Dynamic Wetting of Structured Surfaces

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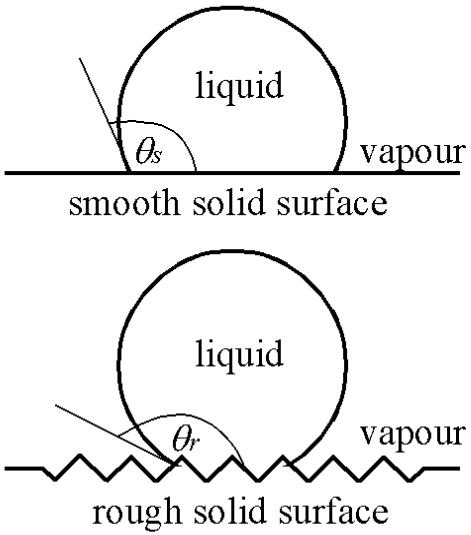
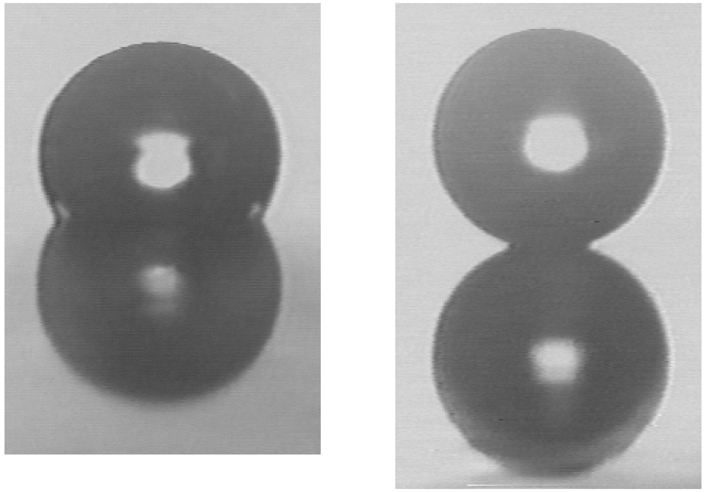
Overview

1. Wetting and Topography
    - Wenzel's Equation (*and Air Trapping*)
    - Super-hydrophobicity and Super-wetting
    - Tanner's Law
2. Experimental
    - Surface Structures - Lithographic Fabrication
    - Dynamics: Super-wetting
    - Equilibrium: Super-hydrophobic
3. Conclusions

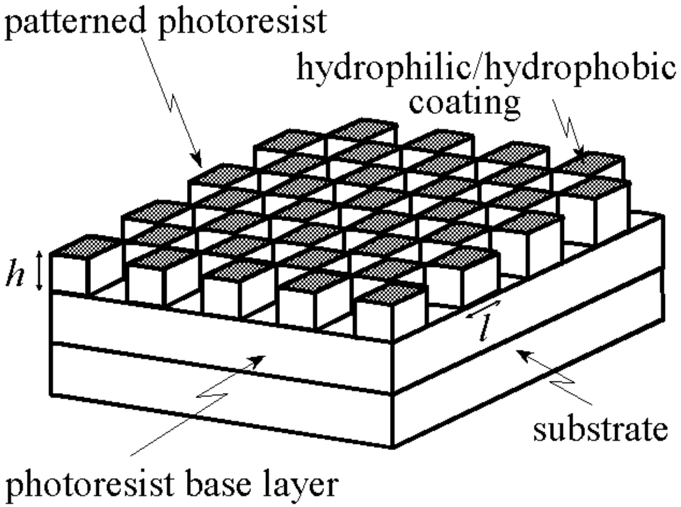
Super-Hydrophobic Surfaces



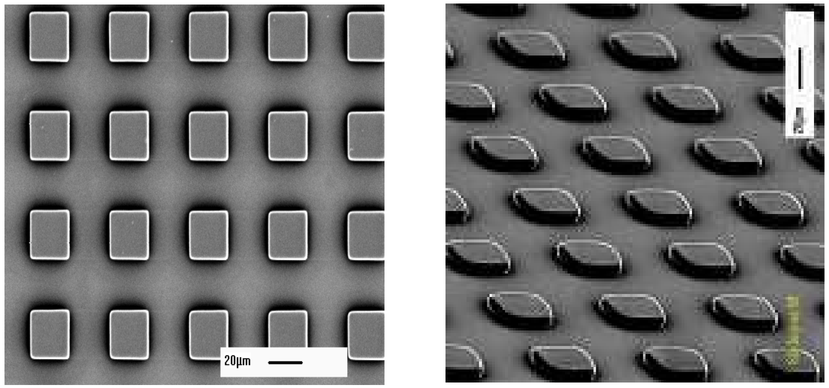
Water Drop (~ 2 mm)



Lithographic Principle

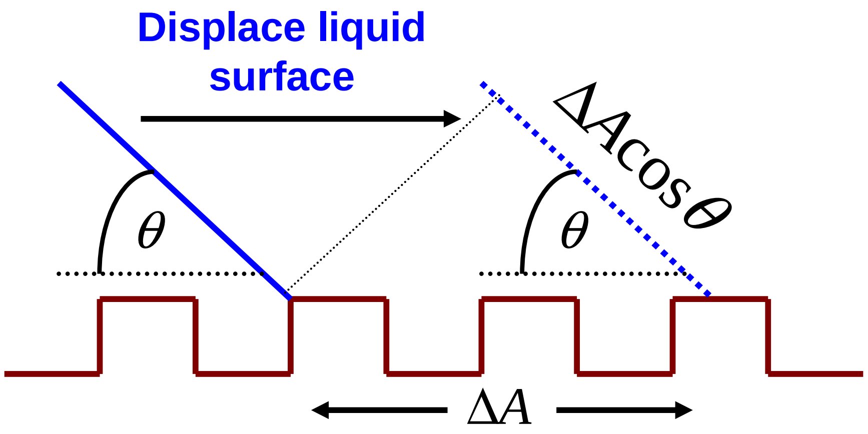


SEM Images

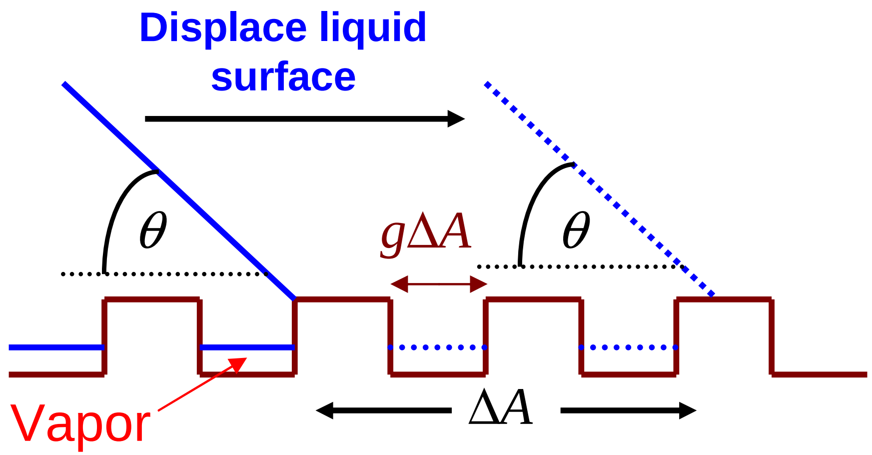


Wetting and Topography

Surface Topography



Air Trapping



Surface Free Energy Changes

$$\Delta F = (\gamma_{SL} - \gamma_{SV})r\Delta A + \gamma_{LV}\cos\theta\Delta A$$

$$\Delta F = (\gamma_{SL} - \gamma_{SV})fr\Delta A + \gamma_{LV}g\Delta A + \gamma_{LV}\cos\theta\Delta A$$

Wenzel's Eqn

$$\cos\theta_e^R = r(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} = r\cos\theta_e^s$$

