18.357: Lecture 15

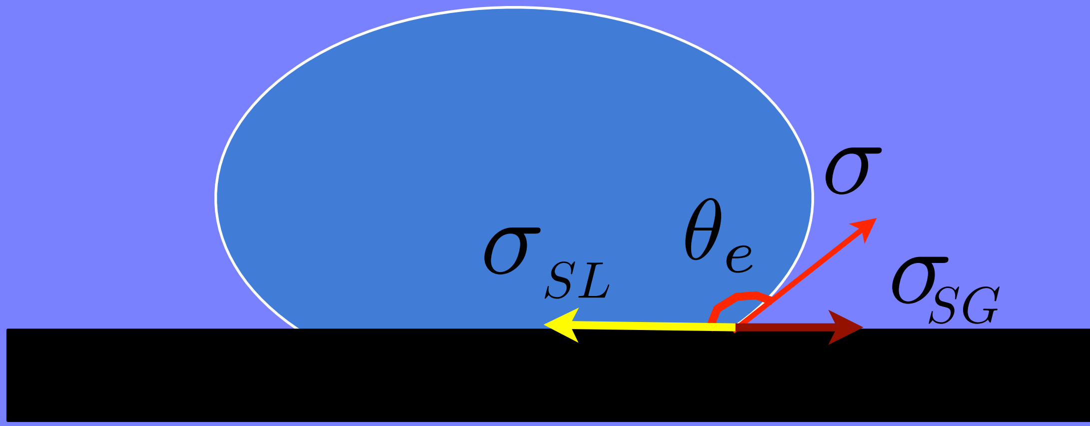
Contact angle hysteresis,

The wetting of textured solids

John W. M. Bush

Department of Mathematics
MIT

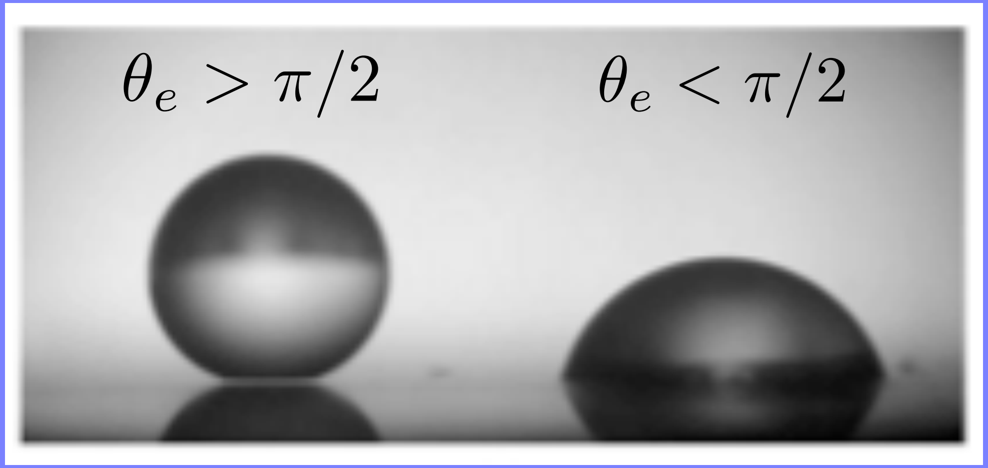
Fluid-Solid Contact: WETTING



Equilibrium contact angle θ_e

Energy differential: $dW = dx\,(\sigma_{SG} - \sigma_{SL}) - dx\,\sigma\,\cos\theta_e$

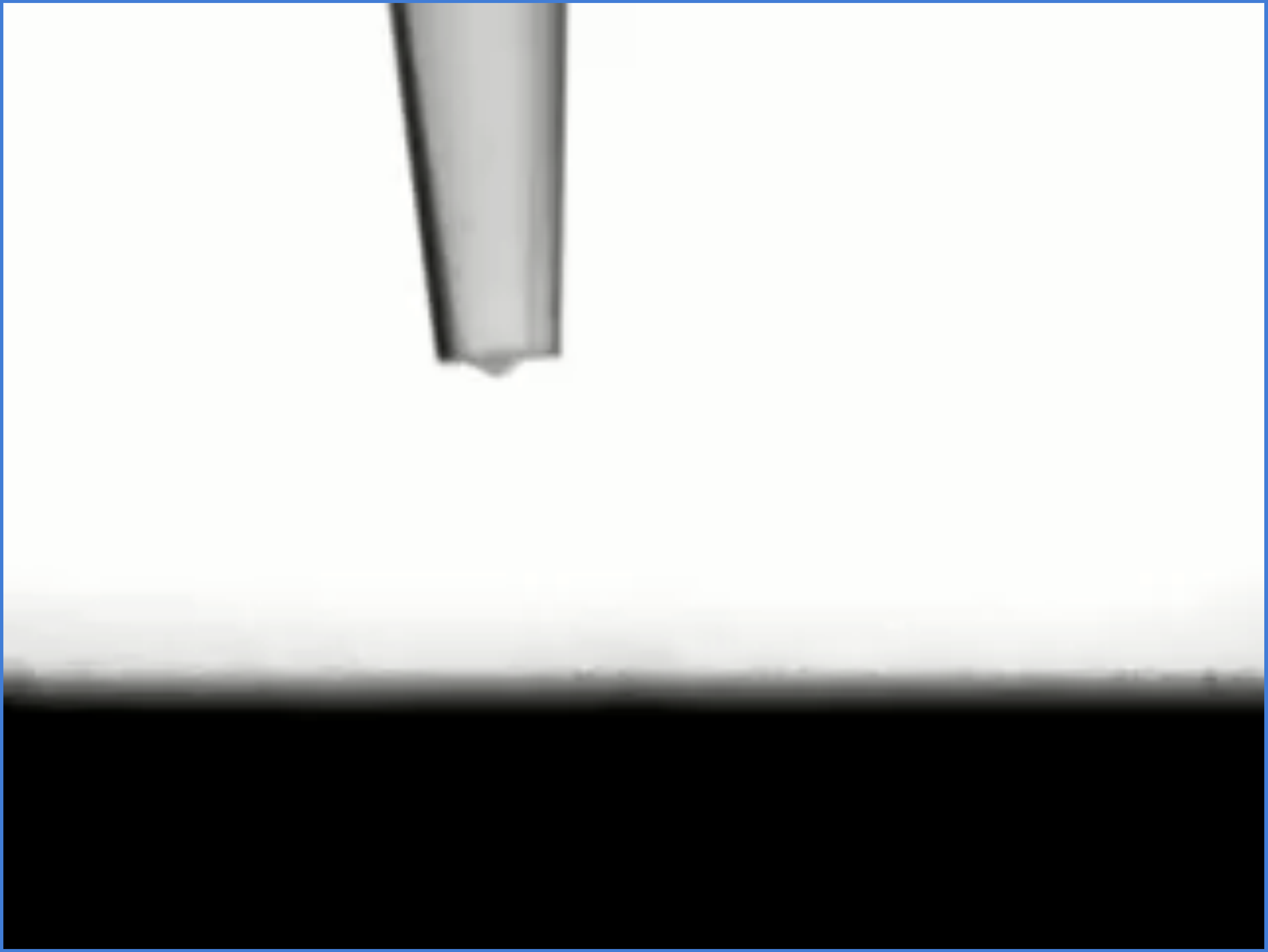
Young's relation: $$\sigma\,\cos\theta_e = \sigma_{SL} - \sigma_{SG}$$



