

# Electrowetting of Liquid Marbles

Glen McHale, Mike Newton,  
Dale Herbertson, Neil Shirtcliffe, Steve Elliott

School of Biomedical & Natural Sciences  
Nottingham Trent University

Email: [glen.mchale@ntu.ac.uk](mailto:glen.mchale@ntu.ac.uk)

# Overview

1. Super-Hydrophobicity
2. Electrowetting of Droplets
3. Electrowetting on S/H Surfaces
4. Liquid Marbles (and Puddles)
5. Electrowetting of Liquid Marbles

# Super-Hydrophobicity

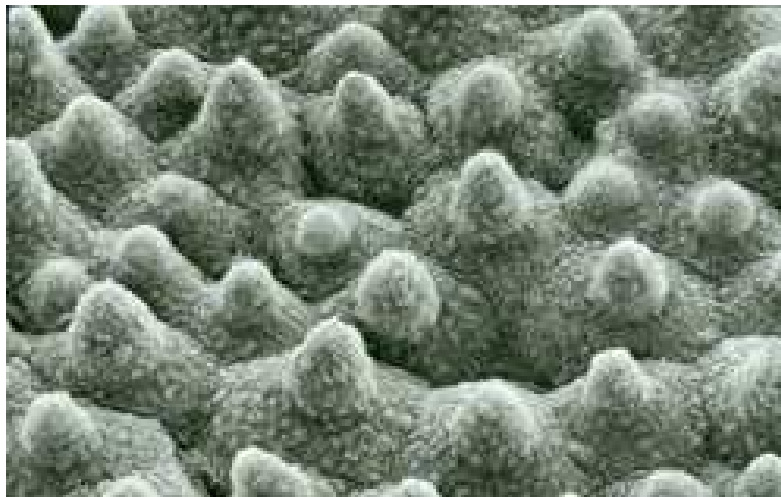
# The Sacred Lotus Leaf

## Plants

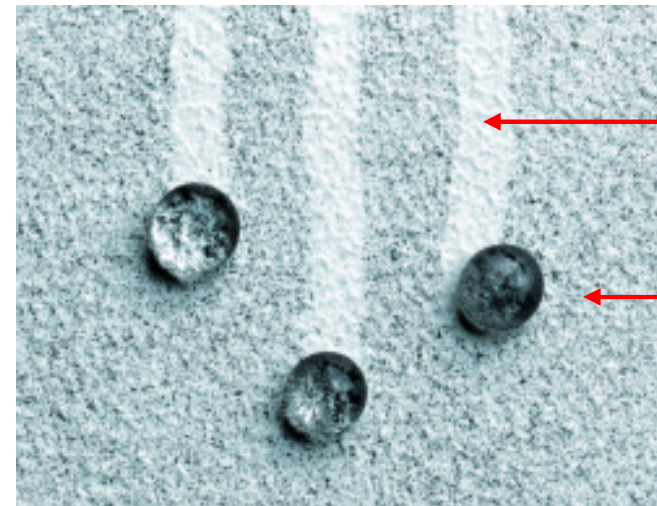
- Many leaves are super-water repellent
- The Lotus plant is known for its purity
- Super-hydrophobic leaves are self-cleaning under the action of rain



## SEM of a Lotus Leaf



## Self-Cleaning



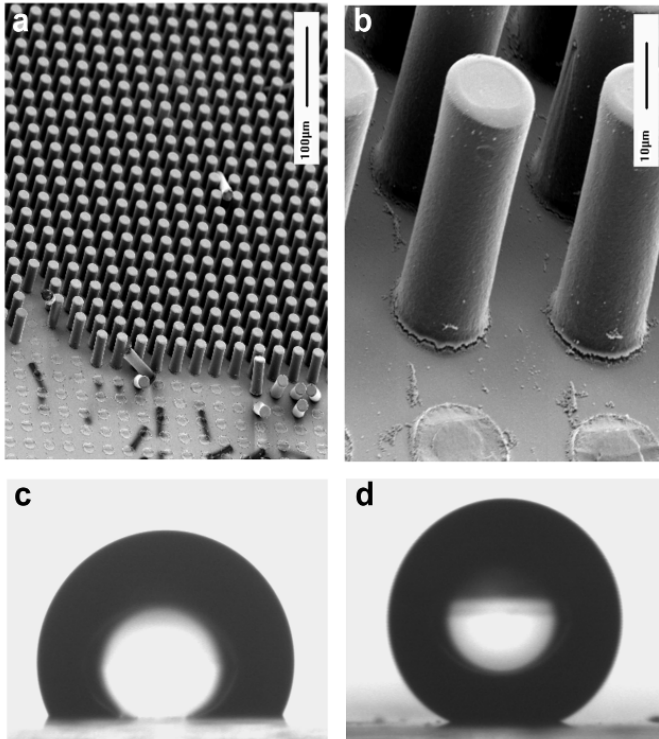
Dust cleaned  
away

Dust coated  
droplet

A “proto-marble”

# Surface Structure

## Effect on Water

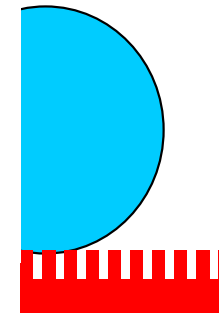


- a), b) Pillars  $D=15 \mu\text{m}$ ,  $L = 2D$   
c) Flat and hydrophobic  
d) Tall and hydrophobic

## “Skating” Droplets

Composite air-solid surface

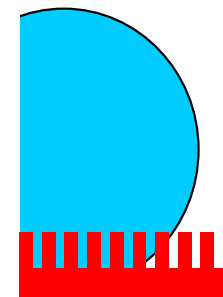
Low hysteresis: “Slippy” surface



## “Penetrating” Droplets

Based on roughness

Large hysteresis: “Sticky” surface



# Electrowetting

# Electrowetting on Dielectric (EWOD)

- **Electrowetting Principle**

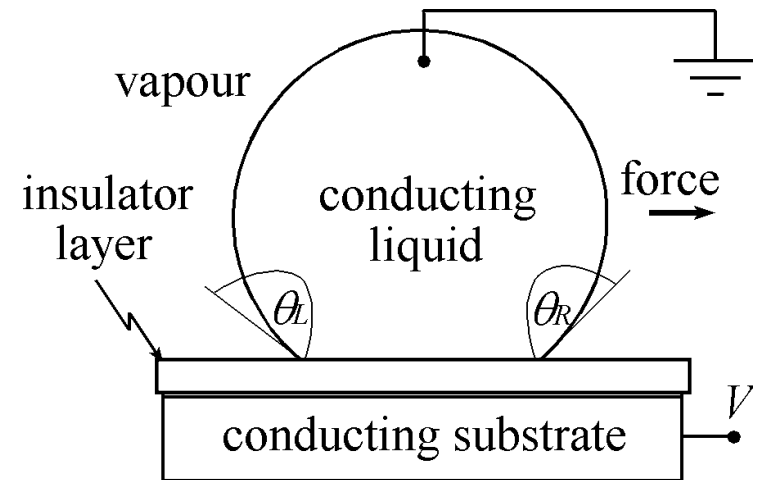
- Conducting liquid on electrical insulator on conducting substrate