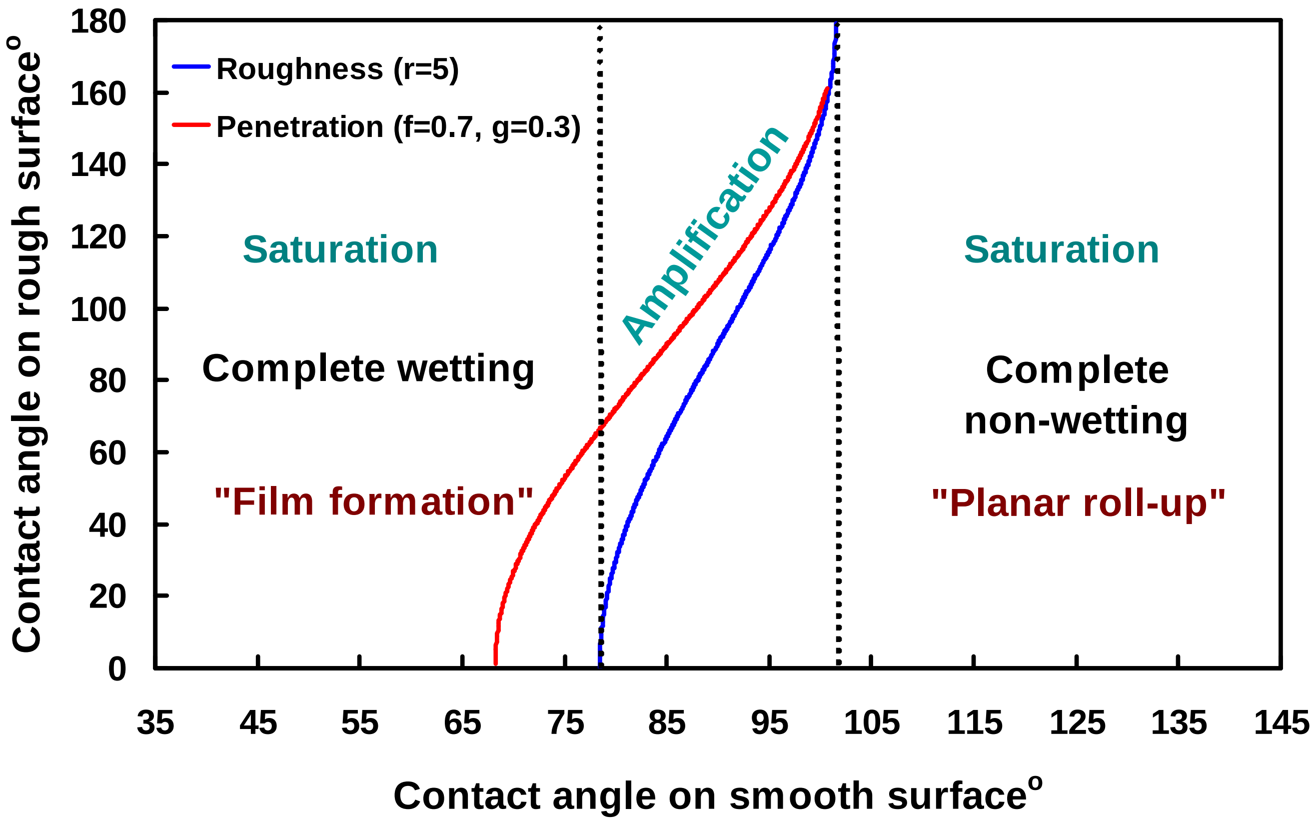
$r = \Delta A_{true} / \Delta A$ = roughness factor

Modified (Cassie Style) Eqn

$$\cos\theta_e^R = rf\cos\theta_e^s - g$$

f = fraction of rough surface wet

Effect of Topography - Equilibrium



Roughness/Topography

θ_e^s > threshold

⇒ enhances hydrophobicity

θ_e^s < threshold

⇒ enhances film formation

Super-wetting

Super-hydrophobic

⇒ equilibrium experiments

Super-wetting

⇒ dynamic experiments

Wenzel and "*Driving Force*"

Smooth Surface

Drop Equilibrium – Young's Law

$\Rightarrow \cos\theta_e^s = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$

Drop Edge Speed Dynamics

$\Rightarrow v_E \propto \theta\, \gamma_{LV}(\cos\theta_e^s - \cos\theta)$

$\Rightarrow v_E \propto \theta\, \gamma_{LV}(\theta^2 - \theta_e^{s2})$

Rough Surface

Drop Equilibrium - Wenzel

$\Rightarrow \cos\theta_e^R = r\cos\theta_e^s$

Drop Edge Speed Dynamics

$\Rightarrow v_E \propto \theta\, \gamma_{LV}(r\cos\theta_e^s - \cos\theta)$

$\Rightarrow v_E \propto \theta\, \gamma_{LV}((r-1)+((\theta^2 - r\theta_e^{s2})/2)$

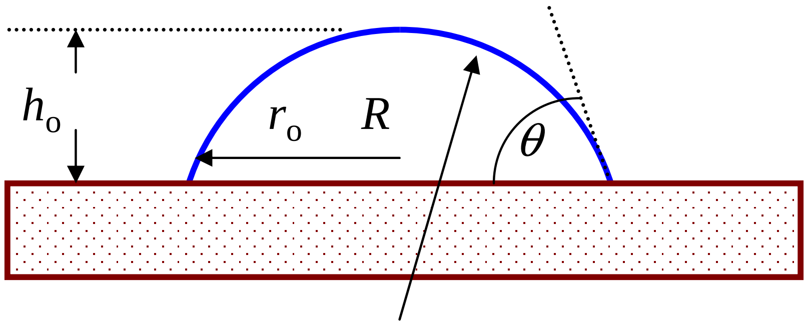
Prediction

Weak roughness or topographic patterning modifies edge speed:

$v_E \propto \theta(\theta^2 - \theta_e^{s2})$ changes towards $v_E \propto \theta$

Dynamics - Frenkel's Method

- Frenkel's Method
  - – Hydrodynamic approach
  - – Spherical cap droplet
  - – Viscous dissipation



Rate of surface free energy change = Viscous dissipation

- Advantages of the Method
  - – On smooth surfaces correct limit for θ_e small
  - – Provides an edge speed-wide angle relation
  - – Covers partial wetting case $\theta_e \neq 0^o$
- Limitations of the Method
  - – Results are for non-volatile liquids
  - – Assumes a spherical cap shape (size<κ^{-1})

Edge Speed - Contact Angle Relation

- Surface Free Energy from Shape
  - Edge speed is $v_E = dr_o/dt$
  - Interfacial areas of spherical cap
  - Topography

$$\frac{dF}{dt} = 2\pi r_o \gamma_{LV}\left[\cos\theta - frI + g\right]v_E$$

$I = (\gamma_{SV} - \gamma_{SL})/\,\gamma_{LV} = \cos\theta_e^s$

- Form of Dissipation
  - Use dimensional argument
  - Poiseuille flow to estimate k

$$\frac{dE_d}{dt} = \frac{k\eta v_E^2 r_o}{\tan(\theta/2)}$$

- Edge Speed - Contact Angle Relation

$$v_E = \left(\frac{2\pi\gamma_{LV}}{k\eta}\right)\tan(\theta/2)\left[fr\cos\theta_e^s - \cos\theta - g\right]$$

- Small Angle Case

$$v_E \propto \theta\left((fr - 1 - g) + \left(\theta^2 - fr\,\theta_e^{s2}\right)/2\right)$$

Hoffmann-de Gennes
when fr=1 and g=0
$v_E \propto \theta\,(\theta^2 - \theta_e^{s2})$

“Roughness” Modified Tanner’s Law

- Dynamics of θ
  - Spherical cap shape at all times
  - Volume of liquid conserved
  - v_E converted to $d\theta/dt$

- Power Law for θ
  - Complete wetting $\theta_e^s=0$
  - Small angle approx
  - Solve for time dep.

$$\frac{d\theta}{dt} \propto -\theta^{7/3}\left[2\left(fr-1-g\right)+\theta^2\right]$$

$$\theta = \frac{B_s}{\left(t+C_s\right)^{3/10}} \sim \frac{1}{t^{3/10}}$$

Tanner’s Law

(fr=1, g=0)

$$\theta = \frac{A_R\left(fr-g-1\right)}{\left(t+C_R\right)^{3/4}} \sim \frac{1}{t^{3/4}}$$