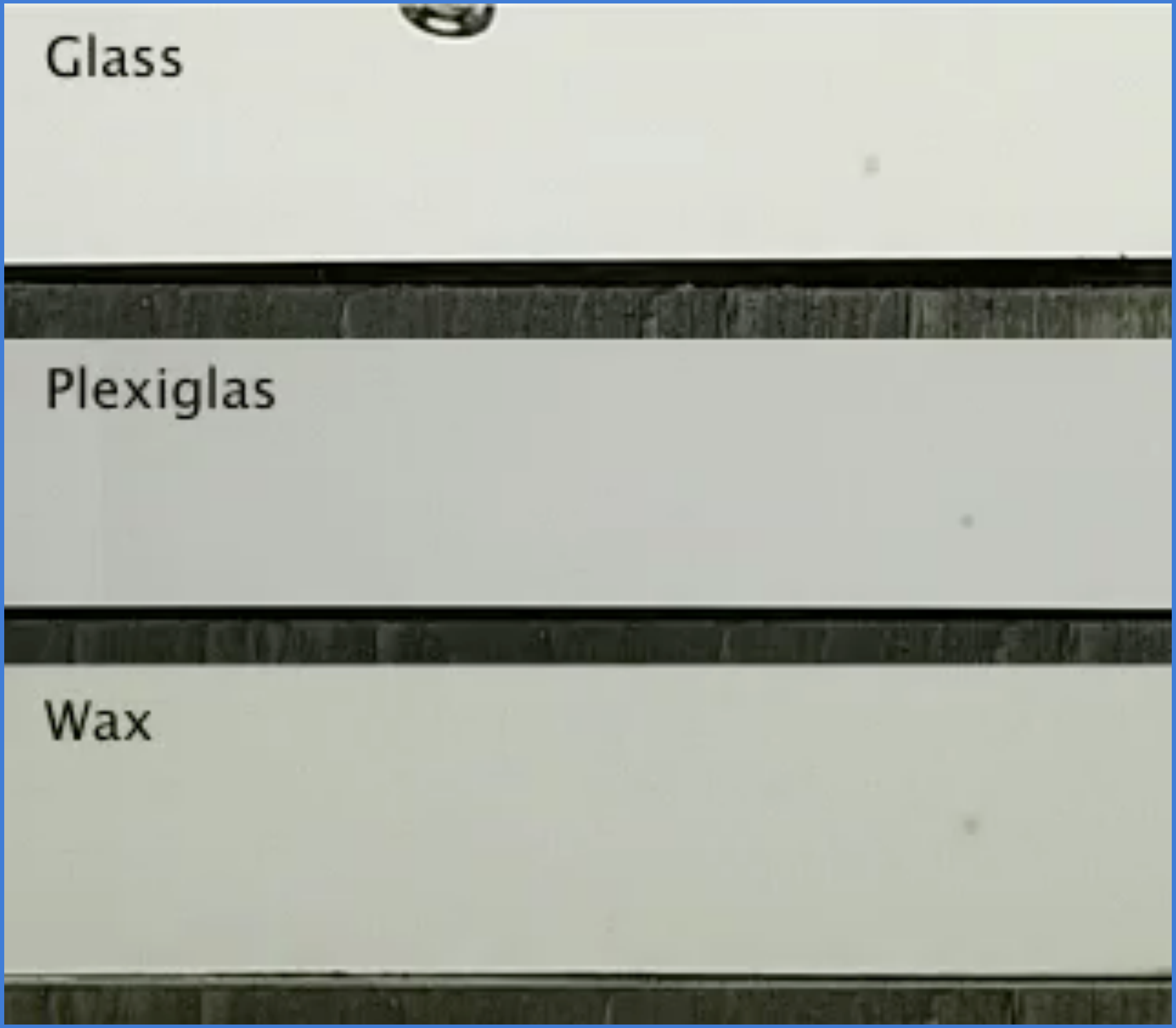
Hydrophobic surface

Hydrophilic surface

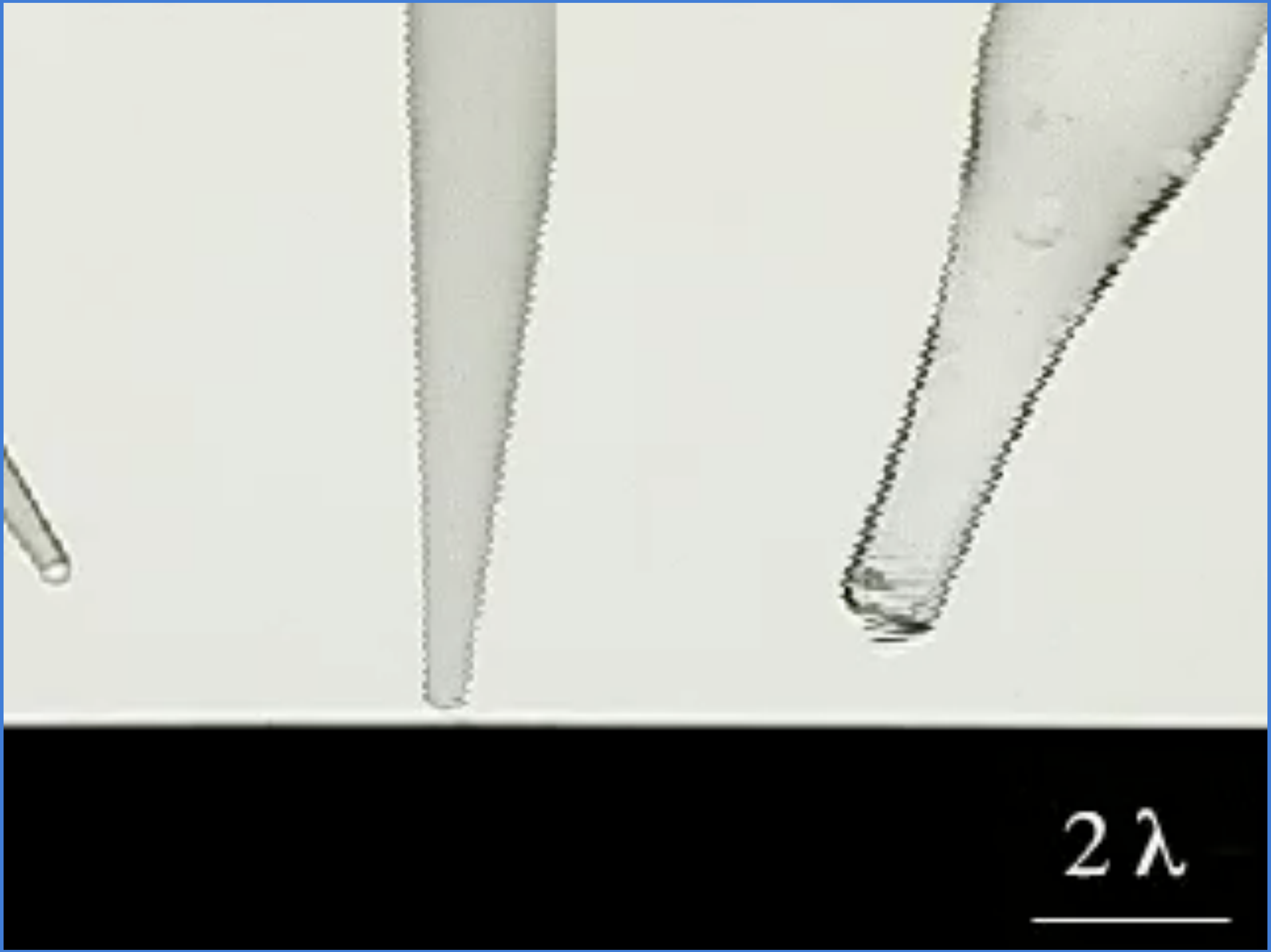
Total wetting on a flat solid

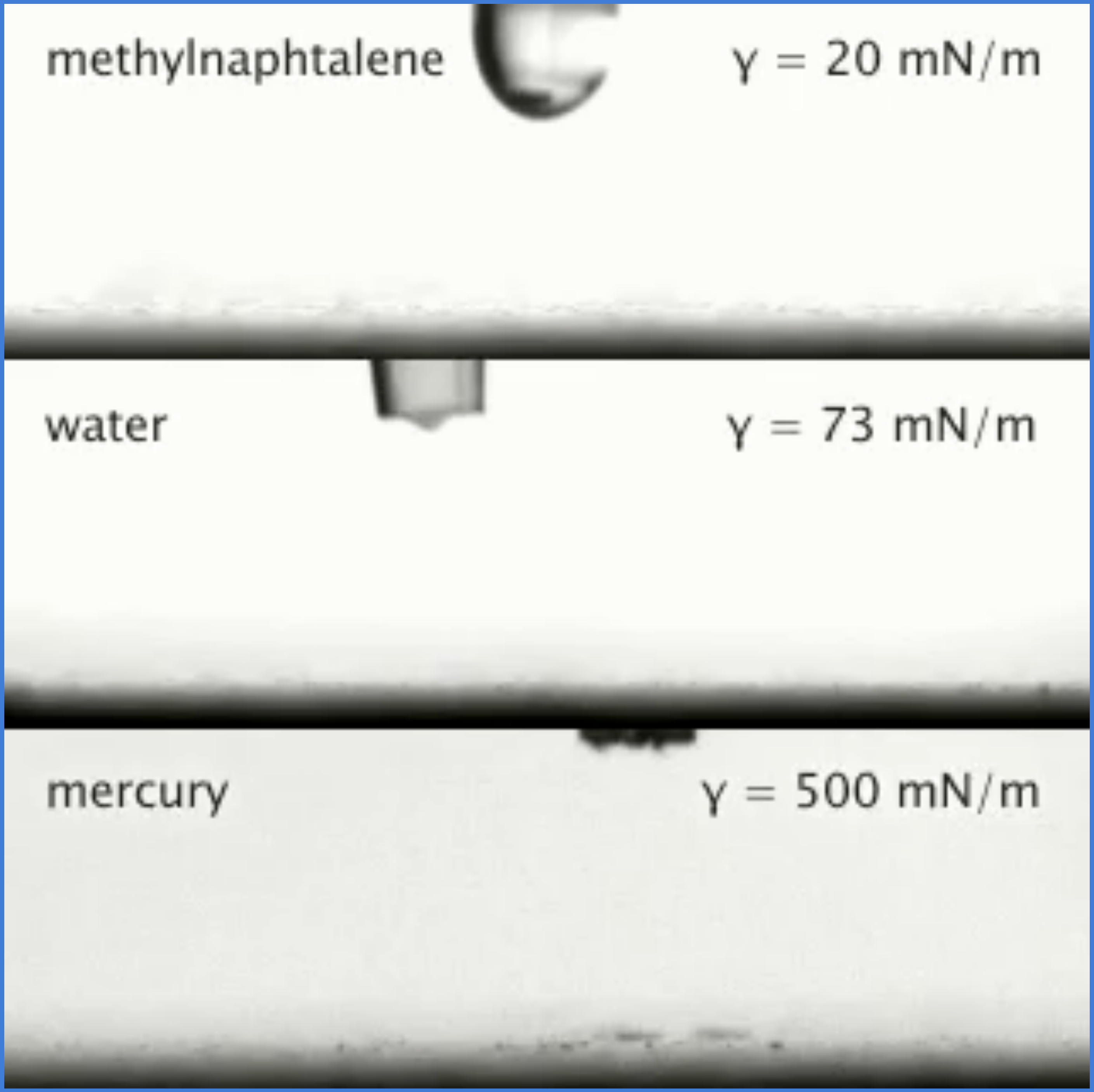


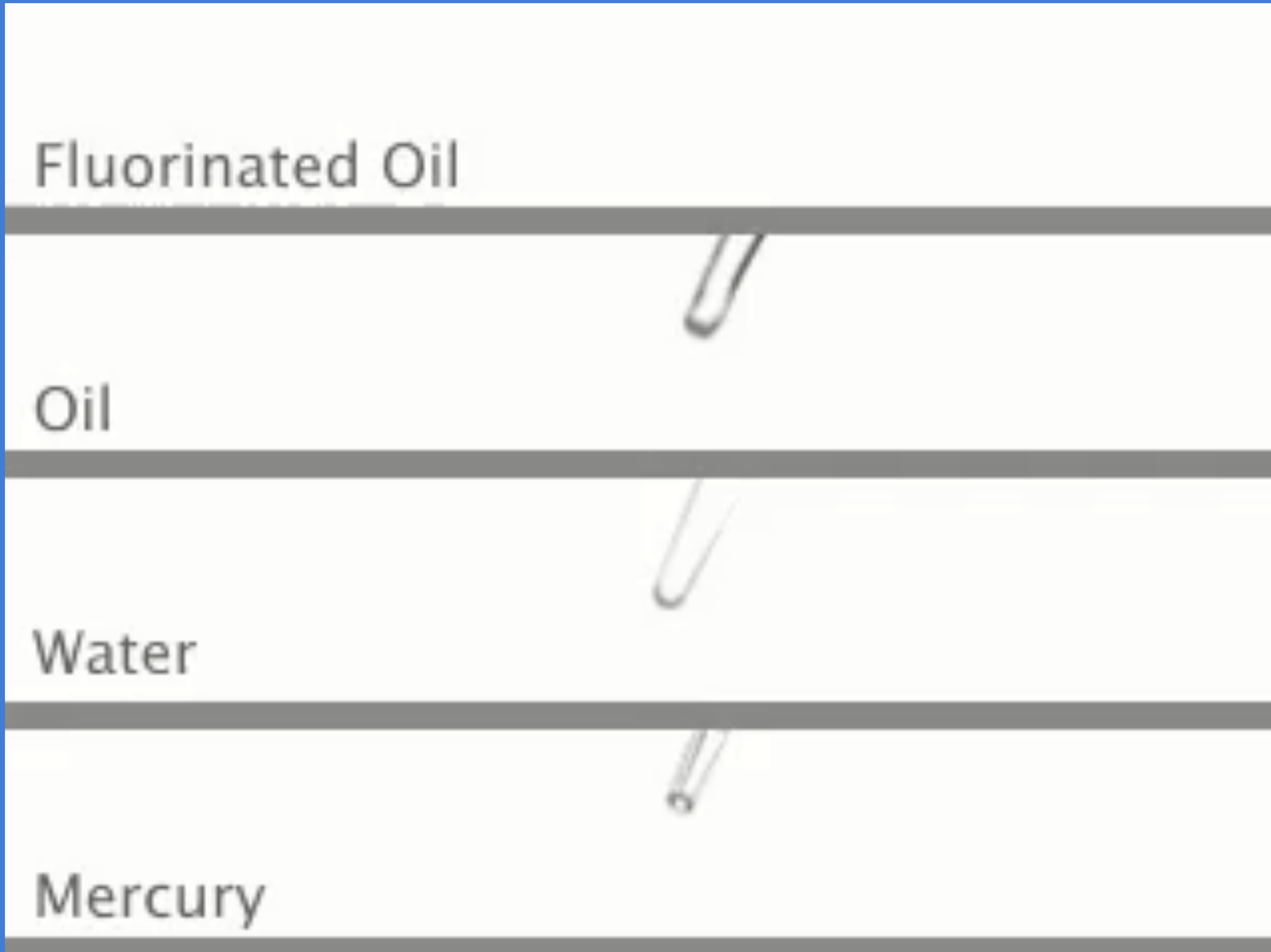
Partial wetting on a flat solid



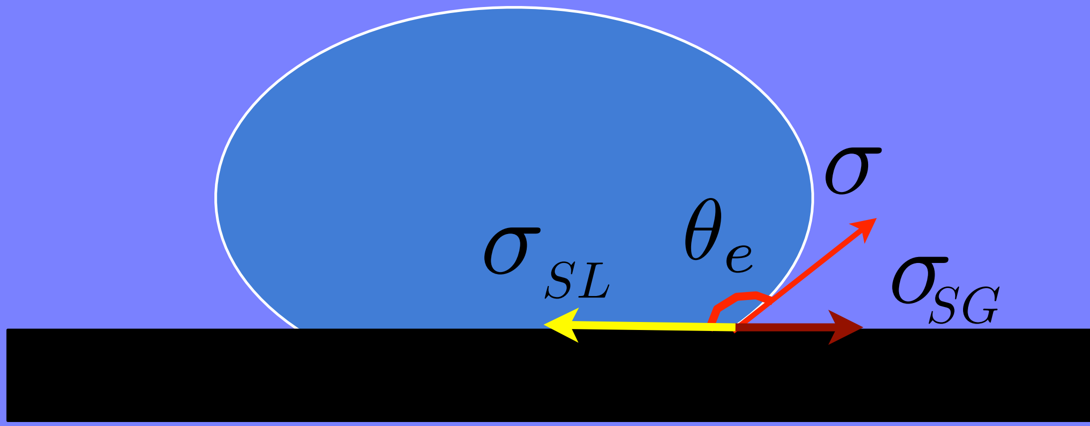