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

- Droplet spreads and contact angle reduces

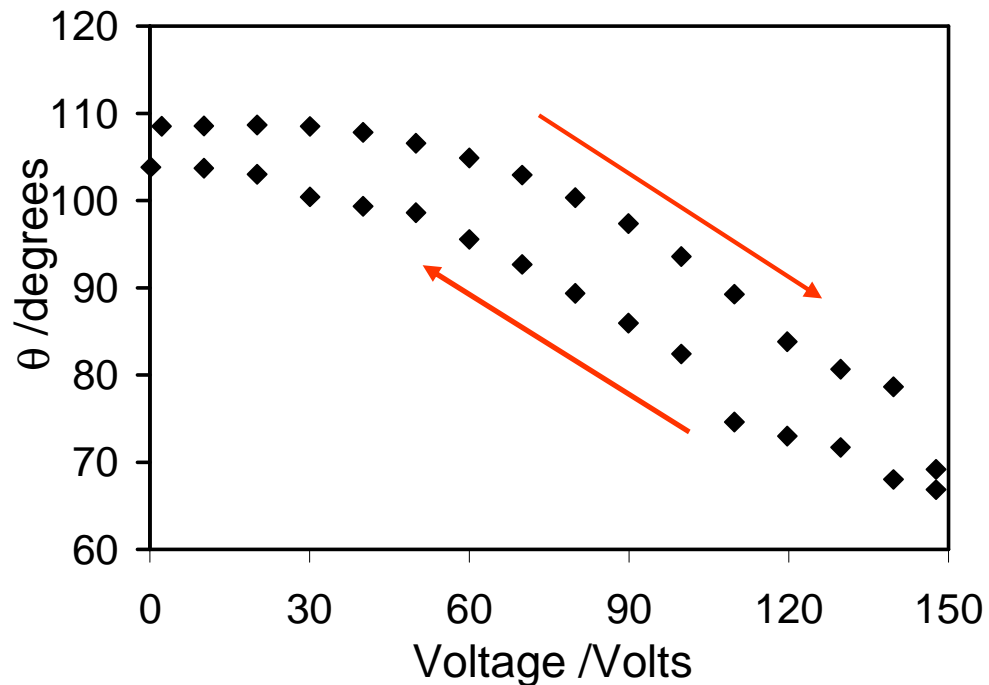
$$\cos \theta_e(V) = \cos \theta_e(0) + CV^2/2\gamma_{LV}$$

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

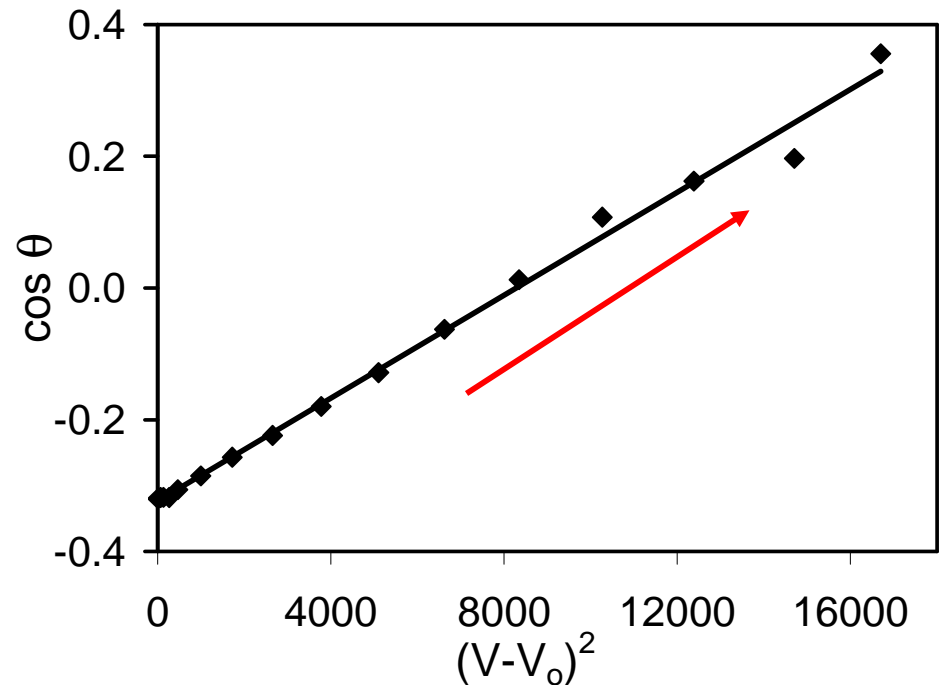


# Results on Flat Hydrophobic SU-8

## Contact Angle



## Fitting



1. Threshold voltage of around 30 V
2. Contact angle hysteresis of around 5°
3. Offset voltage in fit ( $\sim 18.4$  V) represents charging



# Electrowetting on S/H Surfaces

# Super-hydrophobicity & EWOD

- Idea

- Use S-H to gain high initial contact angle  $\theta \uparrow$
- Use electrowetting to tune over full angular range  $\theta \downarrow$

- Thin Insulator,  $d$

- Capacitive energy  $\propto V^2/d$
- Thin insulator for lower voltages

Contradiction 1

But Super-H via patterning insulator → high aspect ratio

- Electrowetting

- Applying voltage causes electrocapillary pressure into surface texture (“Penetrating”)

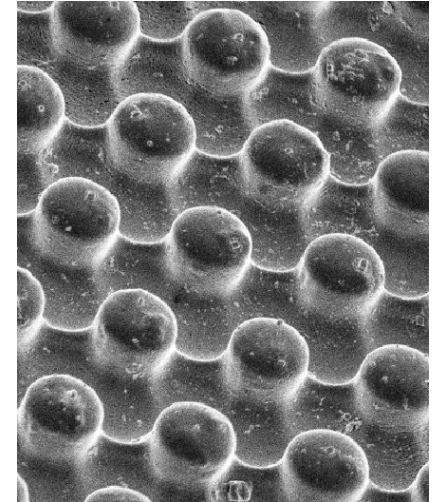
Contradiction 2

But low hysteresis requires “Skating”