Topography Modified

Prediction

Weak roughness or topographic patterning modifies power law:

power law changes from -3/10 towards -3/4

Experimental Approach

- Lithographic Surface
  - SU-8 Photoresist
  - Circular Pillars

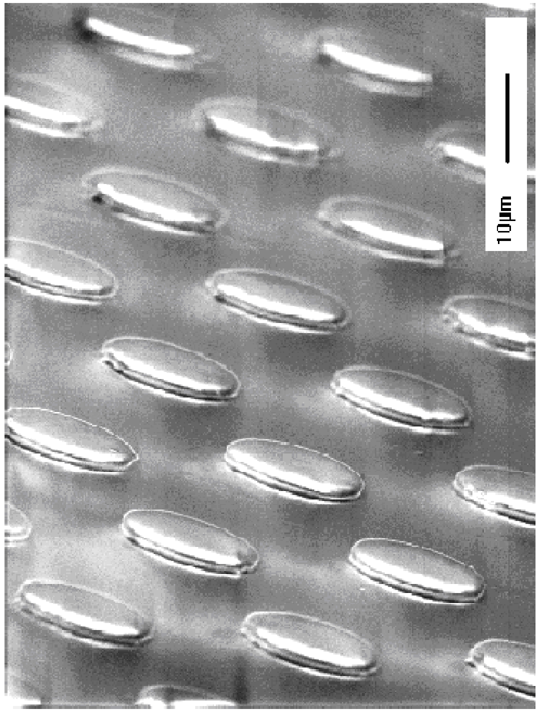
    15 μm diameter

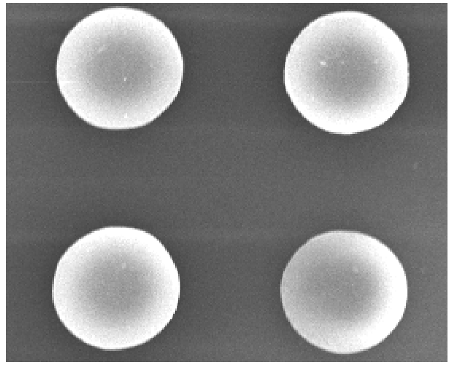
    30 μm centre-centre

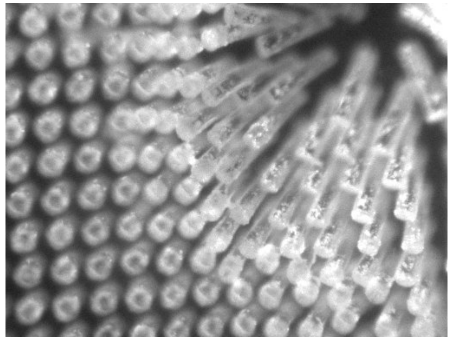
    Square lattice

    Vary height 0 to 30 μm

    (bottom image is 4 μm pattern)







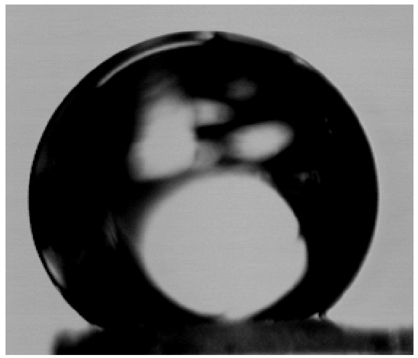
- Contact Angle Measurements
  - Spreading/Wetting

