surface energy
-1 for marble

Gravitational energy gives a drop size factor with $h = h(\theta)$, so non-linear

Capacitive energy from electrowetting

Numerical Results



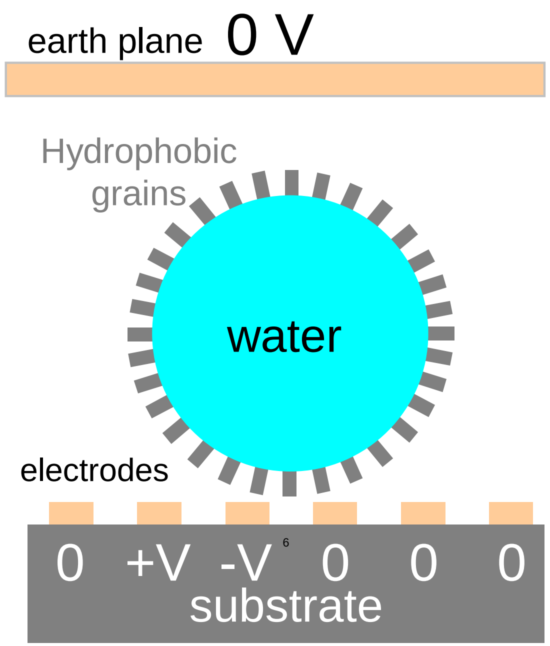


Reference McHale *et al*, Langmuir 23 (2007) 918-924.

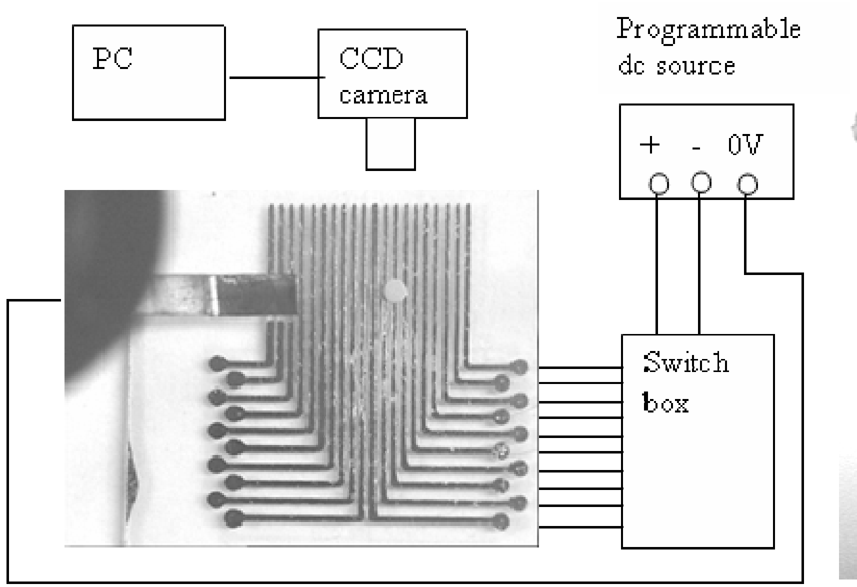
A Hint of Controllable Motion

1. Liquid marble using hydrophobic lycopodium
2. Upper earth plane, planar strip electrodes, pairs switched to ±150 V DC

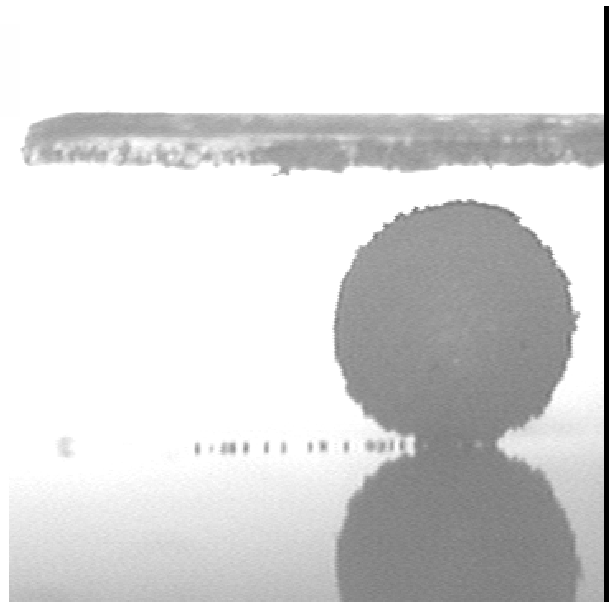
Concept



Method



Results



Reference Newton *et al*, J. Phys. D: Appl. Phys. 40 (2007) 20-24.