Partial wetting


2 λ


methylnaphtalene
γ = 20 mN/m
water
γ = 73 mN/m
mercury
γ = 500 mN/m


Fluorinated Oil
Oil
Water
Mercury

Fluid-Solid Contact: WETTING



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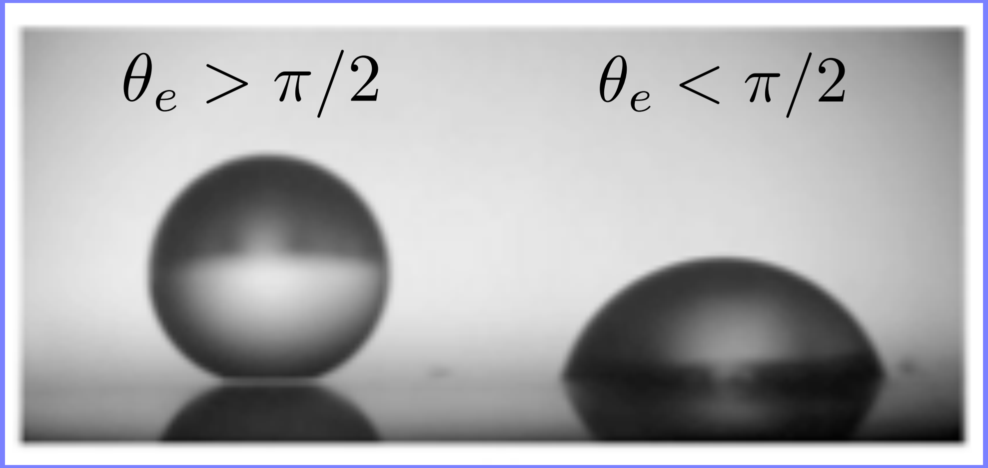
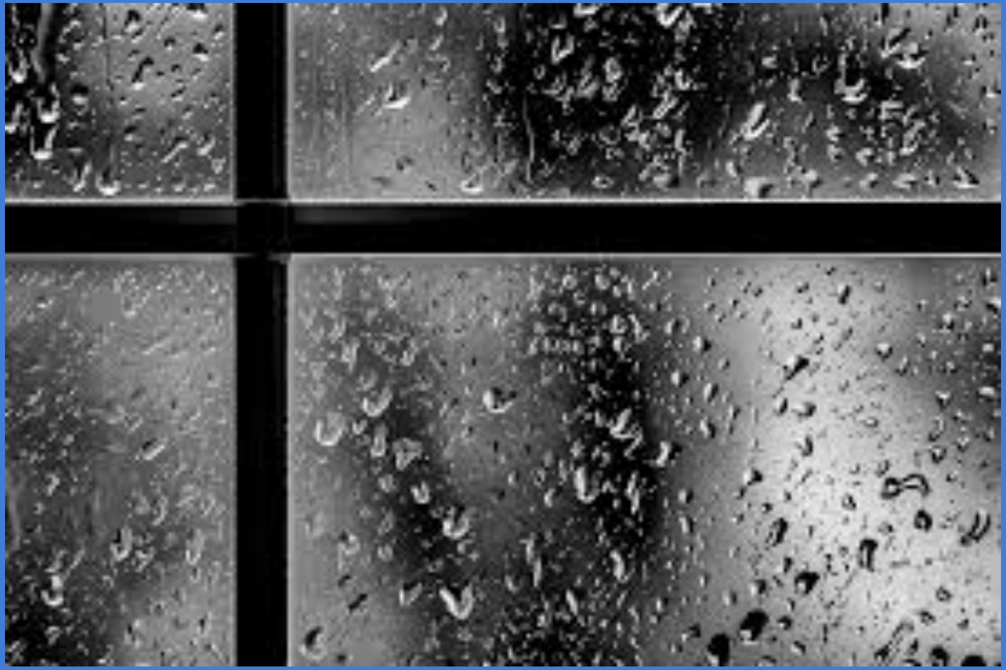