    PDMS Oil 10 000 cSt
  - Super-hydrophobic

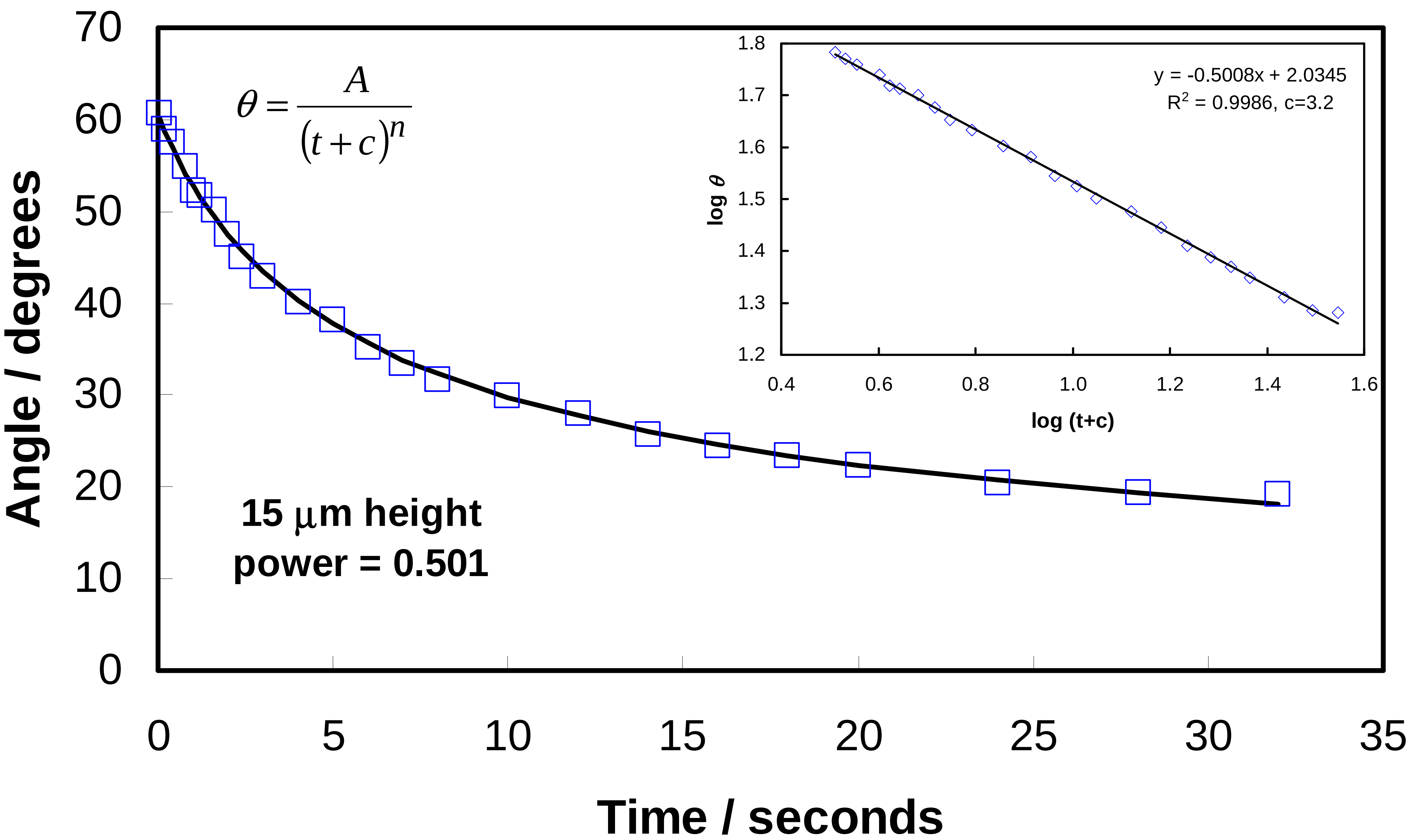
    Hydrophobize surface

    Equilibrium θ_e for water

Water Drop on Hydrophobized 20 μm

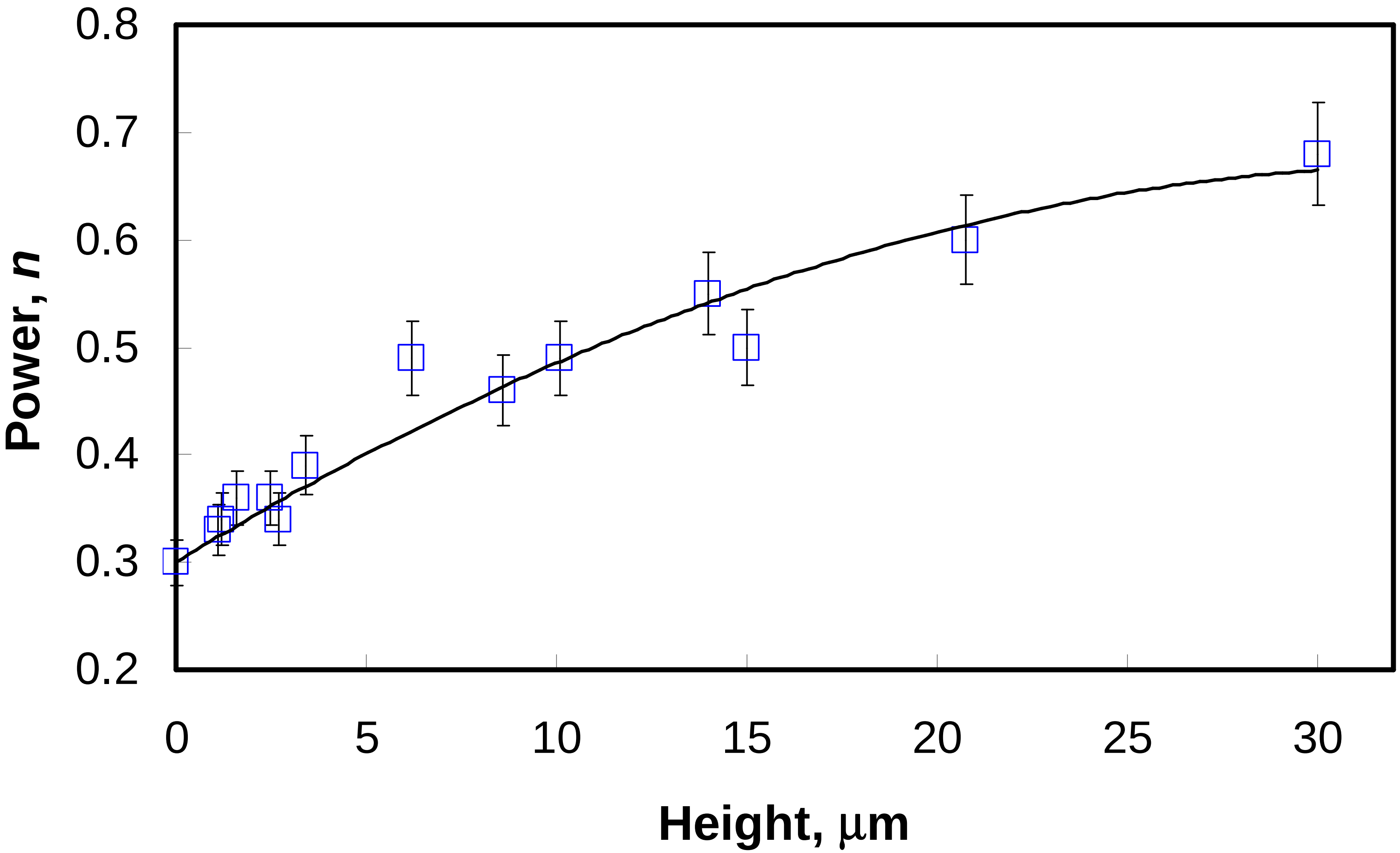


Dynamic Angle - Data and Fit



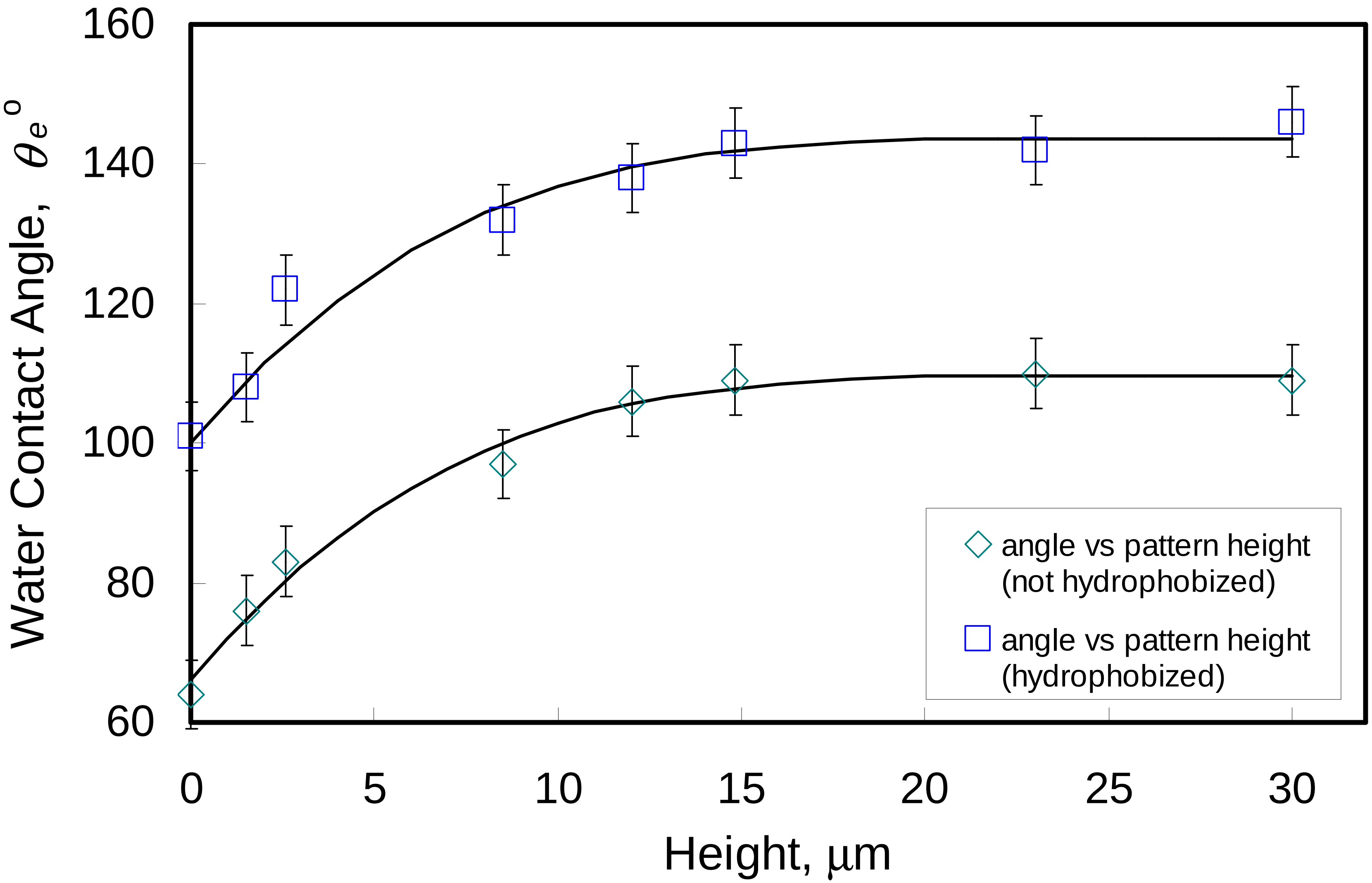
Super-wetting Data

- Exponents from Dynamics
  - PDMS oil and 0 to 30 μm heights



Super-hydrophobic Data

- Water Equilibrium Angles θ_e
  - untreated v hydrophobized patterned surfaces



Conclusions

Achievements

- Theory for Dynamics

  Roughness version Tanner Law

- Controlled Surface Structure

  Simple and systematic

- Super-Wetting

  Dynamics $\Rightarrow$ super-wetting

- Hydrophobic Treatment

  Equilib $\Rightarrow$ super-hydrophobic

Comments

- Simplistic Theory

  Dissipation/fast v slow directions

- Other Types of Surface Possible

  Topographic structuring

- Dynamic Version of Cassie-Baxter

  Pattern by chemical modification

- Foot and Precursor Films

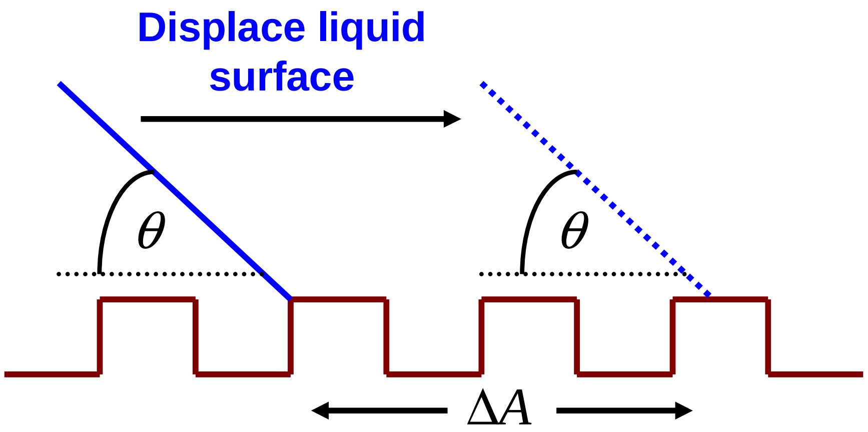
  Symmetry of film v drop

The End

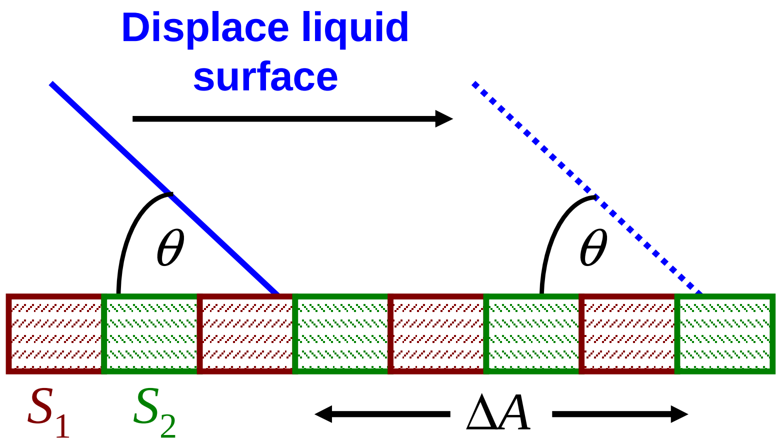
Additional Supporting Slides

Wetting and Topography

Surface Topography



Mixed Chemistry



Surface Free Energy Changes

$$\Delta F = (\gamma_{SL} - \gamma_{SV})r\Delta A + \gamma_{LV} \cos\theta\Delta A$$

$$\Delta F = (\gamma^1_{SL} - \gamma^1_{SV}) f\Delta A + (\gamma^2_{SL} - \gamma^2_{SV})(1 - f)\Delta A + \gamma_{LV}\cos\theta\Delta A$$