Summary

1. Passively Actuated Motion of Droplets

   Appears possible via gradients in θ_{CB}

   Outstanding questions about droplet threshold sizes

2. Voltage Actuated Motion

   Problems remain on superhydrophobic surfaces

   Can be achieved with liquid marbles

The End

Acknowledgements

EPSRC GR/R02184/01 and GR/S34168/01 –Dstl via

EPSRC/MOD JGS

EU COST Action D19 & P21

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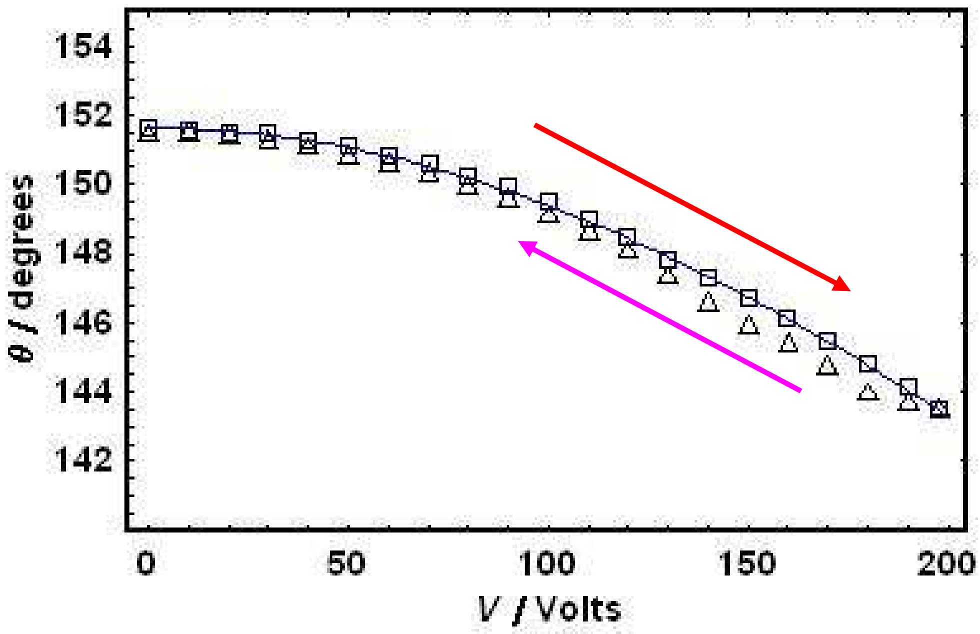
EPSRC Engineering and Physical Sciences Research Council