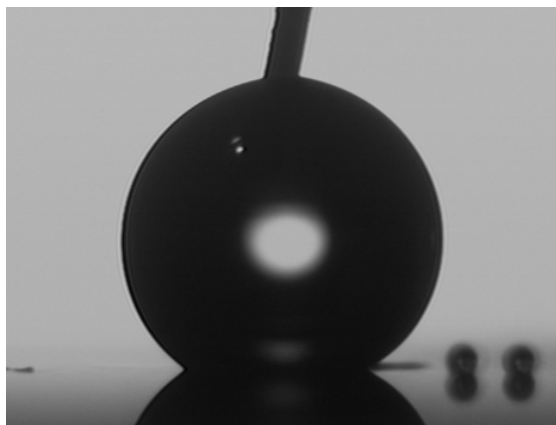
# Irreversible Electrowetting

- **Lithographic System**

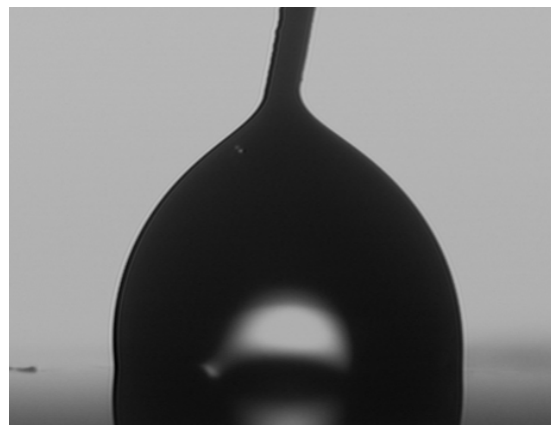
- Ti/Au on glass, SU-8 Pillars 7  $\mu\text{m}$  diameter, 15  $\mu\text{m}$  centre-centre, height 6.5  $\mu\text{m}$  (roughness  $r \approx 1.64$ )
- Spin coated Teflon AF1600 (not perfect,  $r_{\text{estimate}} \approx 1.87$ )
- Droplets of deionised water with 0.01M KCl, DC voltage by steps up to 130 V



Initial Shape



Applied Voltage



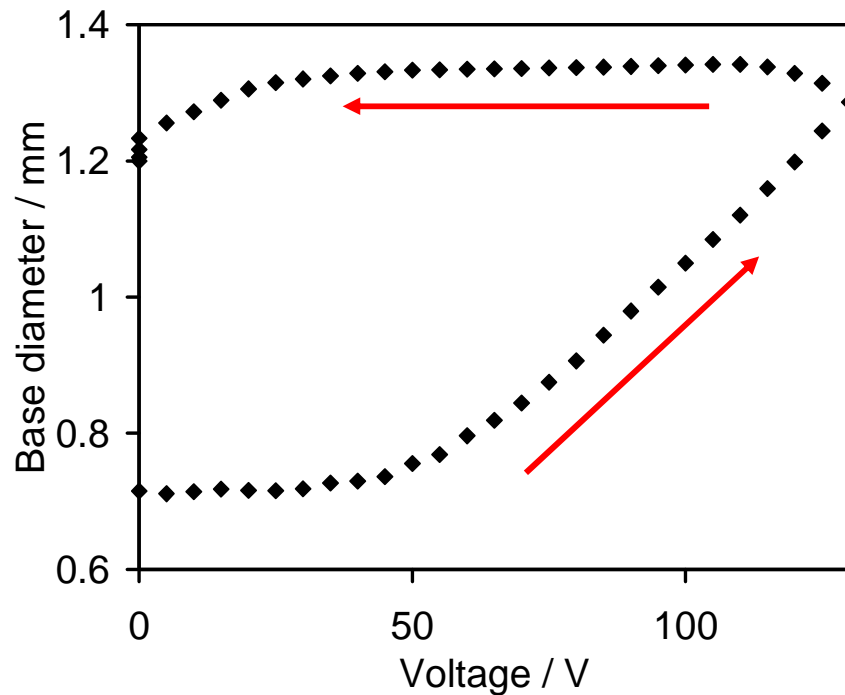
Voltage Removed



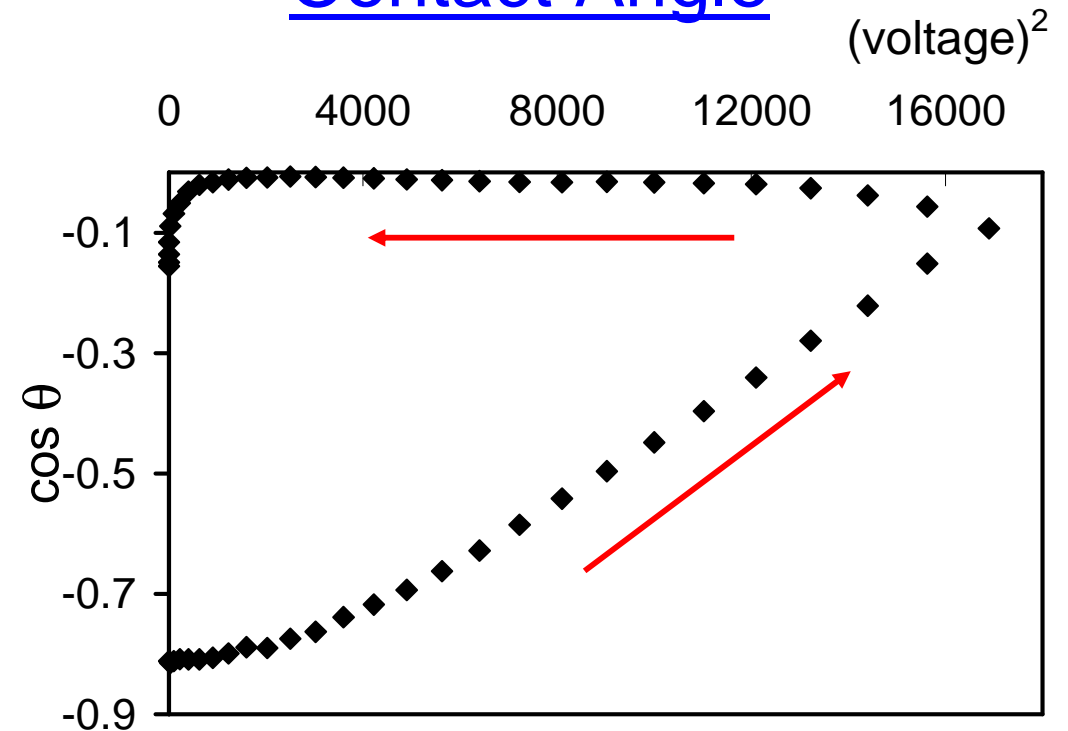
152° ——— irreversible ———> 114°

# Results on SU-8 Pillars

## Base Diameter



## Contact Angle



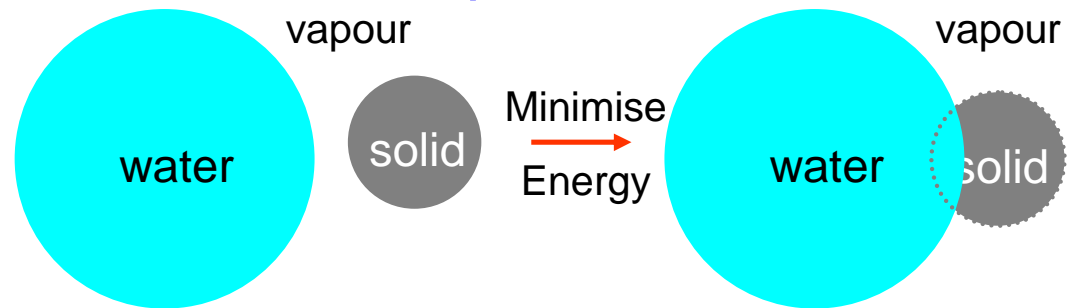
1. Threshold voltage ( $\sim 45$  V) before droplet spreads
2. Irreversible on removal of voltage