Wenzel's Equation

$$\cos\theta = r(\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} = r\cos\theta_e^S$$

Cassie's Equation

$$\cos\theta_e = f\cos\theta_1 + (1 - f)\cos\theta_2$$

Chemically Heterogeneous Case

- Surface Free Energy from Shape

  Edge speed is $v_E = dr_o/dt$

  Interfacial areas of spherical cap

$$\frac{dF}{dt} = 2\pi r_o \gamma_{LV}\left[\cos\theta - fI_1 - (1-f)I_2\right]v_E$$

$I = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV} = \cos\theta_e^s$

- Form of Dissipation

  Use dimensional argument

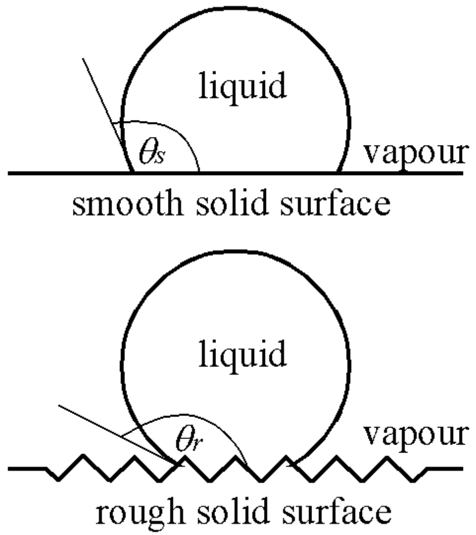
  Poiseuille flow to estimate k

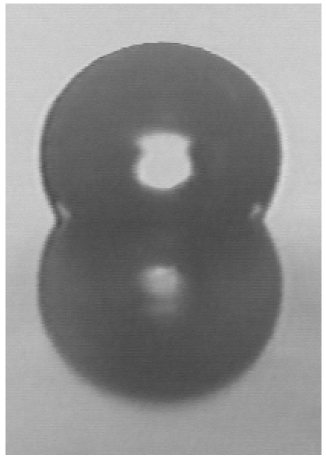
$$\frac{dE_d}{dt} = \frac{k\eta v_E^2 r_o}{\tan(\theta/2)}$$

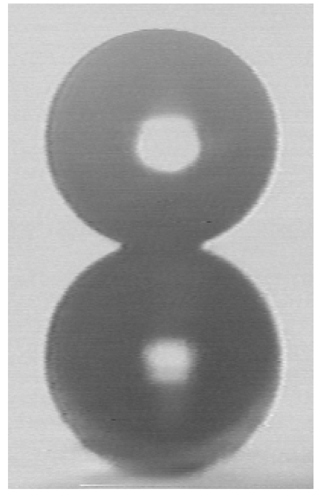
- v_E - θ Relation

$$v_E = \left(\frac{2\pi\gamma_{LV}}{k\eta}\right)\tan(\theta/2)\left[fI_1 + (1-f)I_2 - \cos\theta\right]$$

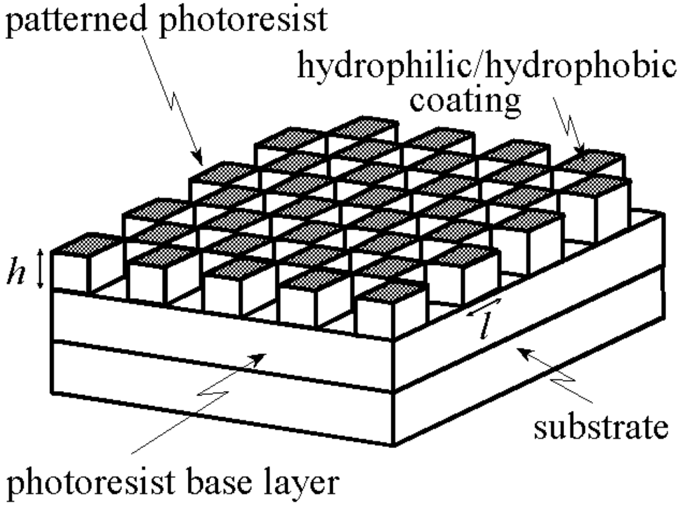
Super-Hydrophobic Surfaces



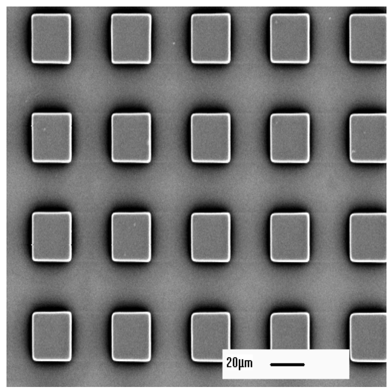


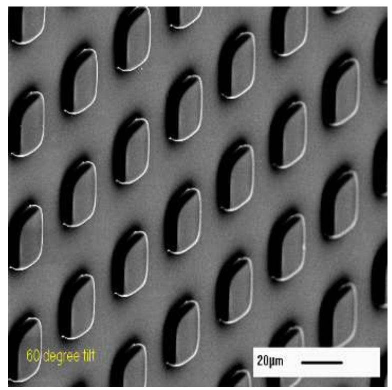


Lithographic Principle



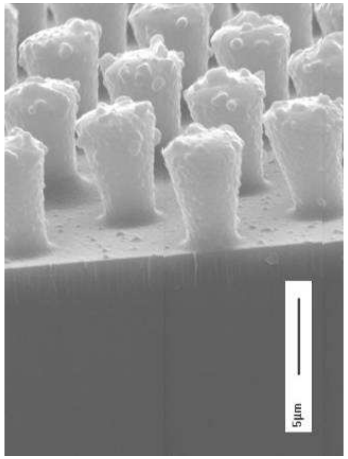
SEM Images

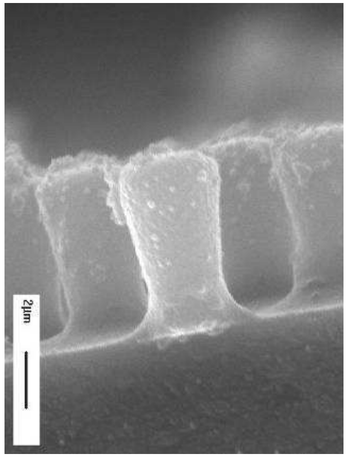


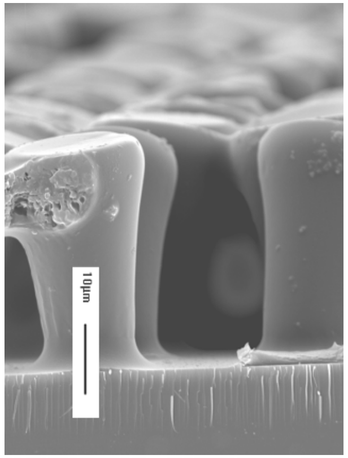


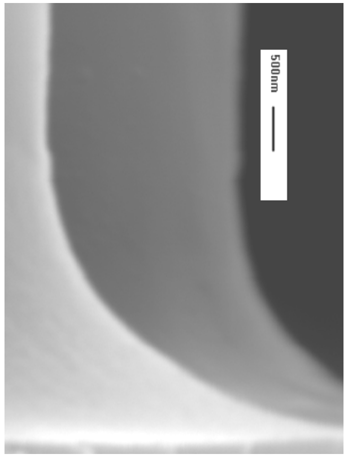
Additional Views of Pillars

- Coated SU-8 Circular Pillars
  - Spin @ 3000 rpm x 2 and no spin (incl. close up)