Hydrophobic surface

Hydrophilic surface

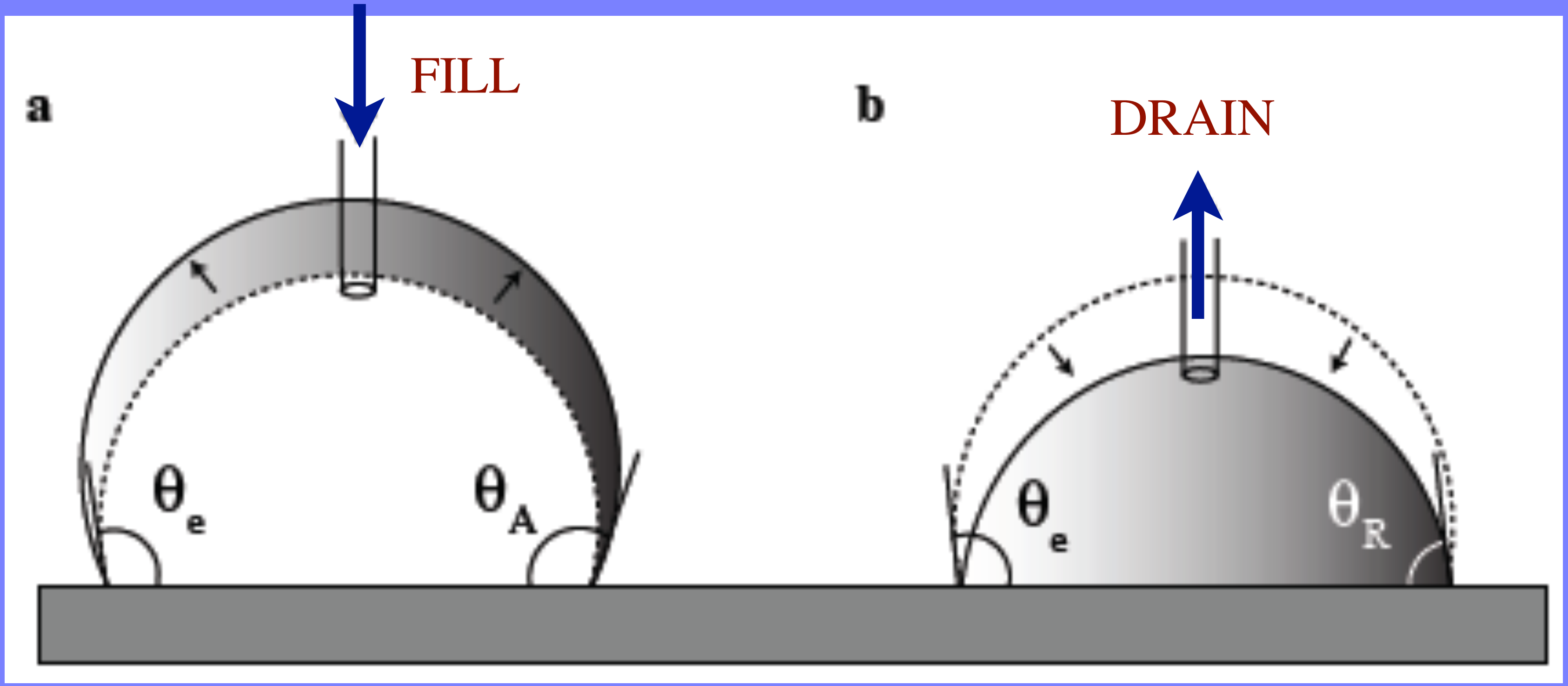
The raindrop paradox



Contact angle hysteresis

Static contact angle is not uniquely θ_e

Reality: drop is stable over a range of $\theta_r < \theta < \theta_a$



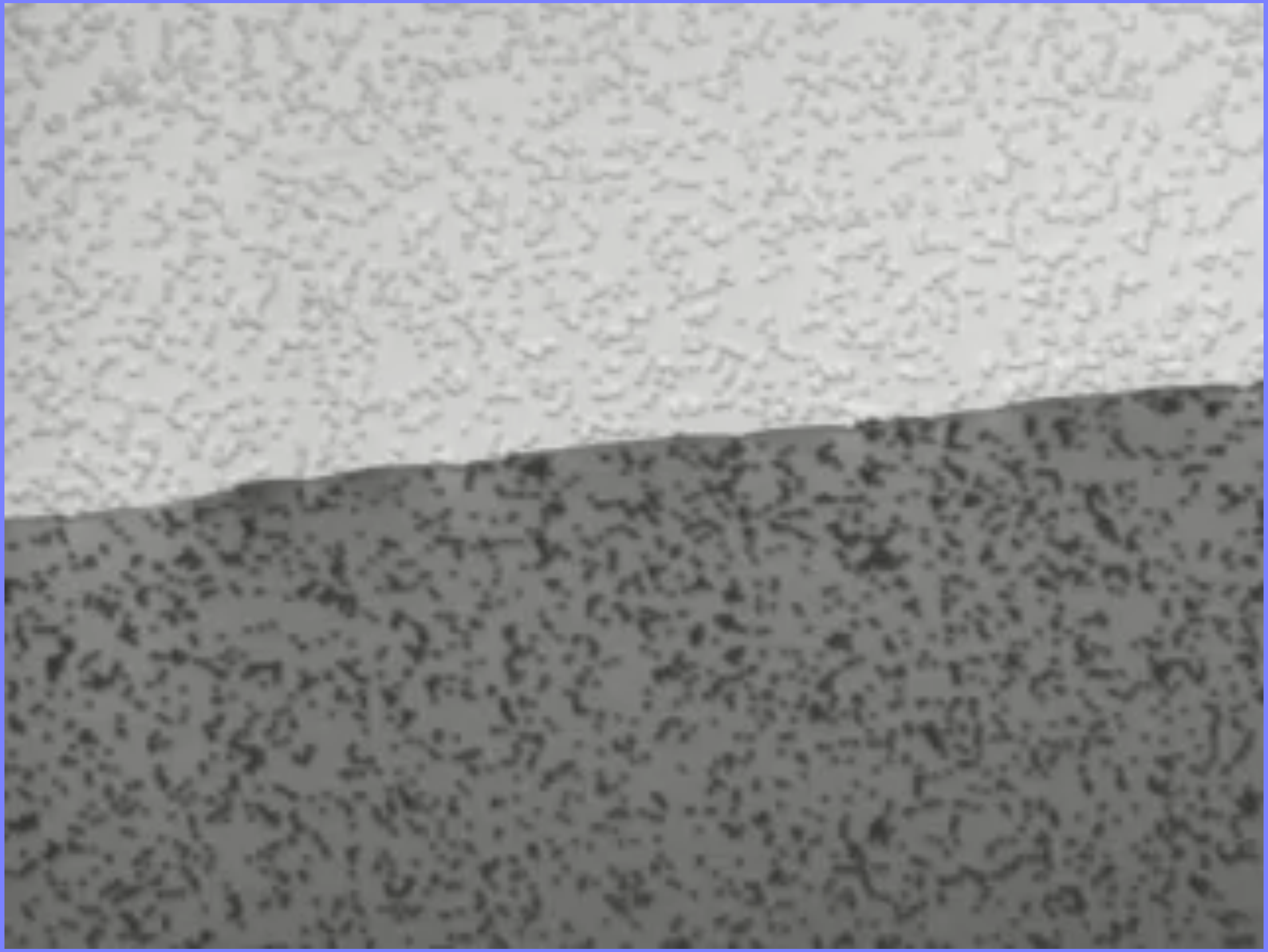
→ FORCE of ADHESION resists drop motion

increases with $\Delta\theta = \theta_a - \theta_r$

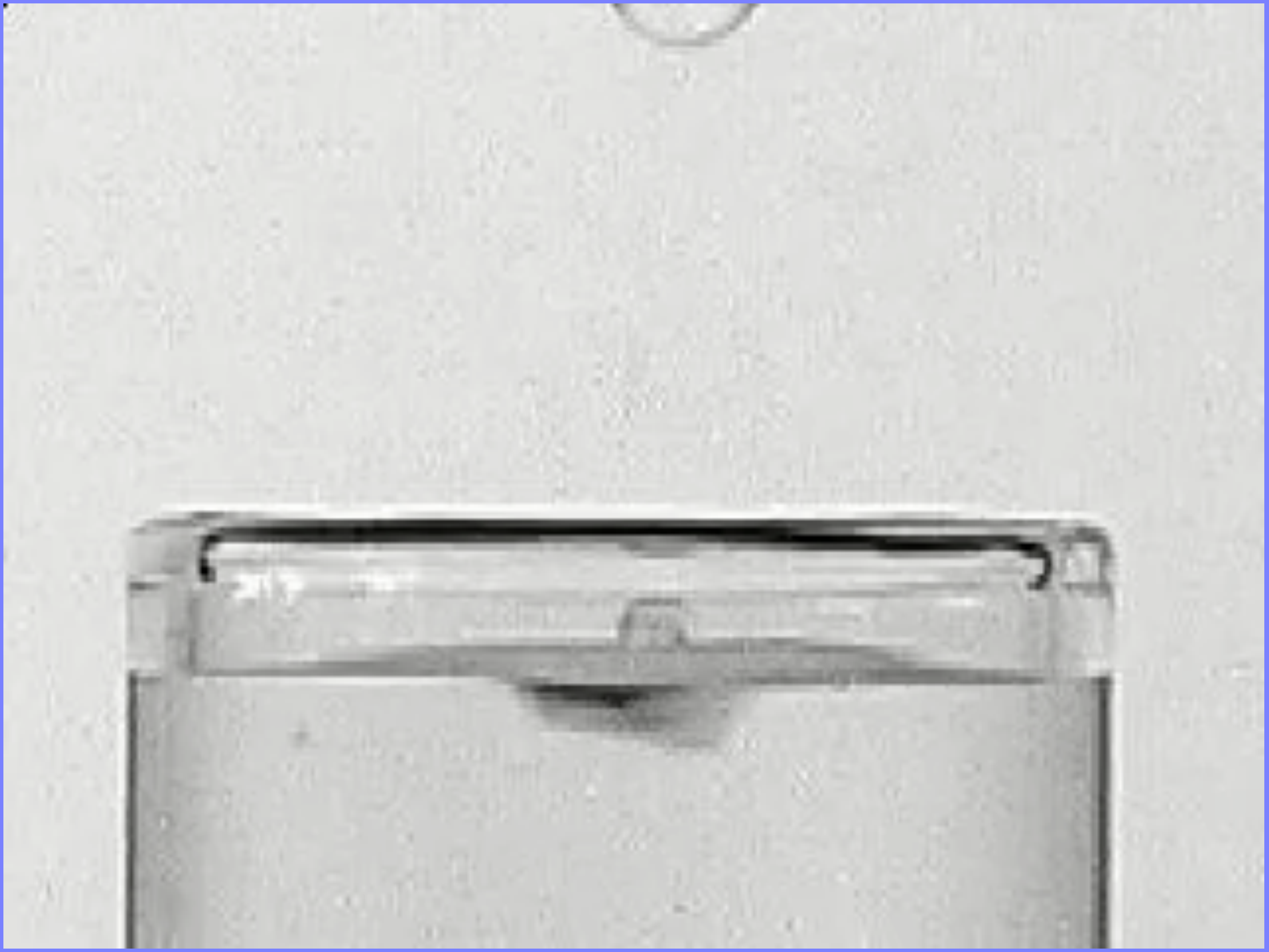
Origins: advancing contact lines pinned on surface irregularities

The origins of contact angle hysteresis

- motion of contact line past chemical/textural irregularities is energetically costly



Contact angle pinning on corners

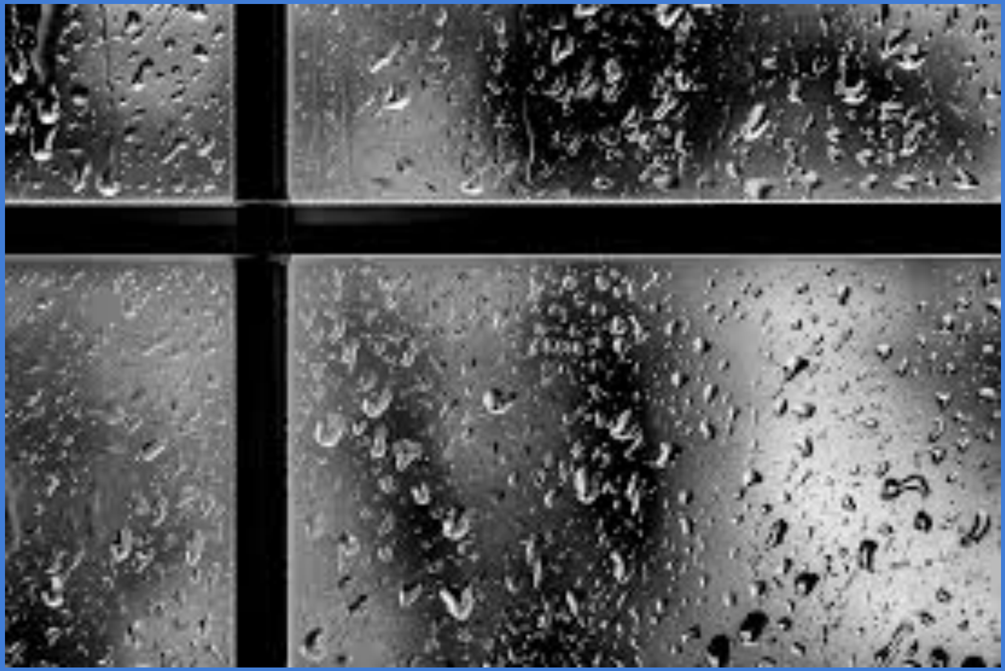


Reduce contact angle hysteresis via cleaning

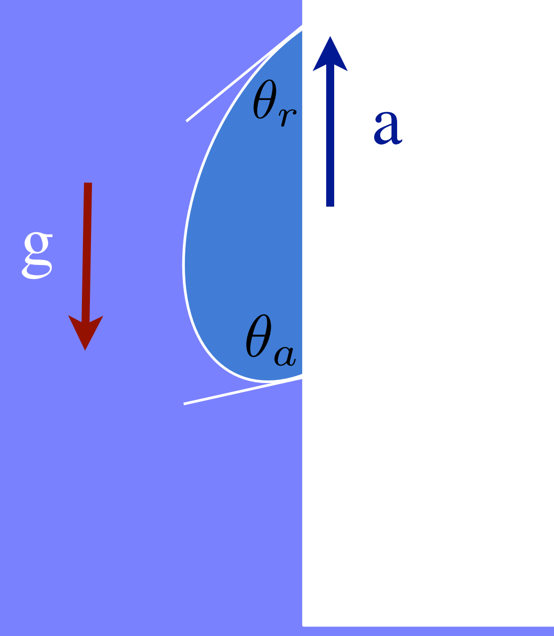
Manifestations of contact angle hysteresis

- liquid slug in a capillary tube
- drops stick to solids

The raindrop paradox



The force of adhesion (Dussan & Chow 1983)



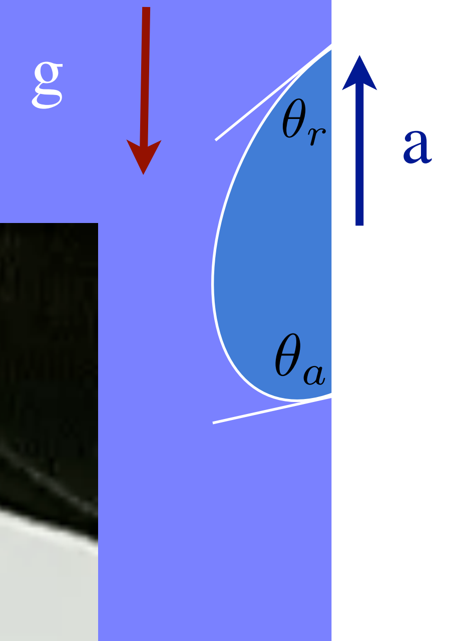
Raindrop stuck on a window

- small drops supported by contact line resistance

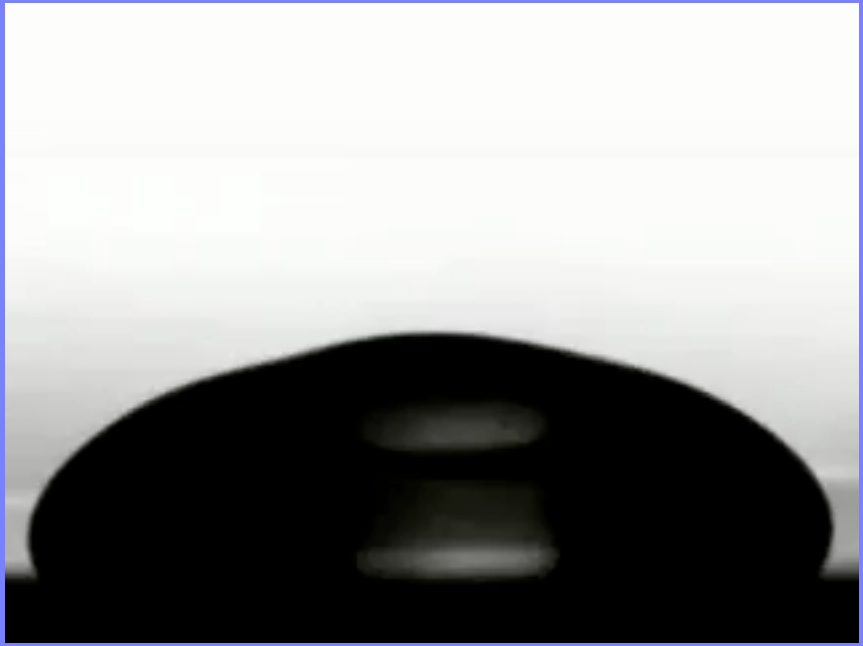
$$F_c \sim 2\pi a \, \sigma \, (\cos \theta_r - \cos \theta_a)$$