# Principles of Liquid Marbles

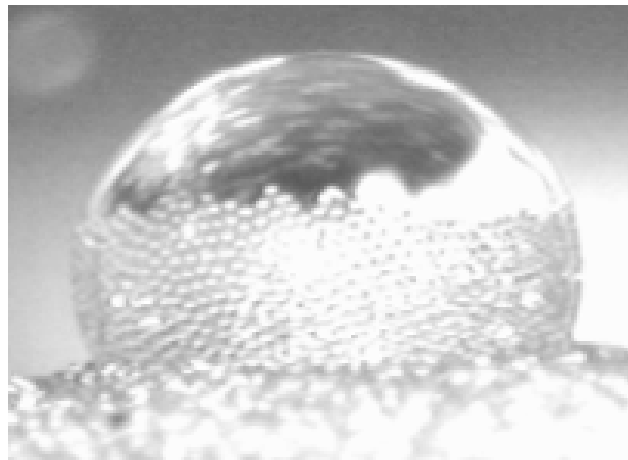
# Liquid Marbles

- Hydrophobic Grains Adhere to the Solid-Liquid Interface

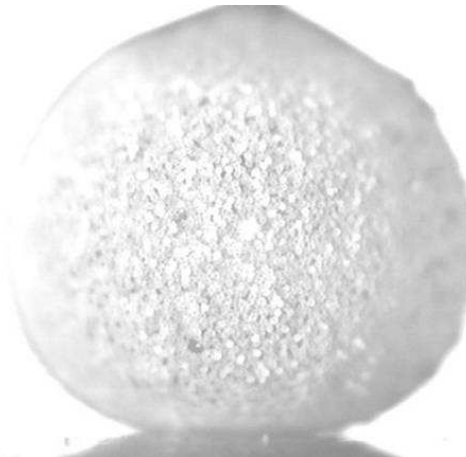
Water droplets can self-coat to create perfect marbles  
Ideal “droplet” (180° contact angle)  
which rolls around on a solid surface



## Large Silica

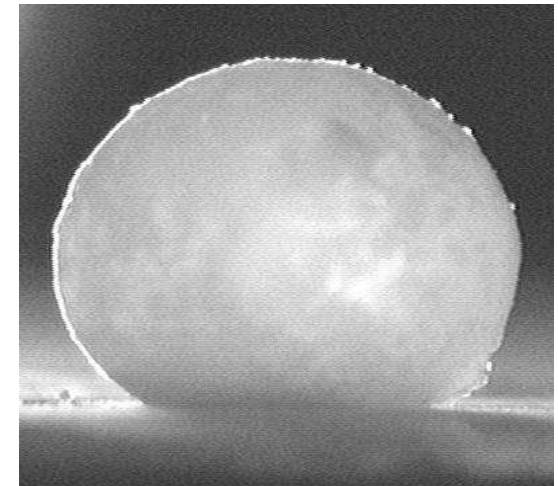


## Lycopodium



Lycopodium grains are 15-19  $\mu\text{m}$ ,  
but monolayers can be achieved

## Silica Powder

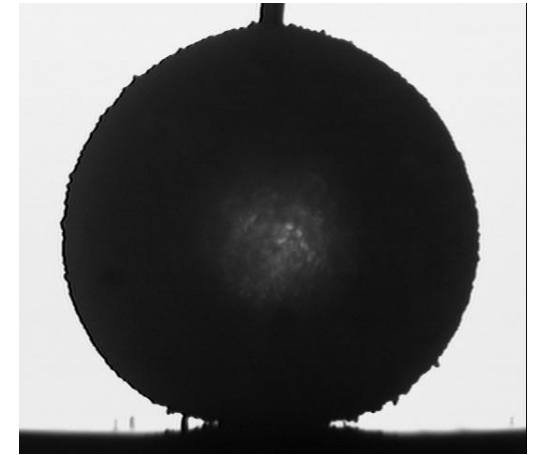


Silica grains are sub- $\mu\text{m}$ ,  
but layer is thick

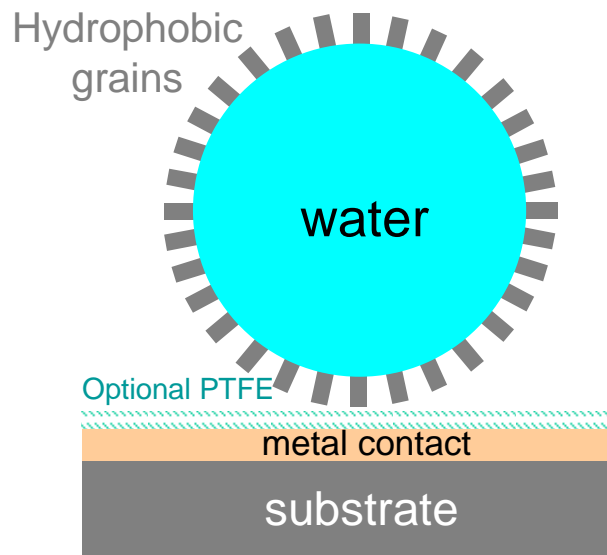
# Electrowetting of Liquid Marbles

- **Reversibility Idea**

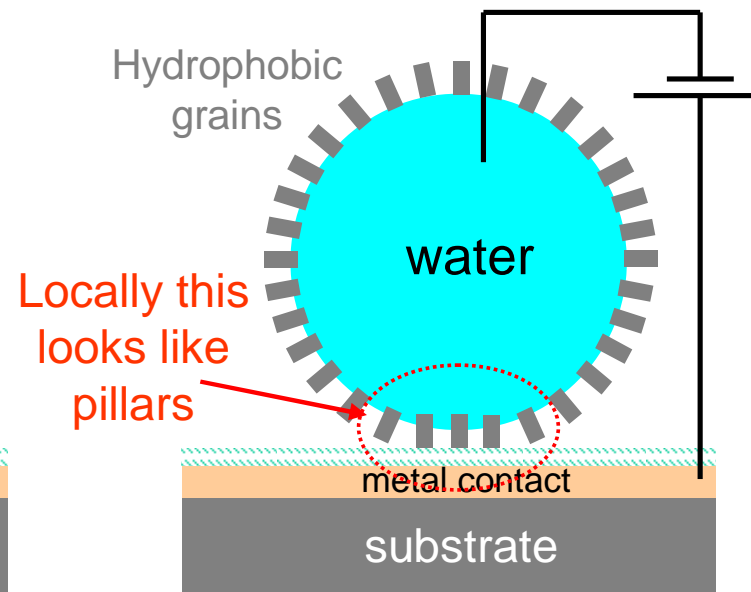
- Make the solid “pillars” adhere more to the liquid than to the substrate
- Provides insulating “pillars” **conformal** to the liquid shape
- More hydrophobic grains “stick out” further (i.e. taller pillars)
- Spin coated Teflon AF1600 on substrate to stop complete breakthrough if granular coating is breached