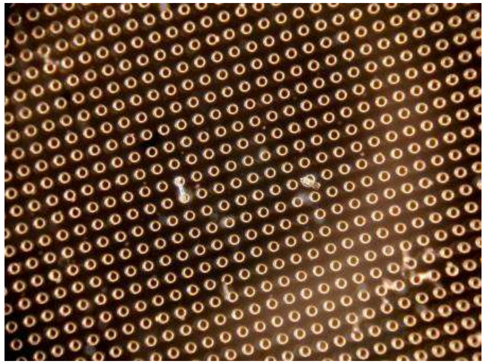
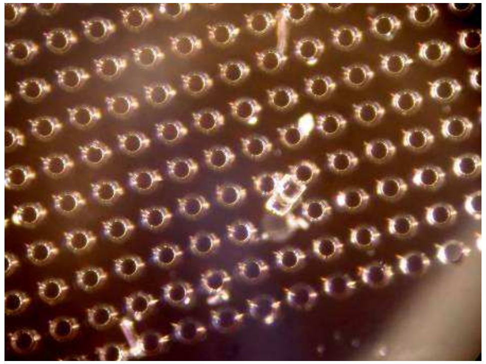
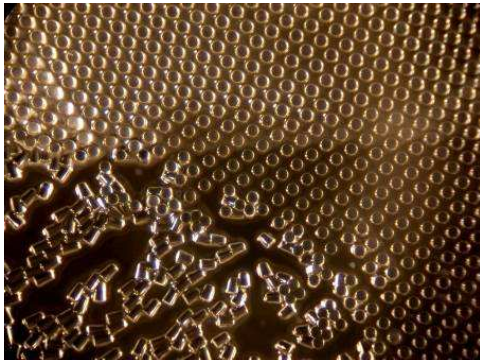
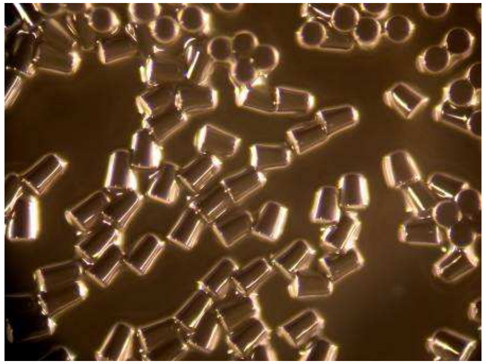








- Pillars - 20 μm Diameter by 40 μm (Samples a,b)

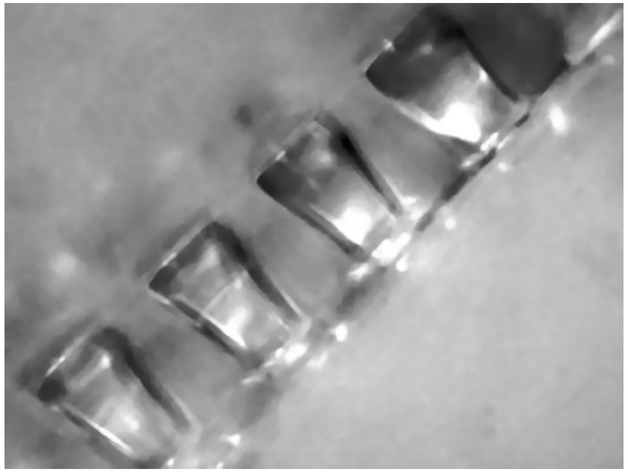
Views Pillars

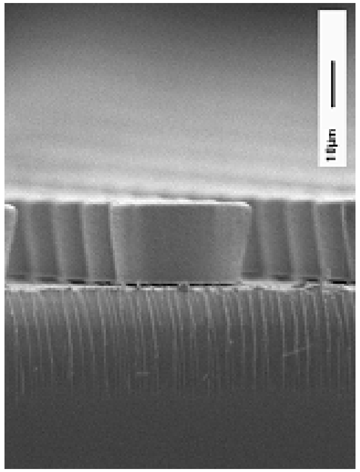
- Lithographic Surface
  - SU-8 Photoresist
  - Circular Pillars

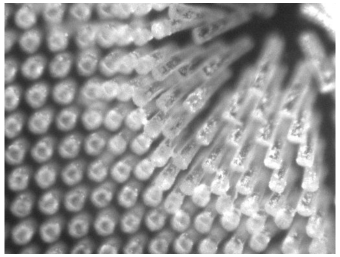
    15 µm diameter

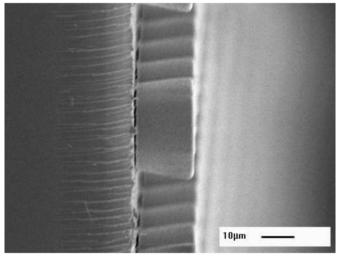
    30 µm centre-centre

    Square lattice

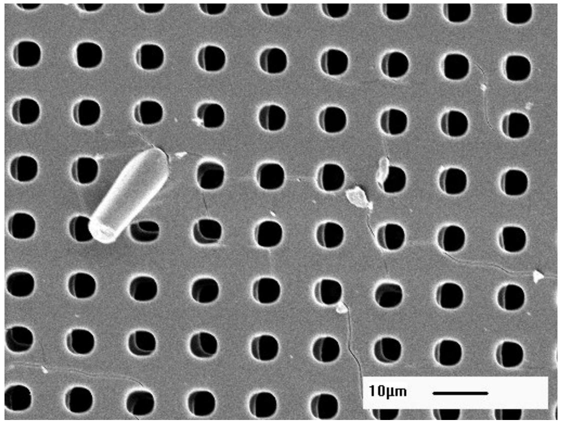






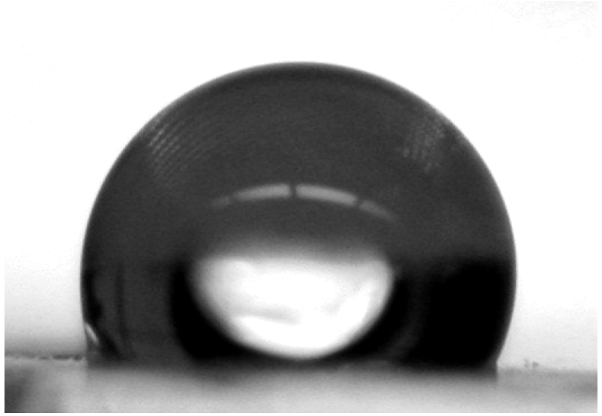


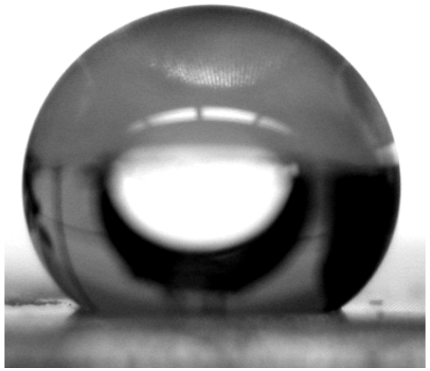
- 4 µm Diameter Pillars



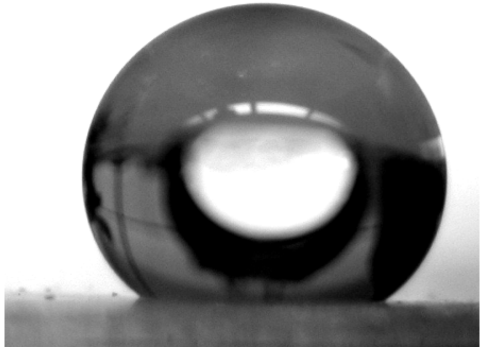
Hydrophobised Patterns of Pillars

- Coated SU-8 Circular Pillars
  - Height is 30 μm, diameter is 15 μm and separation is 15 μm
- Bare and Hydrophobised 30 μm Pattern