- drops grow by accretion until weight prompts rolling

The triumph of gravity over contact forces



Overcoming contact forces via vibration

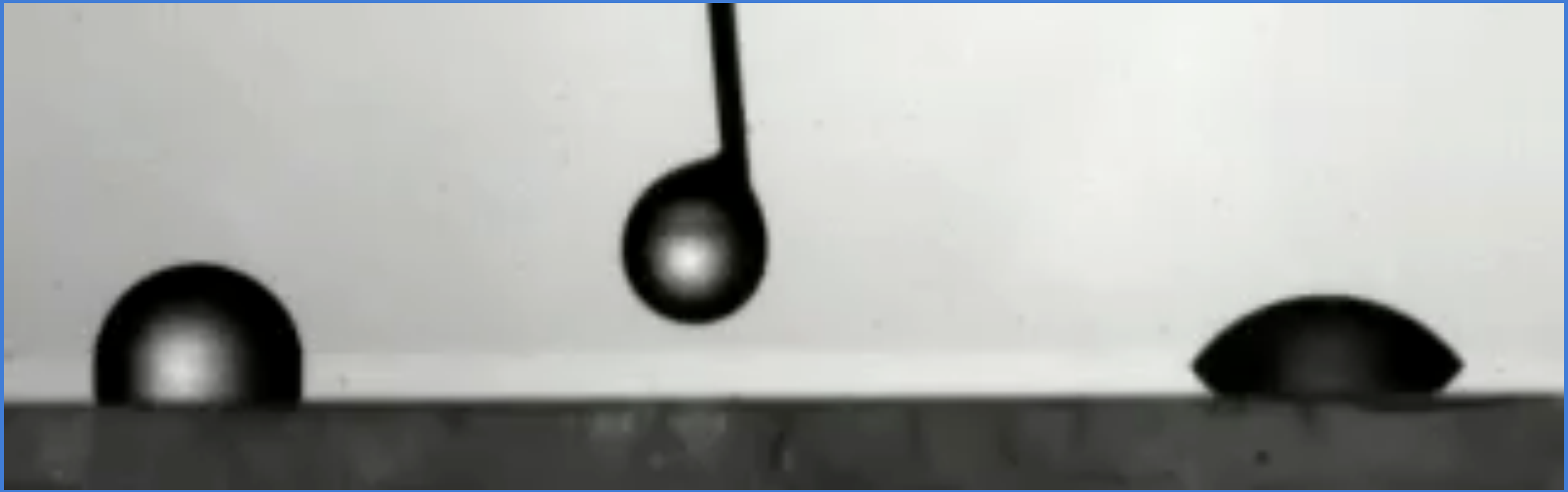


- force at drop's natural frequency

$$\rho U^2 \approx \sigma / R$$

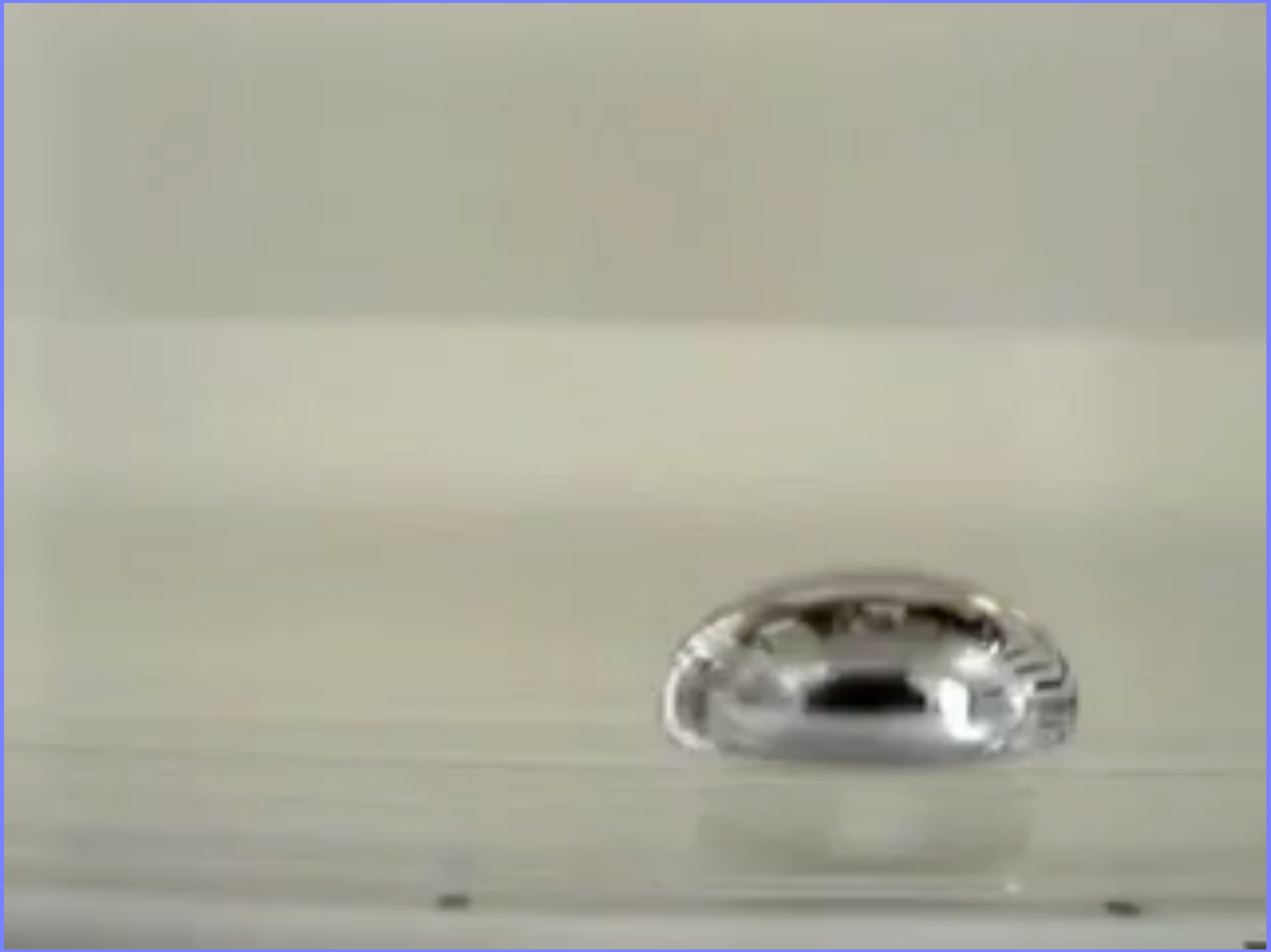
$$\omega \sim \left(\frac{\sigma}{\rho R^3} \right)^{1/2}$$

Spontaneous motion in response to a wettability gradient



- lateral chemical force must overcome contact force

Spontaneous motion in response to a chemical gradient



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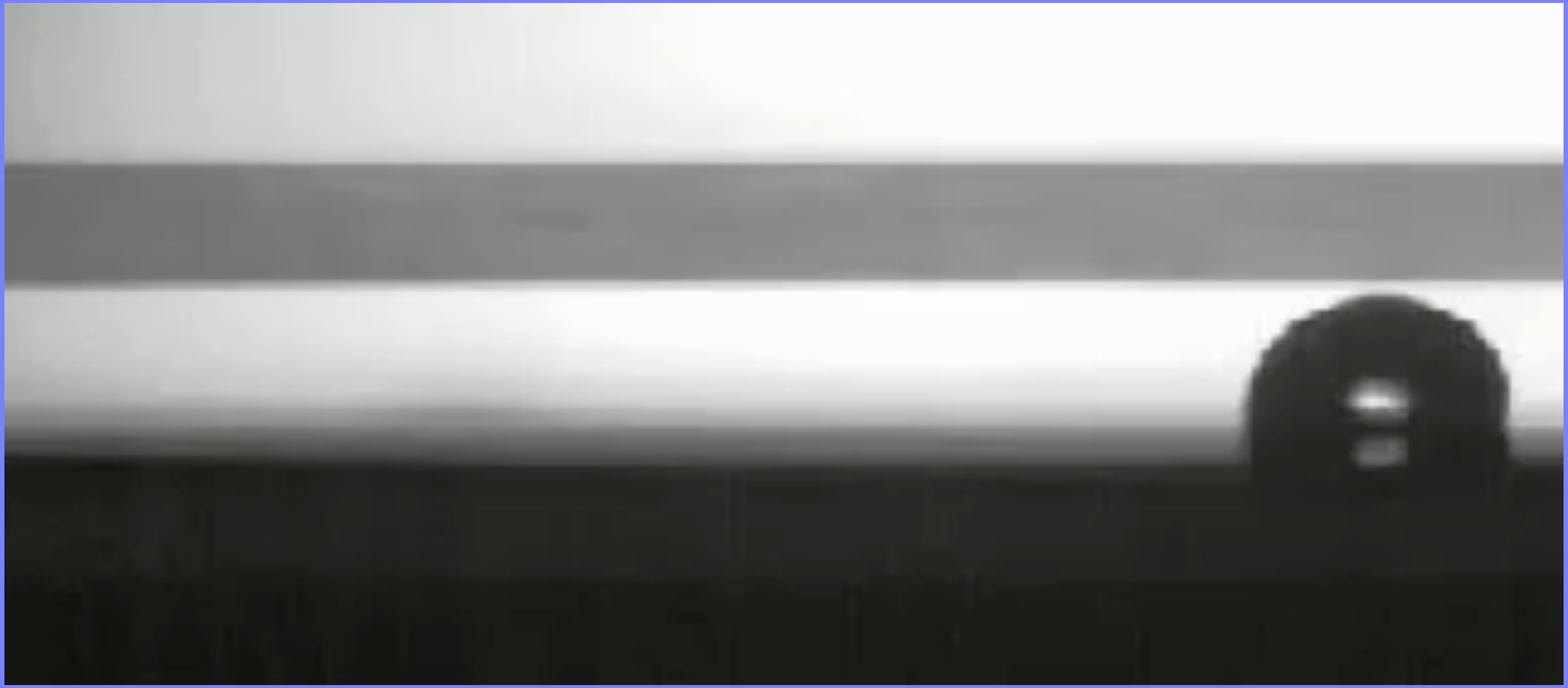
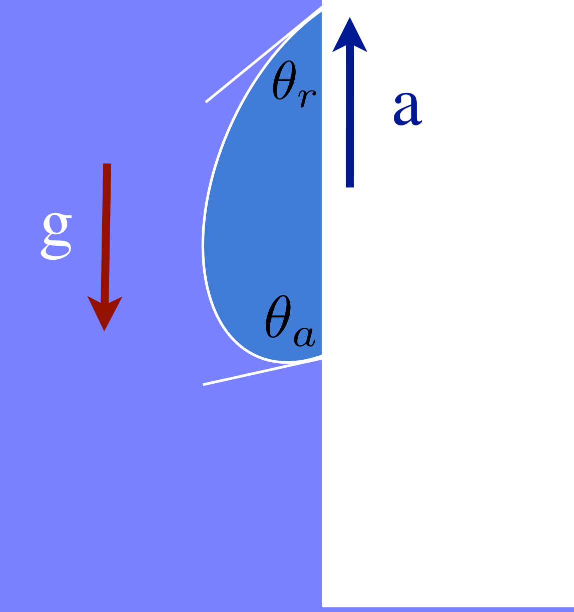
Propulsion via contact angle hysteresis and vibration



- exploited by a class of shorebirds for feeding

The force of adhesion (Dussan & Chow 1983)



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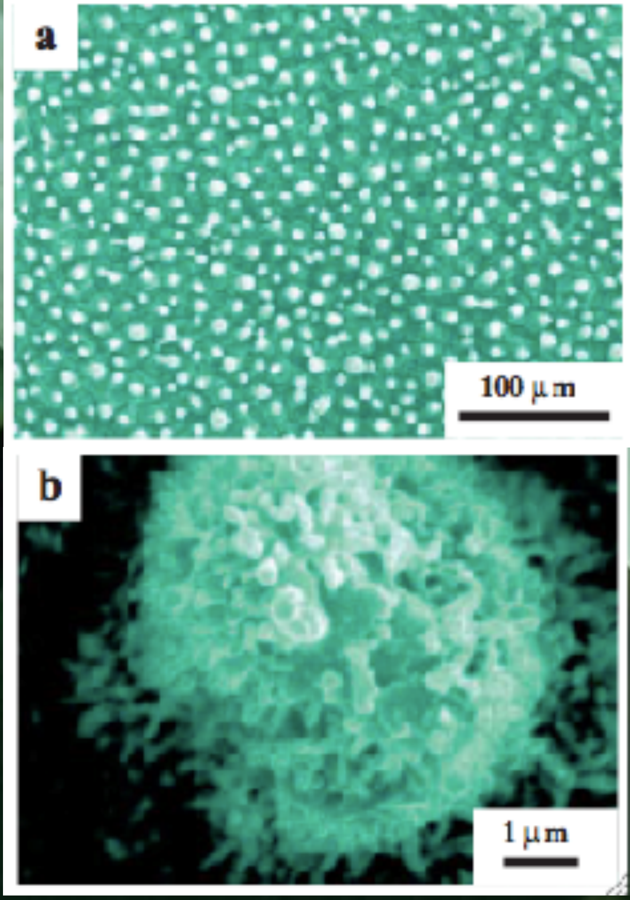
Water-repellency

- impinging drops roll off rather than adhering
- requires large θ_e , small $\Delta\theta = \theta_a - \theta_r$

How can we reduce the force of adhesion?