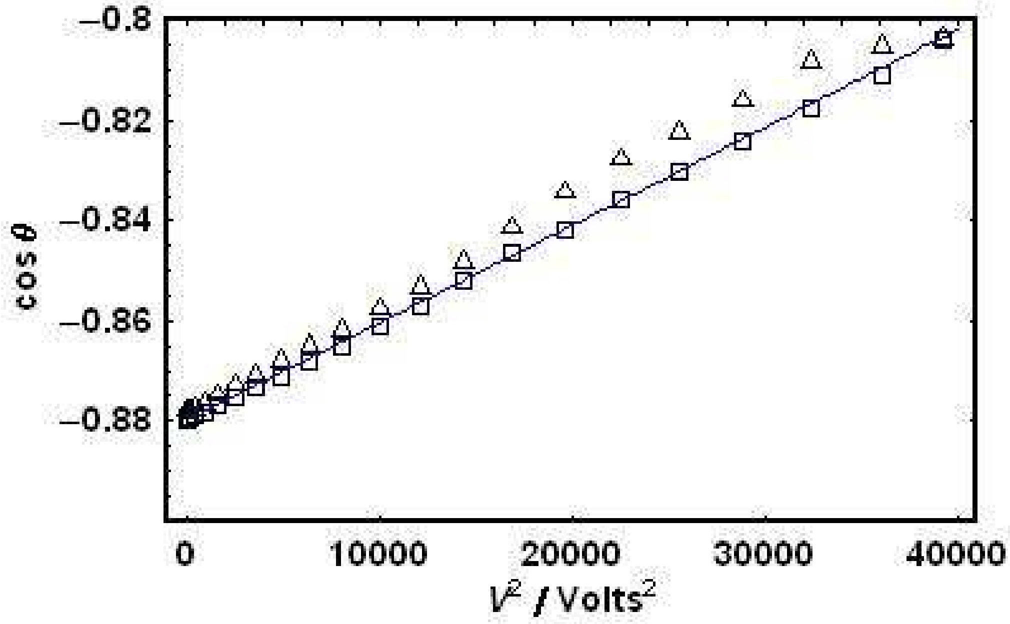
COST

5. Results using Hydrophobic Silica

Contact Angle



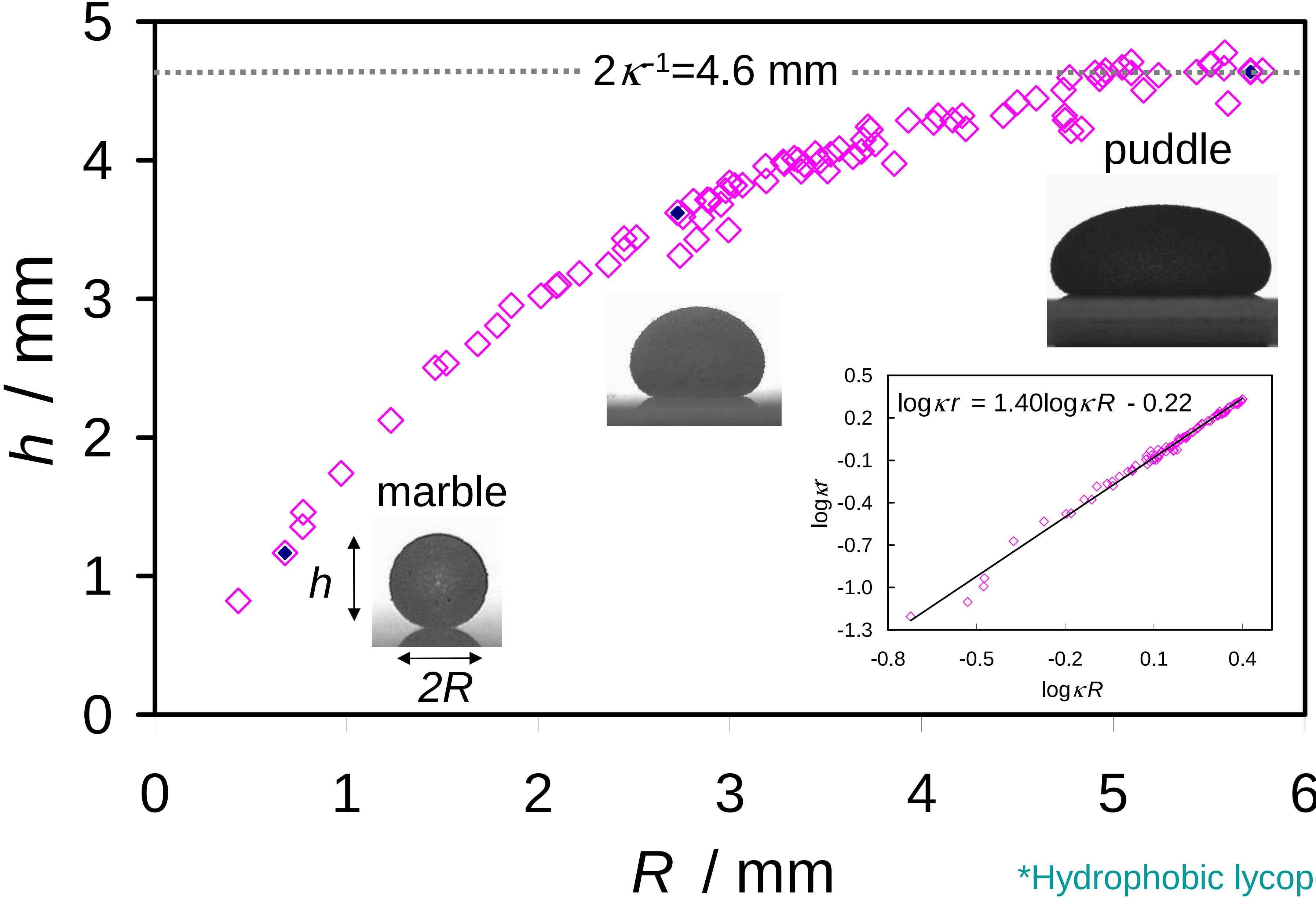
Fitting



1. *No threshold* voltage
2. Virtually *no* contact angle *hysteresis*
3. Experiments show a limited range (155° to 130°)
4. Fit uses κR=0.45

Reference McHale *et al*, Langmuir 23 (2007) 918-924.