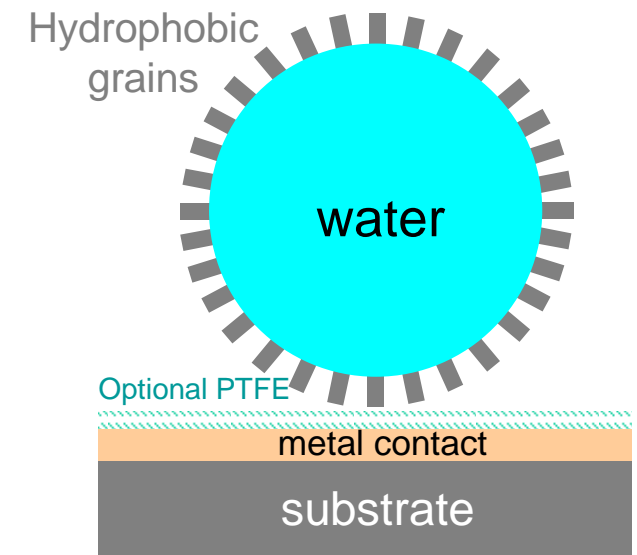
## Initial Shape



## Apply Voltage



## Remove Voltage



# Theory of Liquid Marbles

Minimise total energy of a spherical cap

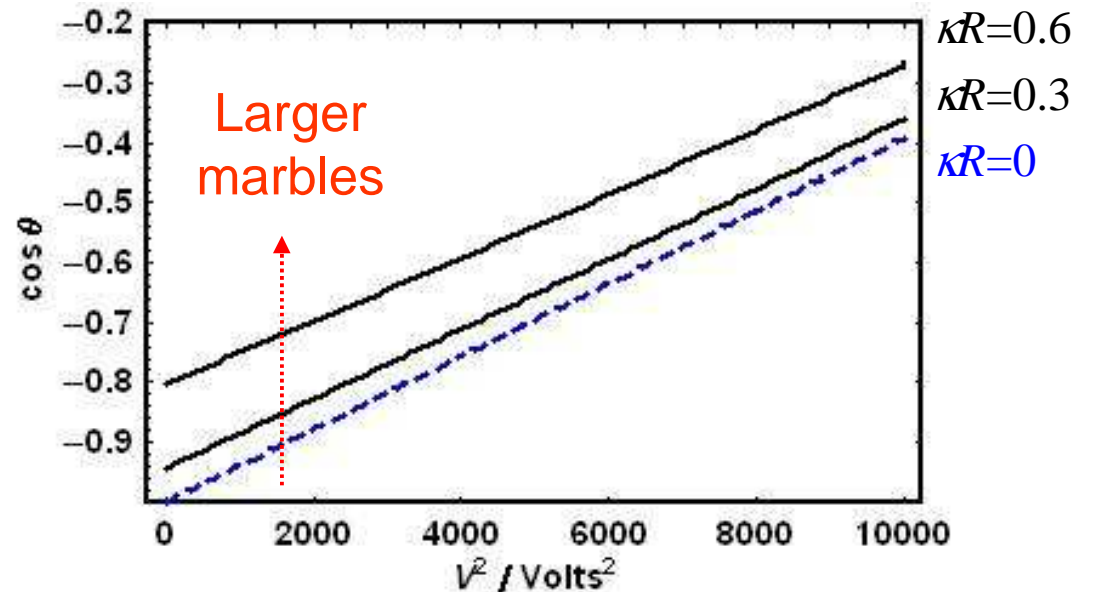
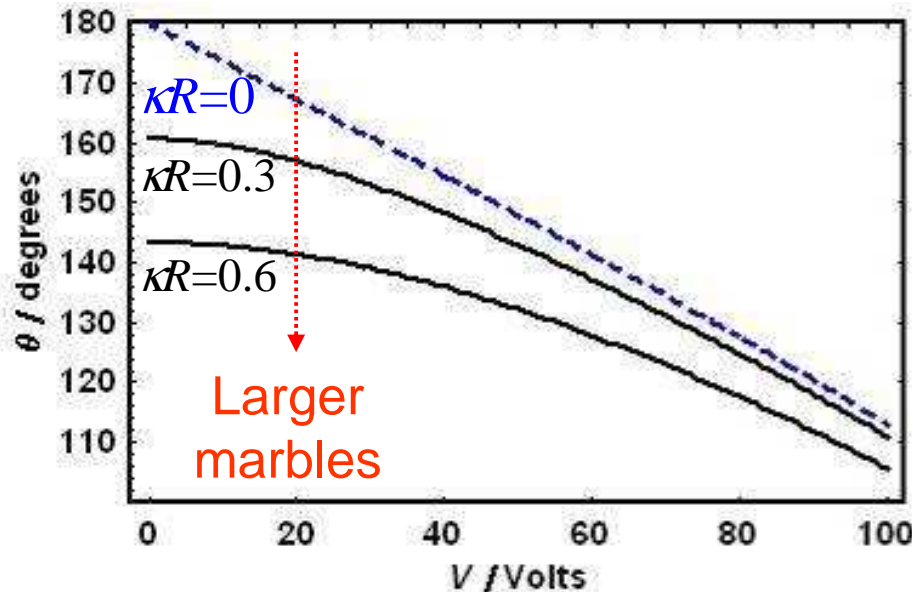
$$\cos \theta = \cos \theta_e + (\kappa h)^2/6 + CV^2/2\gamma_{LV}$$