Water repellency in nature

"One who performs his duty without attachment, surrendering the results unto the Supreme Being, is unaffected by sinful action, as the lotus leaf is untouched by water."
Bhagavad Gita 5.10



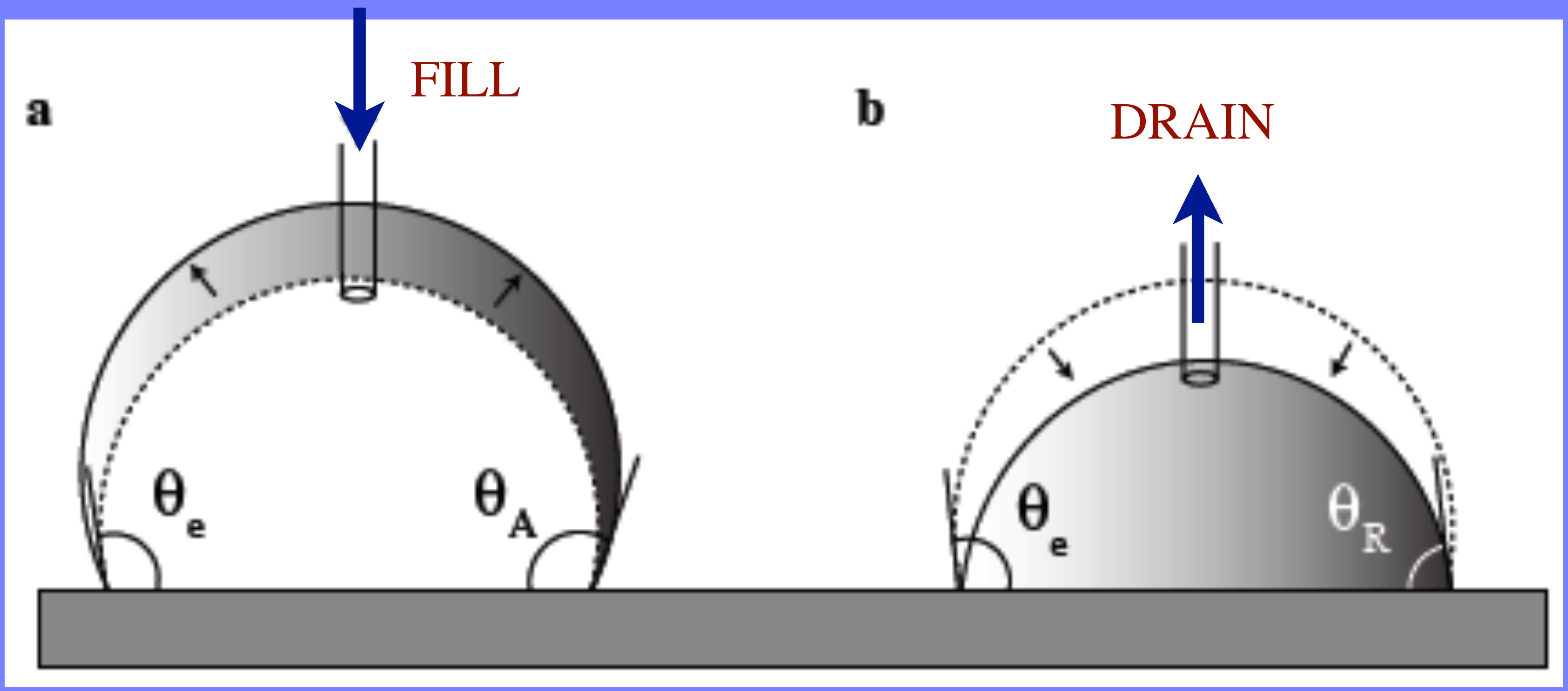
Feng et al. (2004)

- the lotus leaf is superhydrophobic and self-cleaning by virtue of its waxy surface roughness

Contact angle hysteresis

Static contact angle is not uniquely θ_e

Reality: drop is stable over a range of $\theta_r < \theta < \theta_a$



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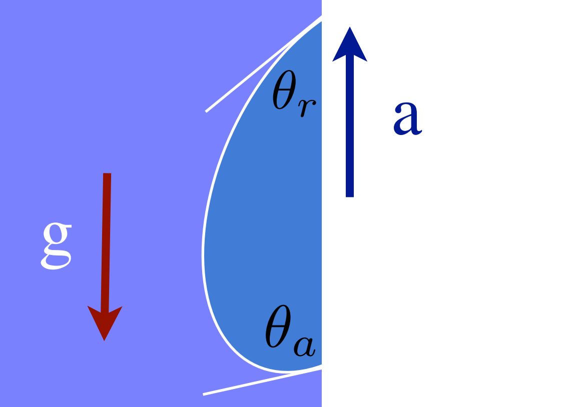

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18.357: Lecture 16

The wetting of textured solids

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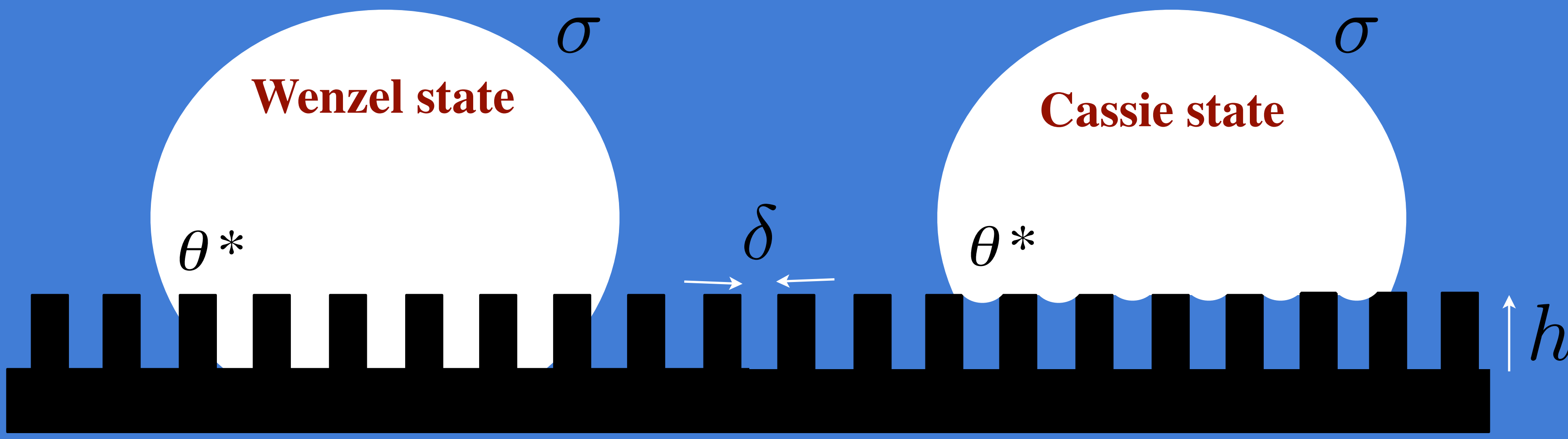
Wetting of a rough hydrophobic surface: Wenzel vs. Cassie



$$dW = r\, dx\, (\sigma_{SG} - \sigma_{SL}) - dx\, \sigma\, cos\theta^*$$

$$\cos\theta^* = r\, \cos\theta$$

where r is total/planar area

θ^* INCREASES, but $\Delta\theta$ INCREASES

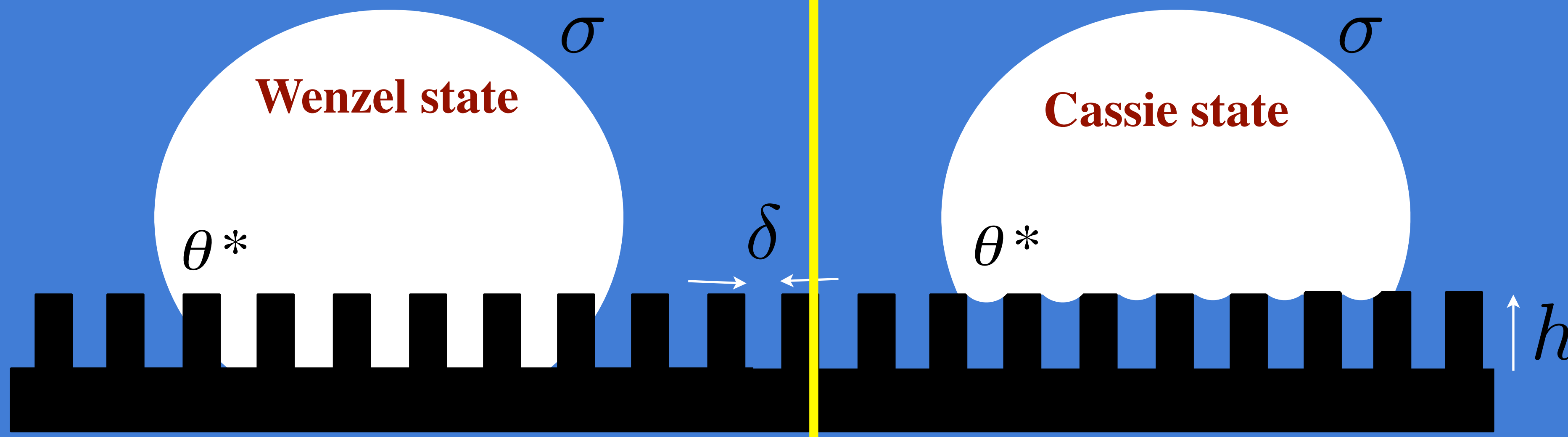
$$\cos\theta^* = -1 + f_s + f_s \cos\theta$$

where f_s is exposed/planar area

θ^* INCREASES

$\Delta\theta$ DECREASES

Wetting of a rough hydrophobic surface: Wenzel vs. Cassie



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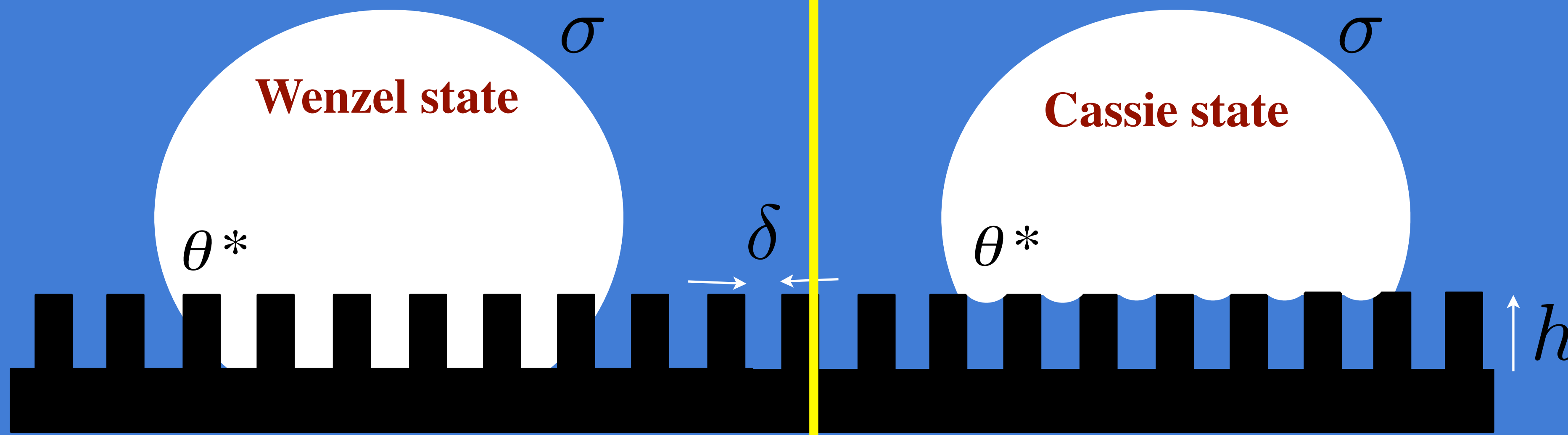