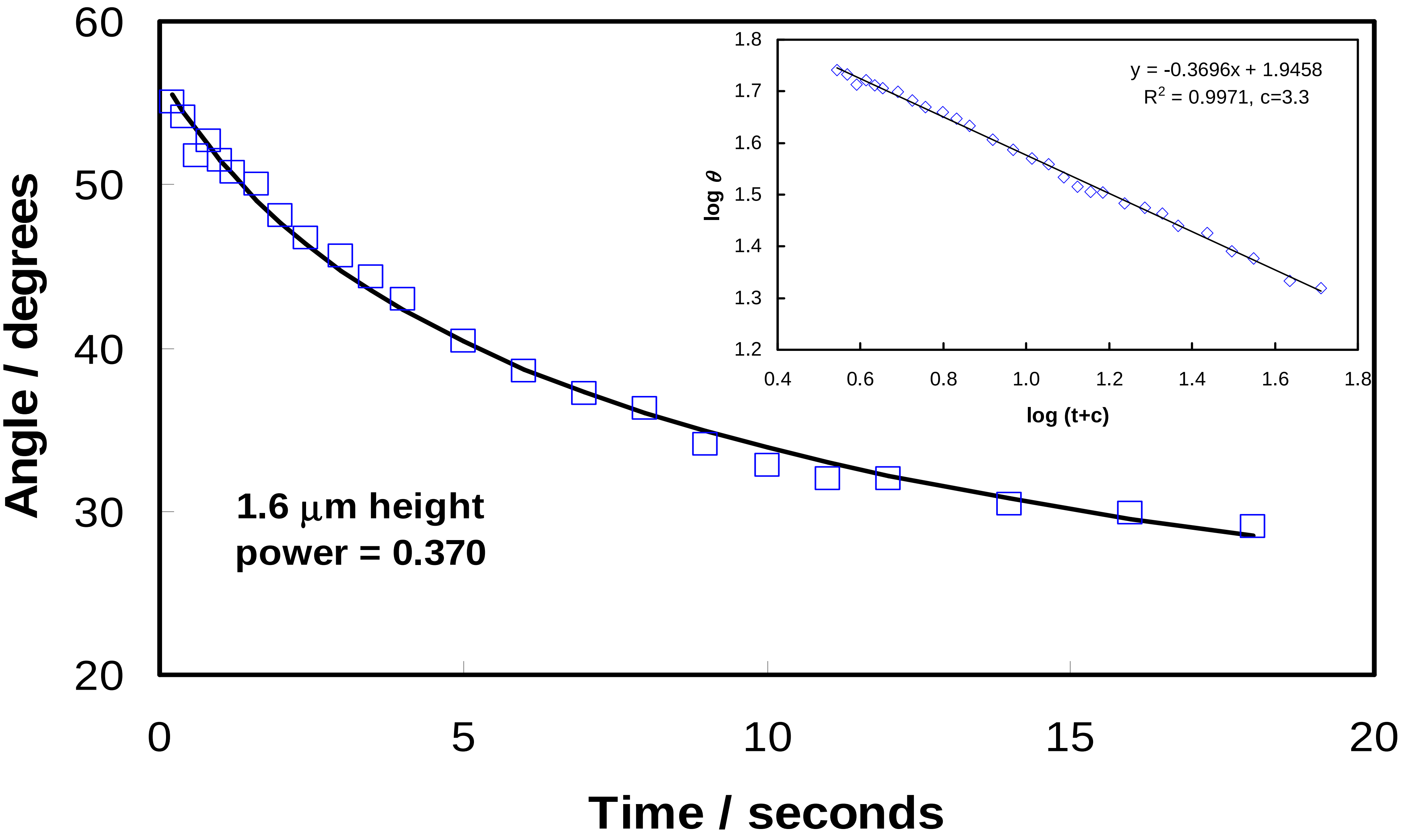




- Hydrophobised 23 μm Pattern



Dynamic Angle - Data and Fit



Alternative Surfaces

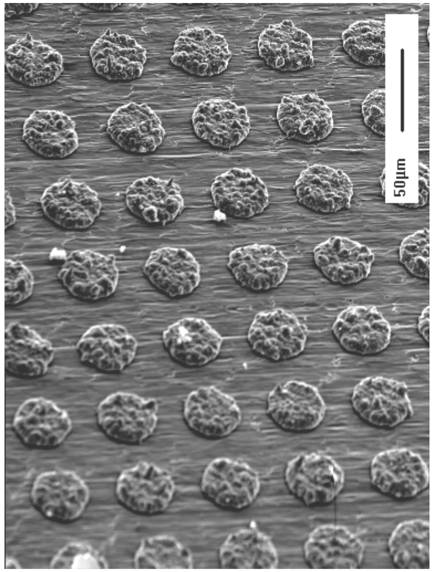
Electrodeposited Surfaces

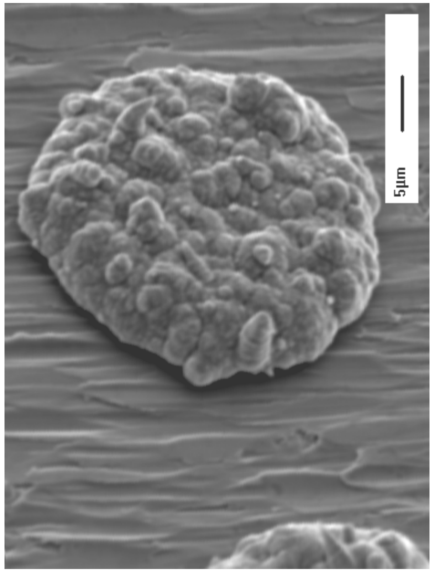
- Cu Deposited Surface
  - Circular “Pads”

    20 µm diameter

    40 µm centre-centre

    Square lattice



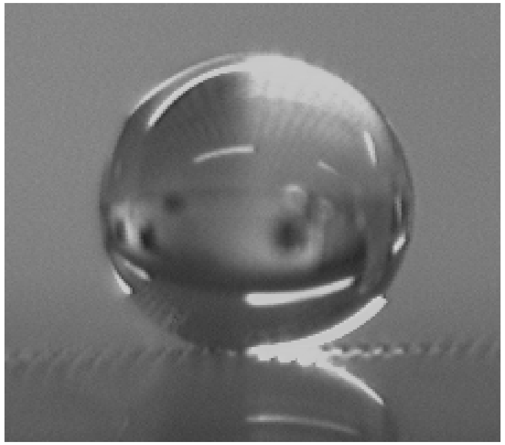


- Super-hydrophobicity
  - Hydrophobize surface

    Gore-tex treatment

    Flutec treatment

Water Drop on Hydrophobized 20 µm



Copper Etched Surfaces

- Etched Copper
  - Chessboard pattern

    20 υm diameter

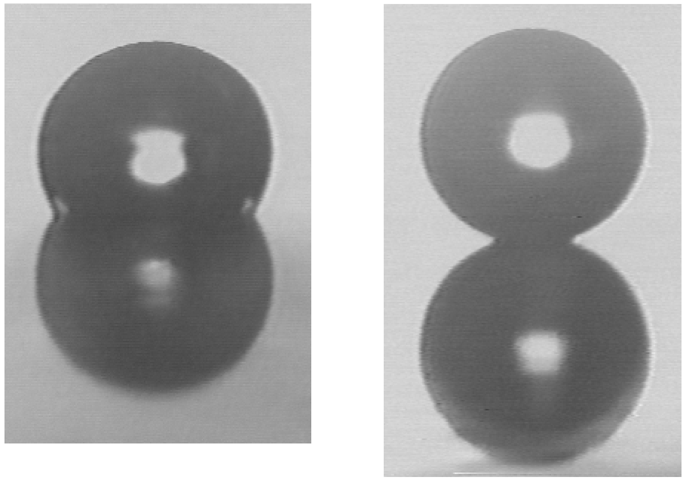


Fig 1. Enhancement of hydrophobicity.

- Evaporation
  - Squares = data on a substrate where the coating is resistant to damage due to exposure to the water.
  - Crosses = data where the hydrophobic

    coating is effectively removed during evap.