From surface energy  
-1 for marble

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

Electrowetting from  
capacitive energy

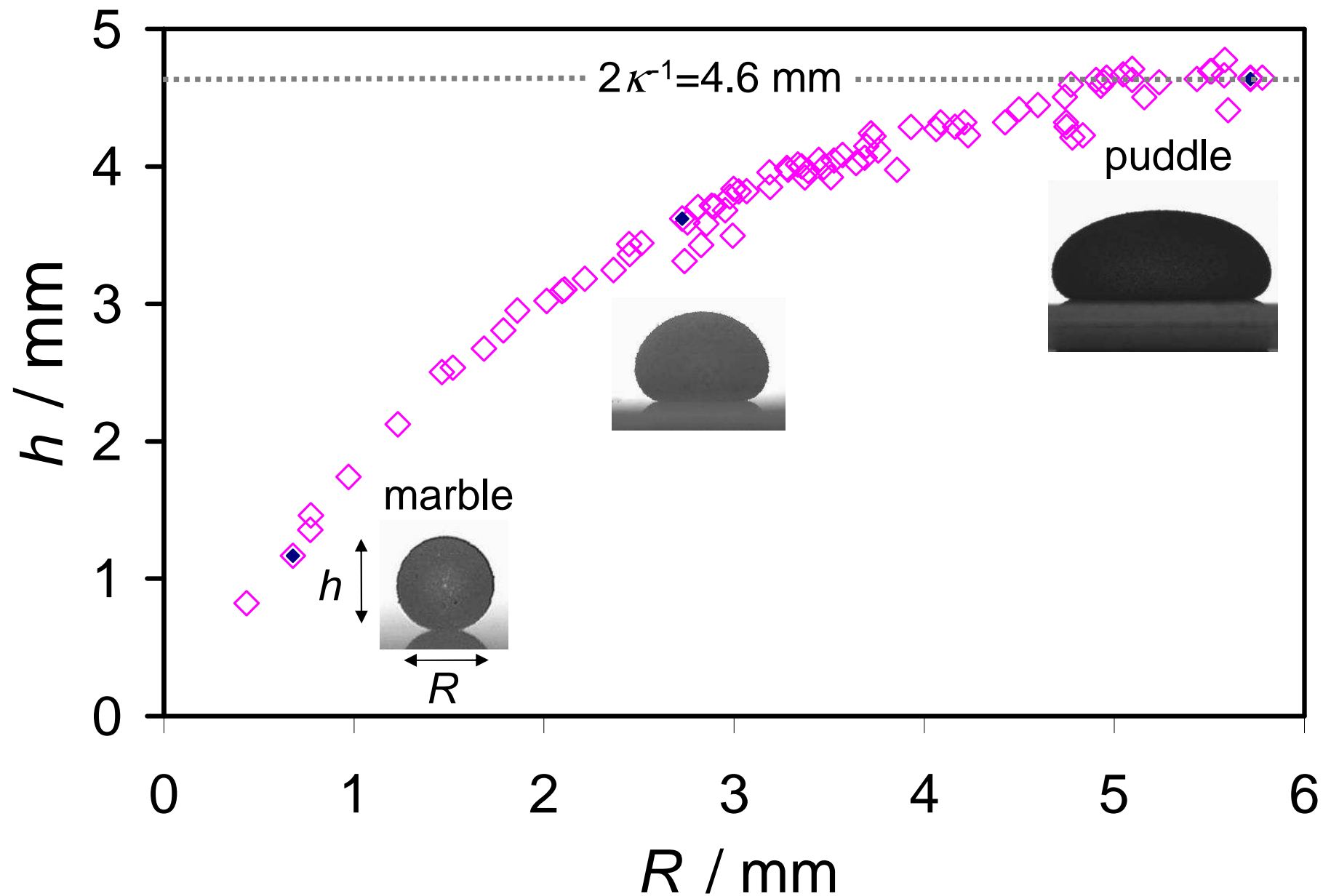
## Numerical Results





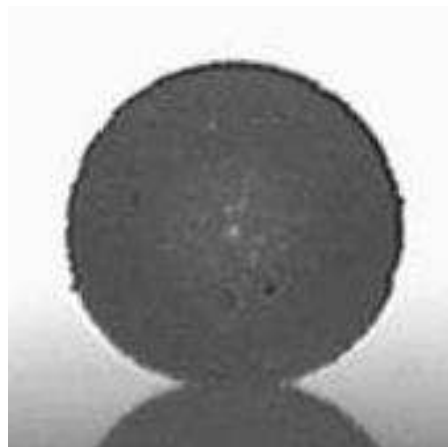
# Experiments on Liquid Marbles

# Size Data (Lycopodium)

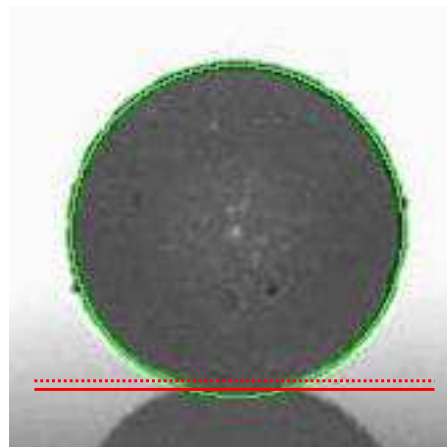


# Accuracy of Measurements

Marble



Circular Fit



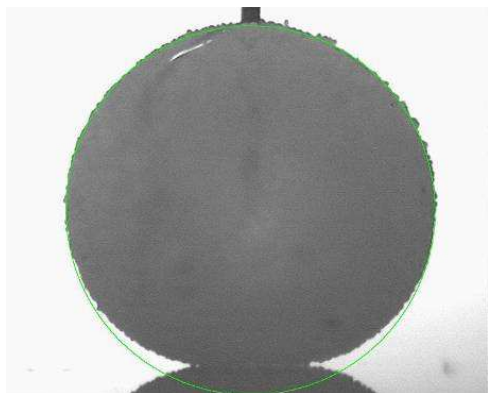
Comments

Almost perfect circle  $\theta \rightarrow 180^\circ$   
Spherical radius,  $R$ , is OK

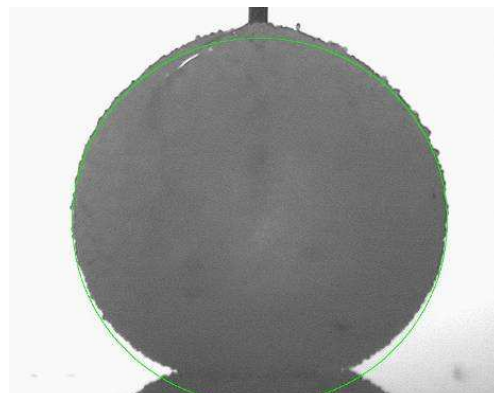
*Baseline difficult due to grains in "skin"*  
Contact radius  $r$ , is sensitive to baseline  
Contact angle  $\theta$ , is sensitive to baseline

