Electrowetting on Super-Hydrophobic Surfaces

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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

Acknowledgement: Neinhuis and Barthlott
Surface Structure

Effect on Water

“Skating” Droplets
Composite air-solid surface (Cassie-Baxter)
Low hysteresis: “Slippy” surface

“Penetrating” Droplets
Based on roughness (Wenzel)
Large hysteresis: “Sticky” surface

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

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 (~ 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

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

- **Contradiction 1**
  - But Super-H via patterning insulator $\rightarrow$ high aspect ratio

- **Contradiction 2**
  - But low hysteresis requires “Skating”
Irreversible Electrowetting

- **Lithographic System**
  - Ti/Au on glass, SU-8 Pillars, Mask: 7.5 μm circles, 15 μm centre-centre, height 6.5 μm
  - Spin coated Teflon AF1600 (θₑ=114°)
  - 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 (~ 45 V) before droplet spreads
2. **Irreversible** on removal of voltage

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. $V_o=28V$ represents charging
2. Conversion from “skating” to “penetrating” regime
3. Fitted $\theta_e(0)$ gives Wenzel angle of 143° and predicts roughness of $r=1.92$
**Determination of Roughness Factor**

**SEM Measurements**
- Pillar diameter = 7.5±0.5 µm
- Centre-centre separation 15 µm
- Height = 6.5±1.3 µm
- Unintended “ribs”
- Teflon on flat surface $\theta_e = 114^\circ$

**Comparison to EWOD Data**
- Cassie-Baxter solid factor of
  \[ \cos \theta_{CB} = f \cos \theta_e - (1-f) \Rightarrow \theta_{CB} = 152^\circ \pm 1^\circ \]
  \[ f = 0.12 \pm 0.02 \quad Pre-electrowetting \quad \theta_{CB} = 152^\circ \]
- Ignoring “ribs” Wenzel factor is
  \[ r = 1.7 \pm 0.1 \quad EWOD \; Intercept \]
- Assuming ribs are ~ 1/2 pillar heights
  \[ r \sim 1.9 \]
  \[ r = 1.92 \]
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**
  - **Silica Powder**

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

  Silica grains are sub-µm, but layer is thick.

Acknowledgement
David Quéré, College de France, Paris.
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 grains coating is breached

**Initial Shape**
- Hydrophobic grains
- Water
- Optional PTFE
- Metal contact
- Substrate

**Apply Voltage**
- Hydrophobic grains
- Water
- Locally this looks like pillars
- Metal contact
- Substrate

**Remove Voltage**
- Hydrophobic grains
- Water
- Optional PTFE
- Metal contact
- Substrate
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
Capacitive energy from electrowetting

Numerical Results

Larger marbles

\[ \kappa R = 0 \]
\[ \kappa R = 0.3 \]
\[ \kappa R = 0.6 \]
Experiments on Liquid Marbles
Size Data (Lycopodium)

\[ 2\kappa^{-1} = 4.6 \text{ mm} \]

\[ \log \kappa r = 1.40 \log \kappa R - 0.22 \]

Graph showing the relationship between \( h \) and \( R \) with \( h \) in mm on the y-axis and \( R \) in mm on the x-axis. The graph includes data points for marble and puddle, with a linear regression line fitting the data.
Mobility of Liquid Marbles

Video’s:

“Small on WatchGlass avi”
“Large on WatchGlass avi”

Displayed in Separate Program
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**
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

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

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

External
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