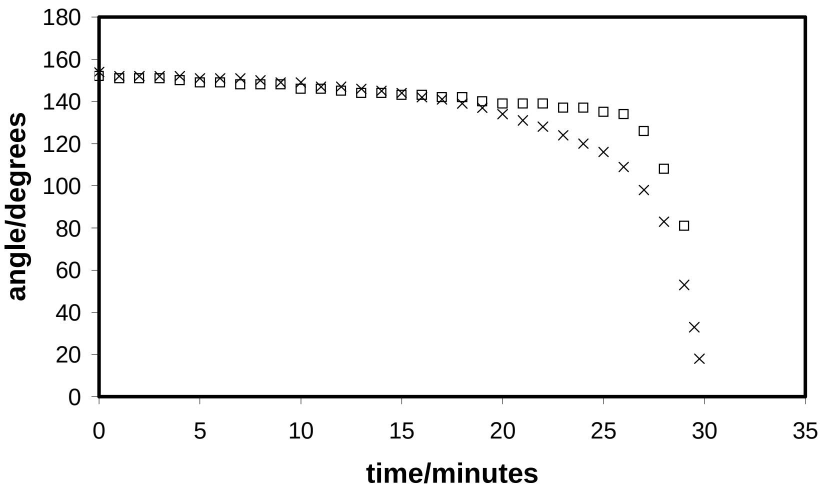


Fig. 2 Evaporation sequences.

Sol-Gel Surfaces

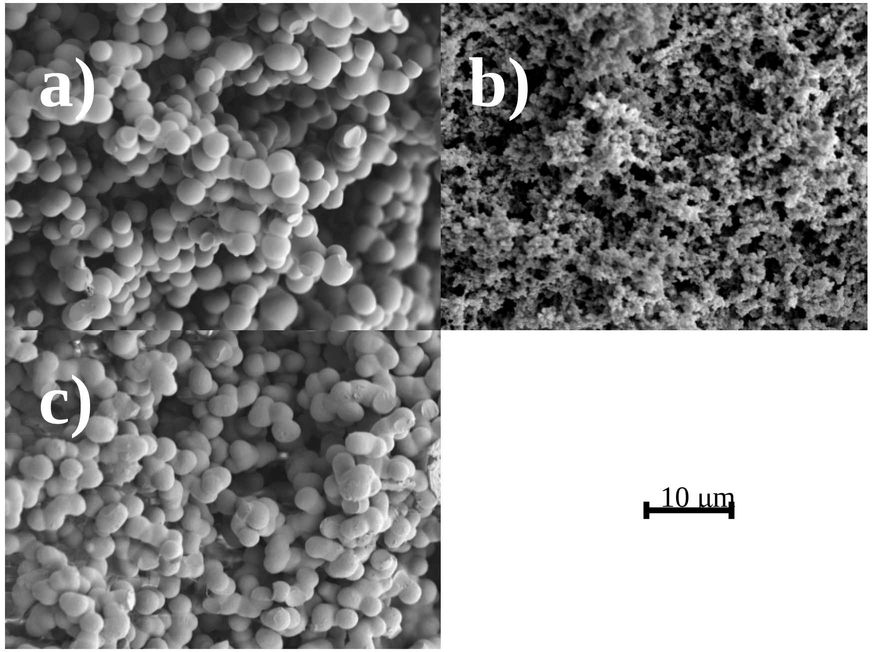
- Phase-Separation
  - Control via chemistry

    nm to 20 μm pores

    a) MTEOS with 1.1 M ammonia, heated to 300°C;

    b) MTEOS with 2.2 M ammonia, heated to 300°C;

    c) PTEOS/MTEOS with 22 M ammonia, heated to 300°C

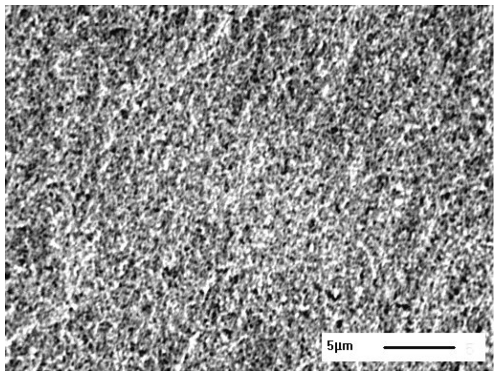


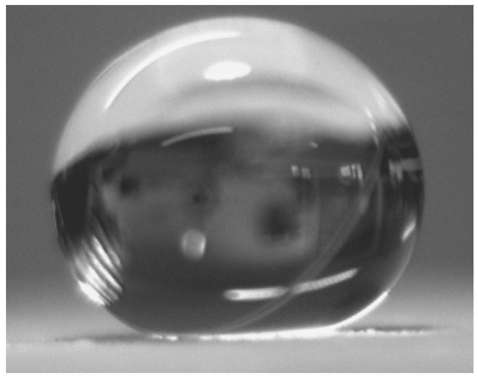
- Super-hydrophobicity
  - no need to hydrophobize

    heating converts surface

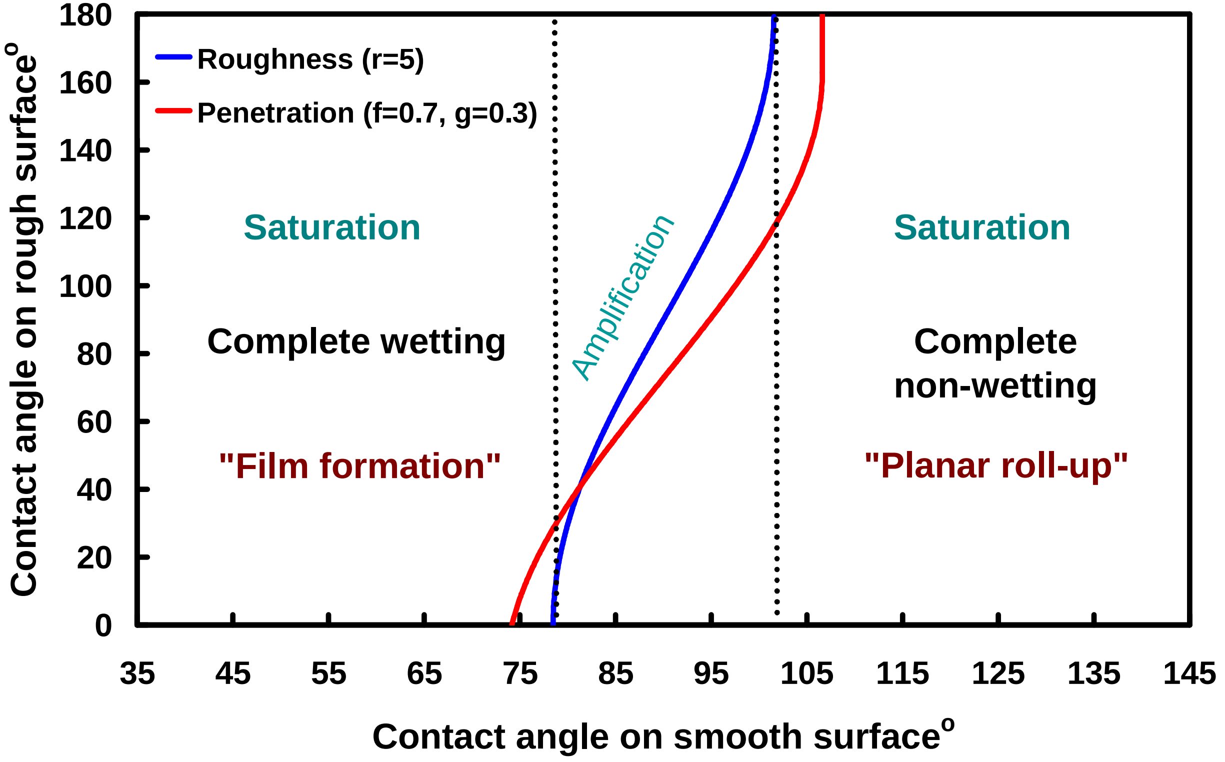
    Completely imbibes water

    Chemical treatment regains super-hydrophobicity





Effect of Topography - Equilibrium



Roughness/Topography

θ_e^s > threshold

$\Rightarrow$ enhances hydrophobicity

θ_e^s < threshold

$\Rightarrow$ enhances film formation

Super-wetting

Super-hydrophobic

$\Rightarrow$ equilibrium experiments

Super-wetting

$\Rightarrow$ dynamic experiments