With Needle/Contact Wire

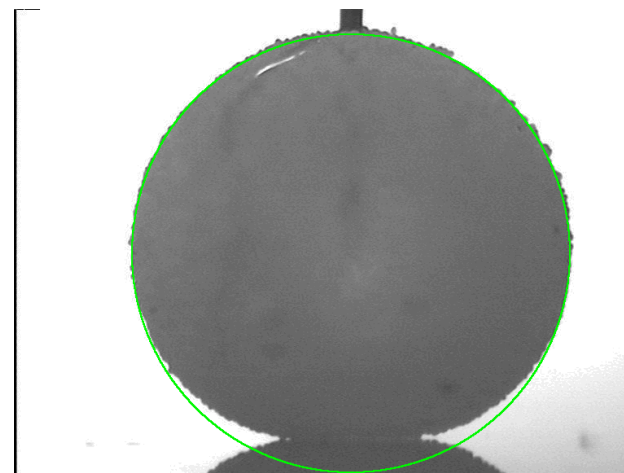
No Voltage



With Voltage

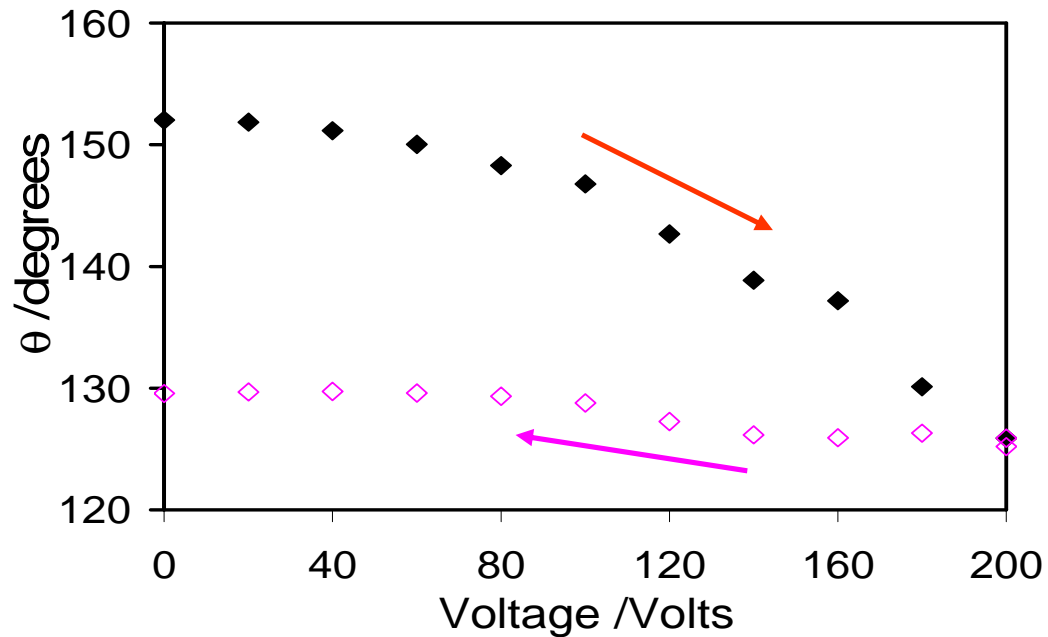


Reversibility – Low V Cycle

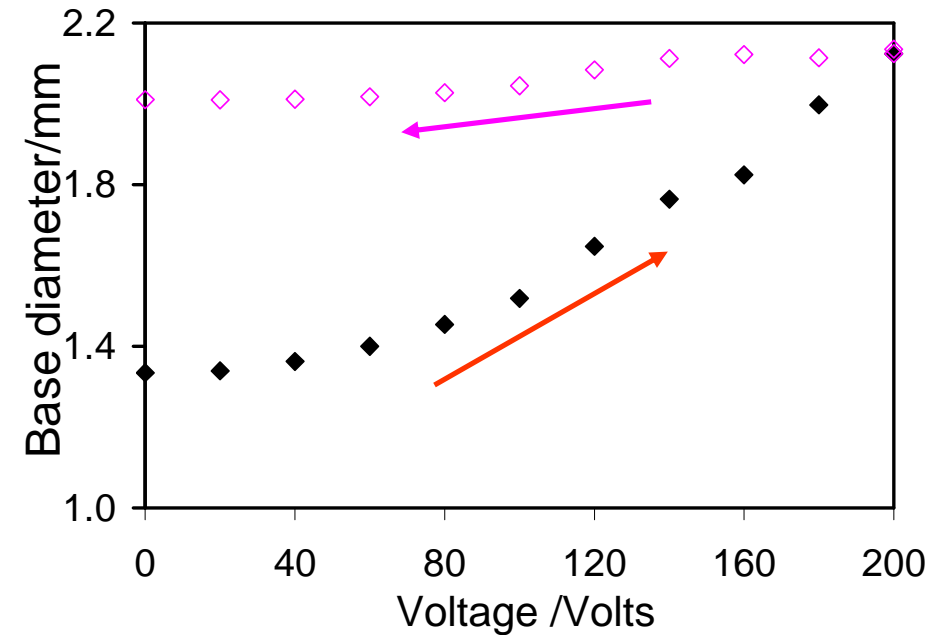


# Results using Hydrophobic Lycopodium

## Contact Angle



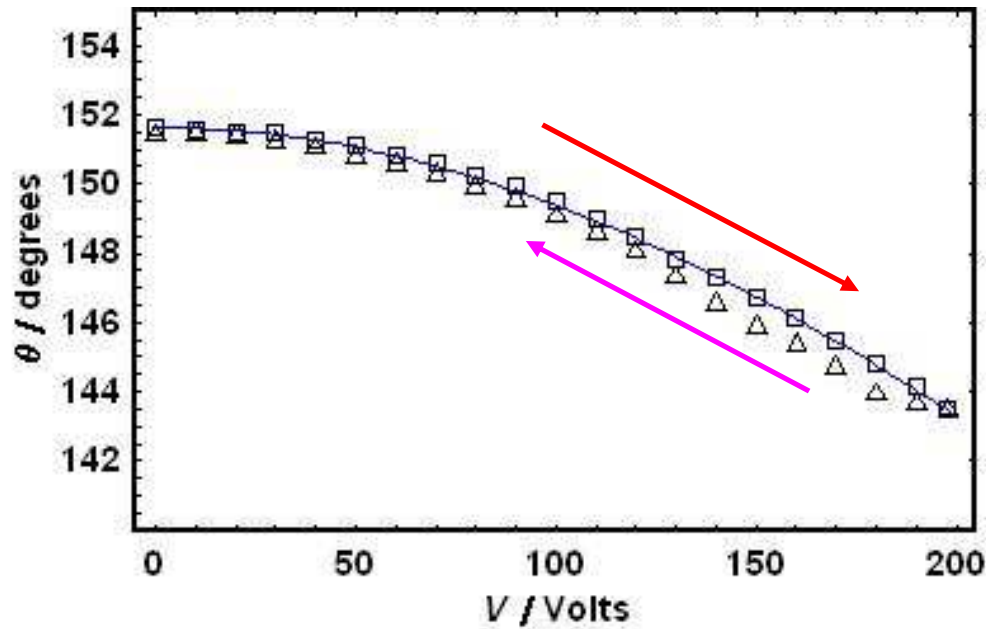
## Base Diameter



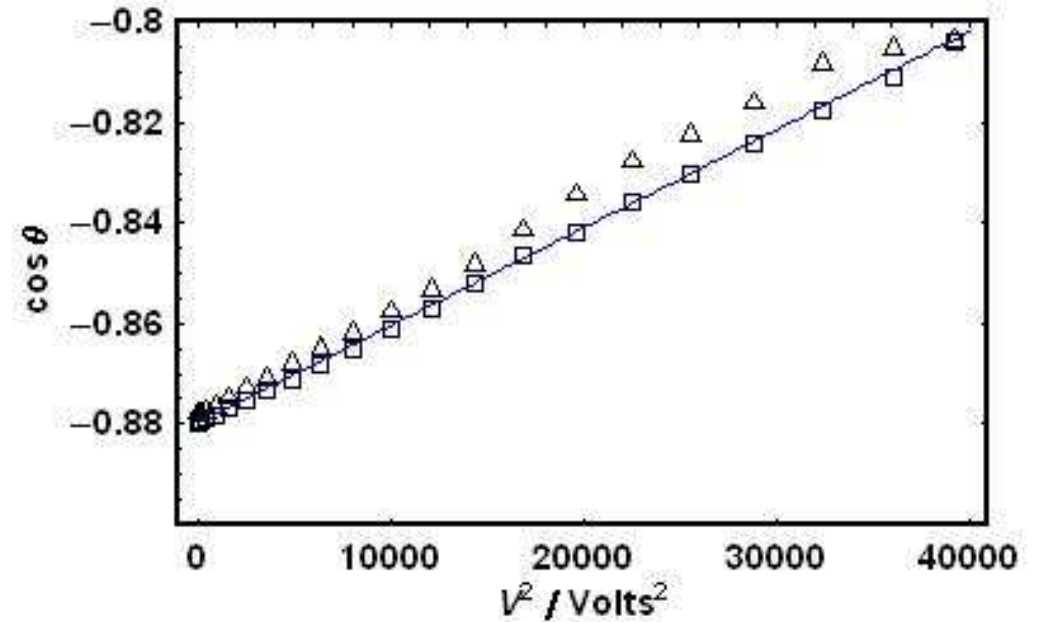
1. No significant threshold voltage
2. Reversibility is compromised at highest voltages due to contact area becoming pinned – “*liquid breakthrough*”

# Results using Hydrophobic Silica

## Contact Angle



## Fitting



1. *No threshold* voltage
2. Virtually *no* contact angle *hysteresis*
3. Current experiments show a limited range (155° to 130°)
4. Fit uses  $\kappa R=0.45$

# Future Work

## 1. Structure of Liquid Marbles

Greater stability

Reduction of charging

Size ranges for marbles/puddles

## 2. Droplet Motion

Non contact mode of generating contact angle changes

Droplet actuation – Different left v right side contact angles