Perfect Non-Wetting Marbles*



*Hydrophobic lycopodium

Electroplated Copper Surfaces

- Copper acid bath

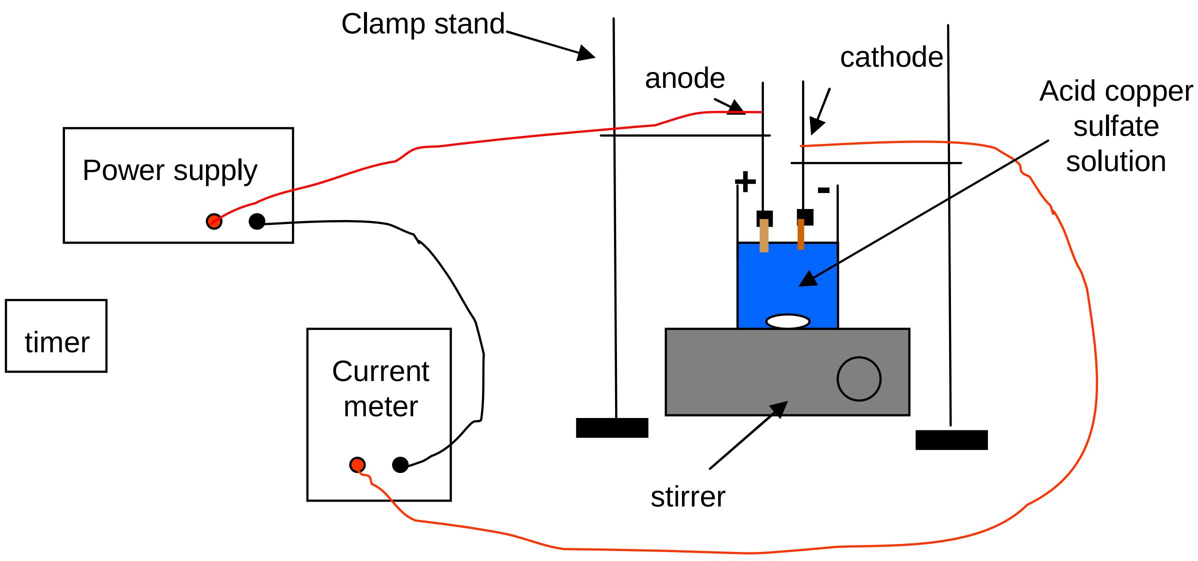
  Copper sulphate ($CuSO_4$) and sulphuric acid (H_2SO_4)

Current density

Slightly rough to highly rough (Fractal)

Masking

Mask and grow pillars in Cu on Cu



Setup for the copper plating