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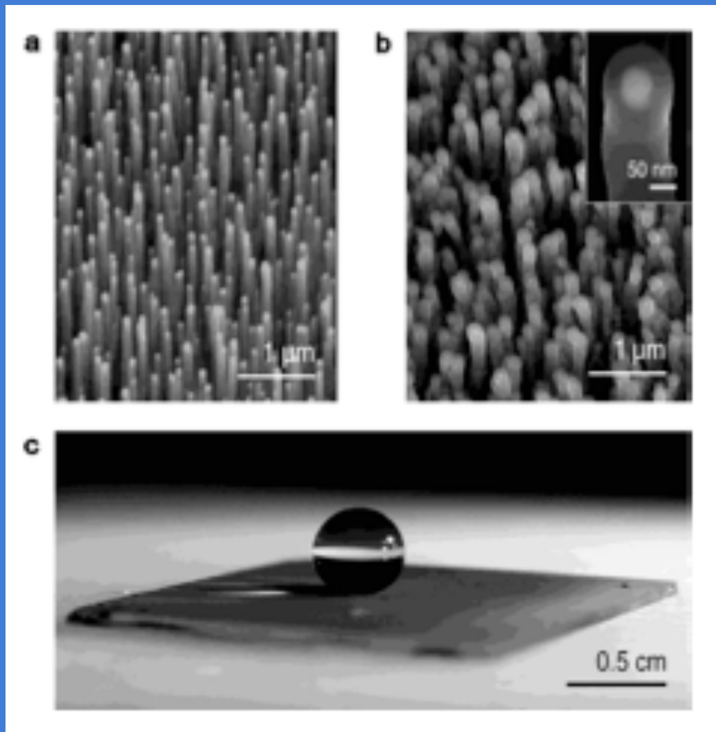
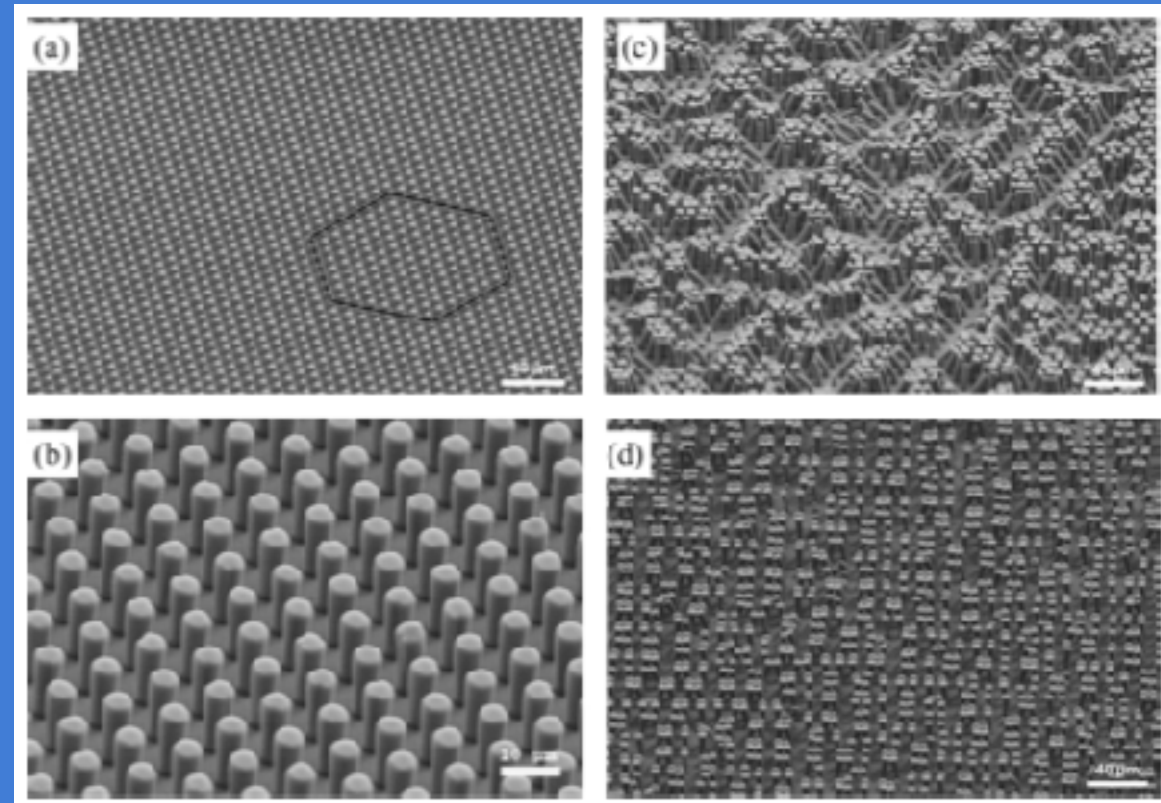
Water-repellency: requires the maintenance of a Cassie state

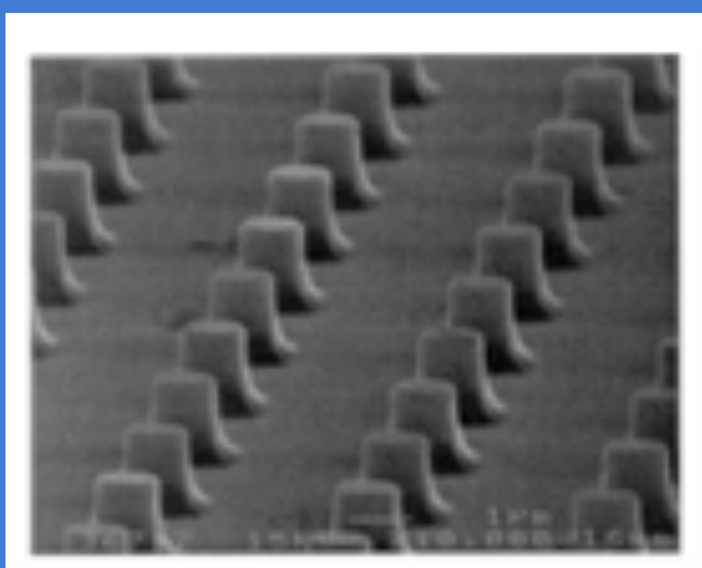
Biomimetic water-repellent surfaces: viable with new microfab techniques



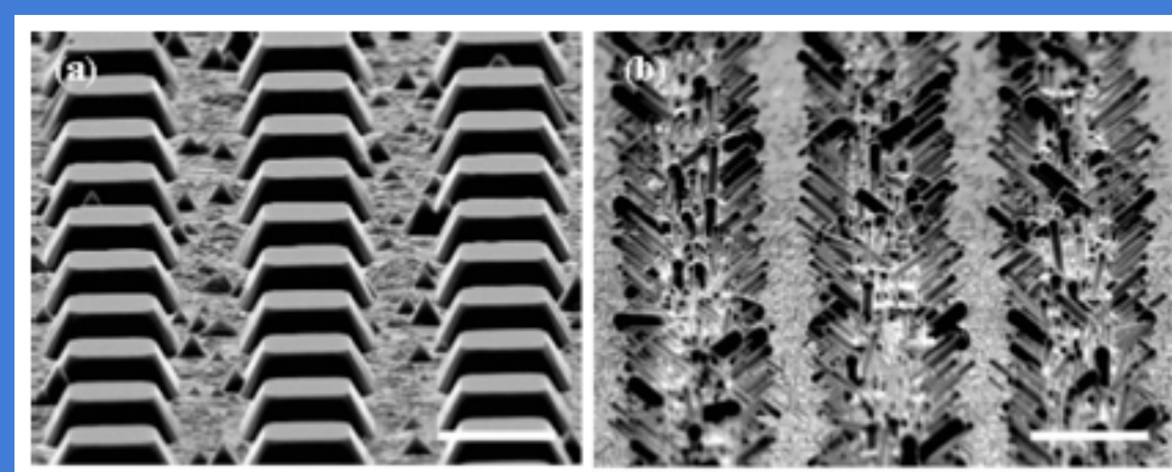
Lau et al. (2003)



Greiner et al. (2007)



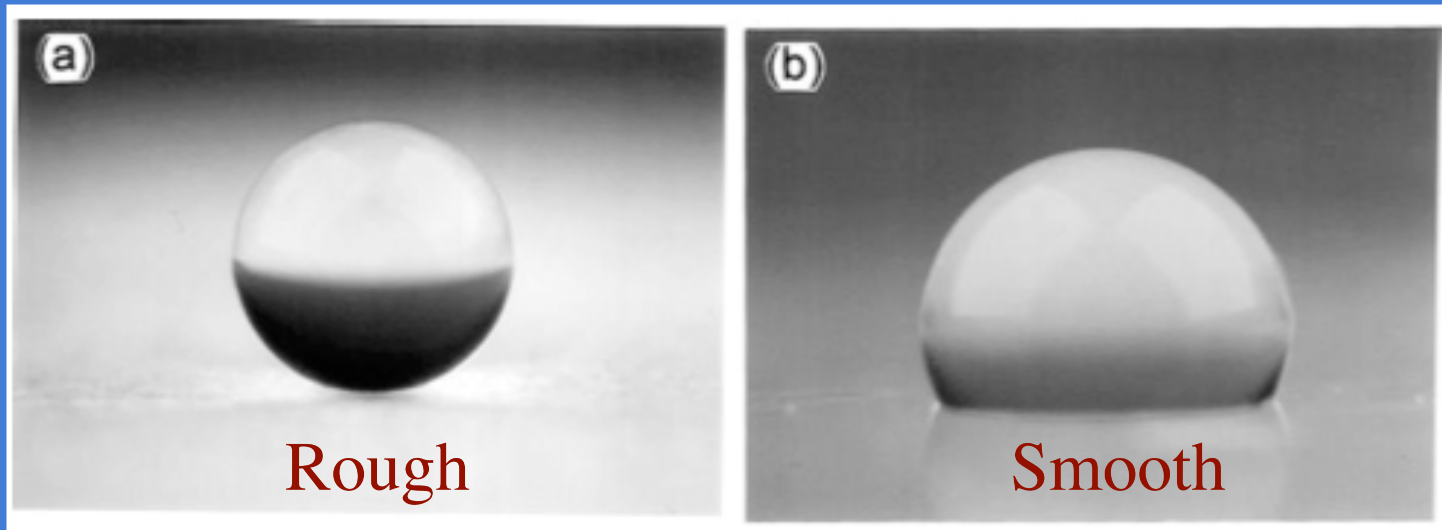
Bico et al. (1999)