Magnetic powder

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The End

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# Acknowledgements

## External Collaborators

Prof. Mike Thompson (Toronto), Prof. Yildirim Erbil (Istanbul)  
Dr Stefan Doerr (Swansea), Dr Andrew Clarke (Kodak)

## Funding Bodies

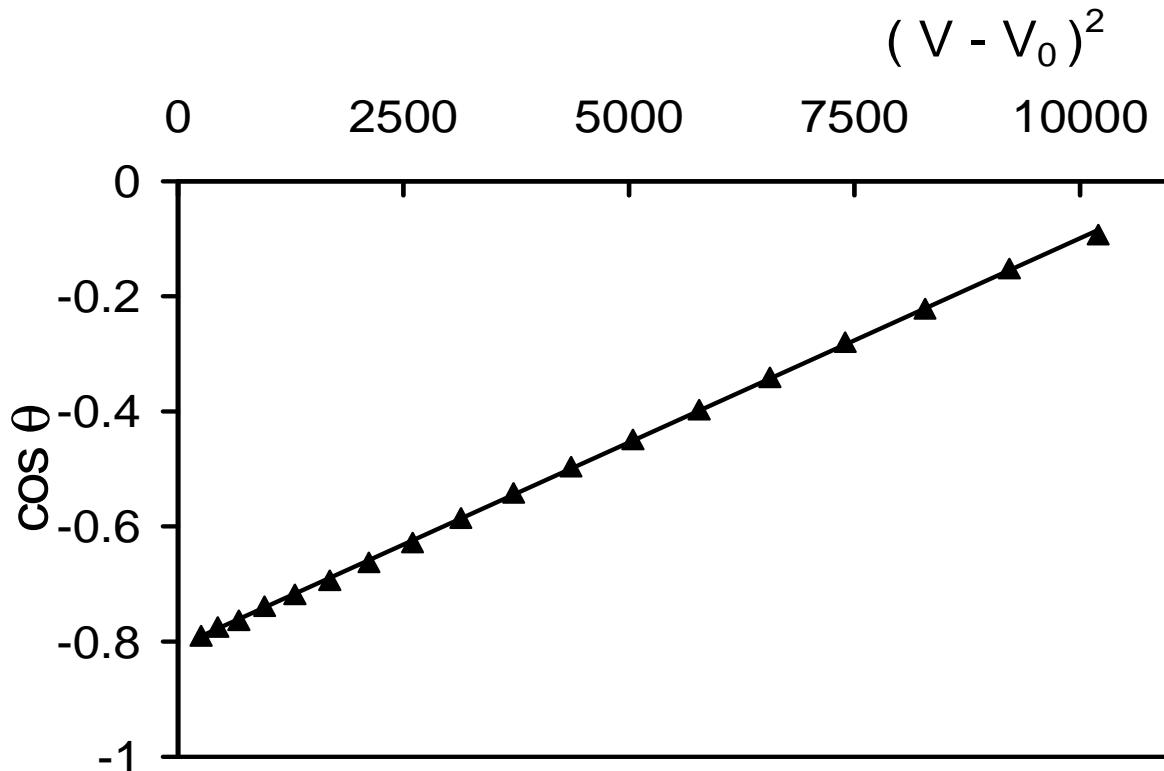
GR/R02184/01 – Super-hydrophobic & super-hydrophilic surfaces  
GR/S34168/01 – Electrowetting  
EP/C509161/1 – Extreme soil water repellence  
Dstl via EPSRC/MOD JGS  
EU COST Action D19 - Chemistry at the nanoscale

# Fitting of Results

- Increasing Voltage Half Cycle

- Advancing droplet charges substrate before contact with liquid
- Modified fitting equation to include a constant  $V_o$

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



## Interpretation

1. Conversion from “skating” to “penetrating” regime
2.  $V_o=28V$  represents charging
3. Fitted  $\theta_e(0)$  gives Wenzel angle of  $143^\circ$  and predicts  $r=1.92$  (SEM image 1.87)