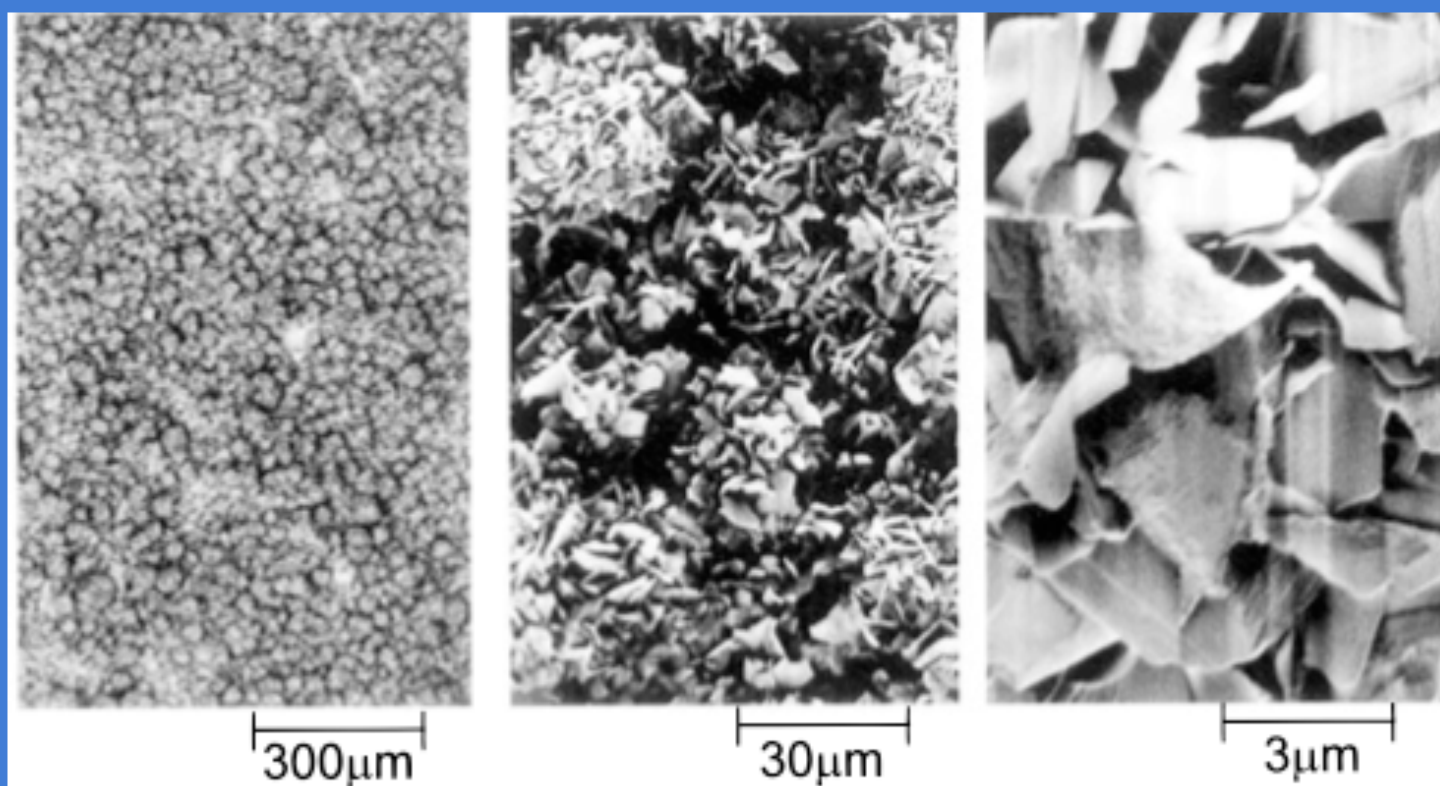


Cao et al. (2007)

Superhydrophobic surfaces achieved with fractal texturing

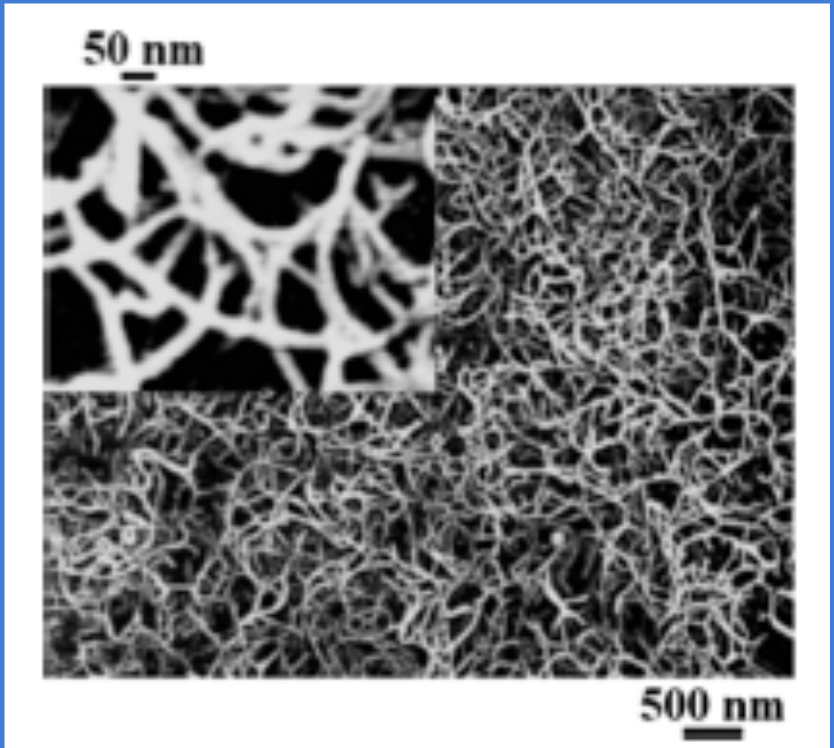
Shibuichi et al. (1996), Onda et al. (1997), Herminghaus (2000)





A perfectly hydrophobic surface

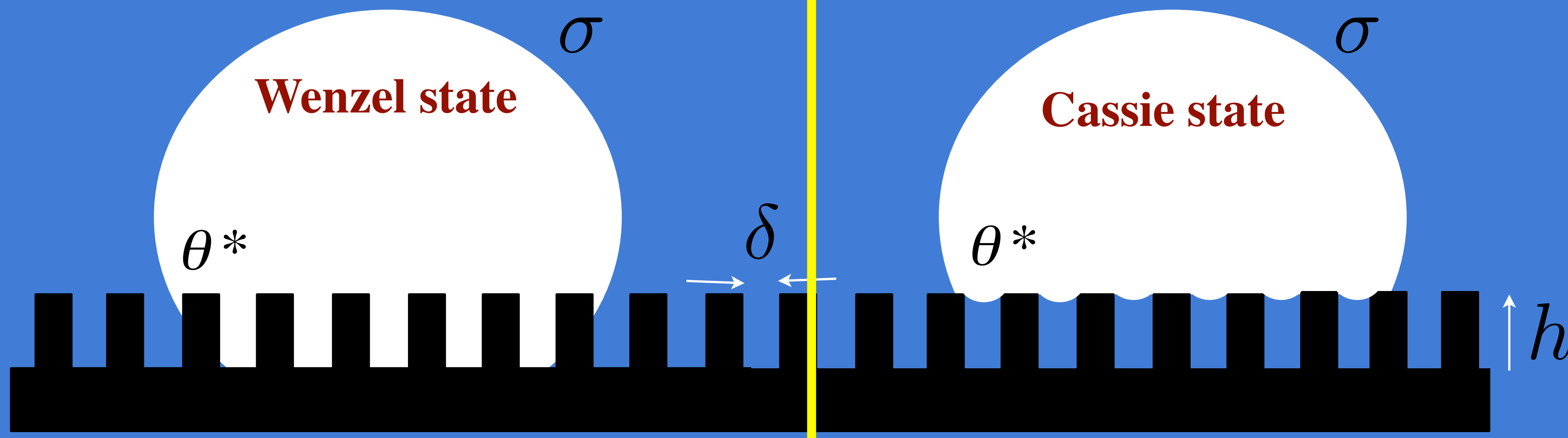
Gao & McCarthy (2006)



"The Lichao surface"

$$\theta = \theta_A = \theta_R = 180^\circ$$

Wetting of a rough hydrophobic surface: Wenzel vs. Cassie



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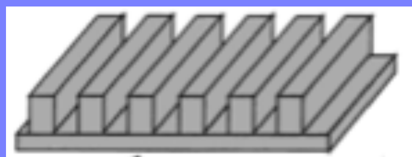
Water-repellency: requires the maintenance of a Cassie state

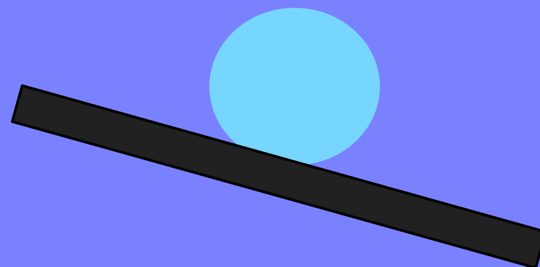
$$\rightarrow \quad P_{applied} < \sigma \left(\frac{1}{\delta}, \frac{h}{\delta^2} \right)$$

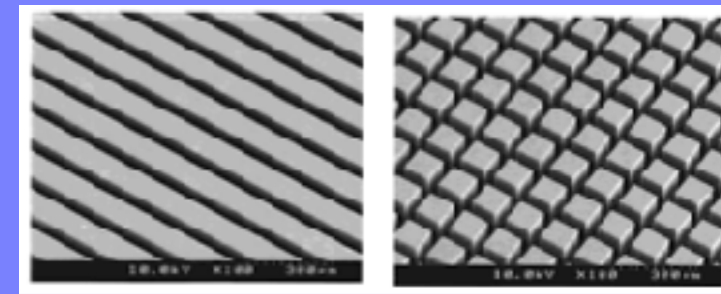
Bartolo et al. (2006)
Reyssat et al. (2007)

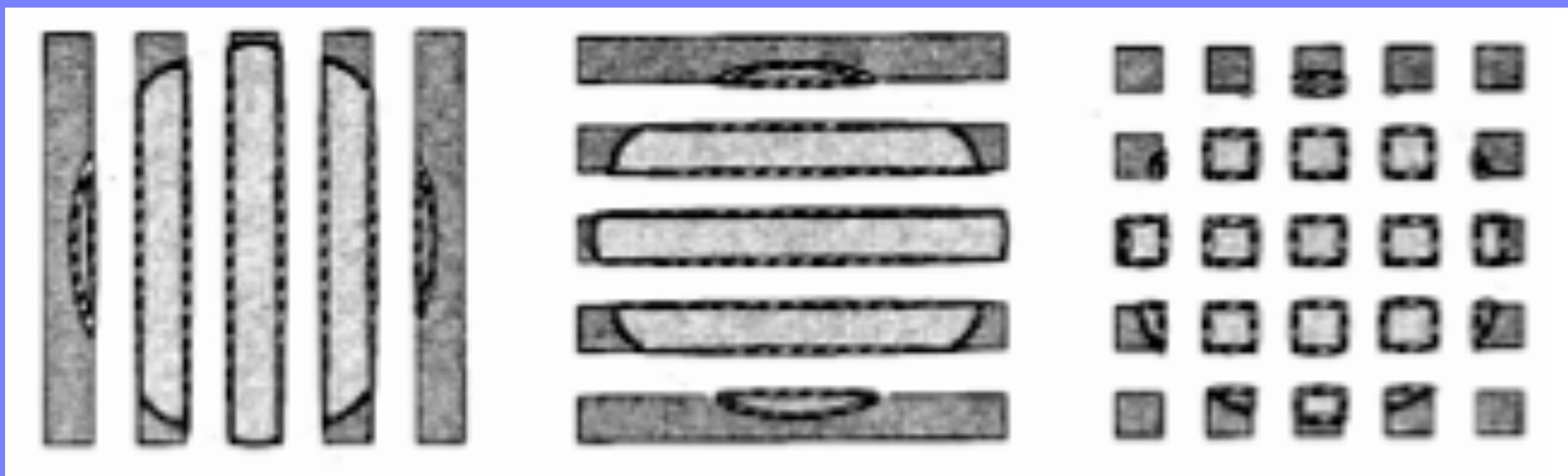
Surface texturing and directional adhesion

Yoshimitsu et al. (2002)







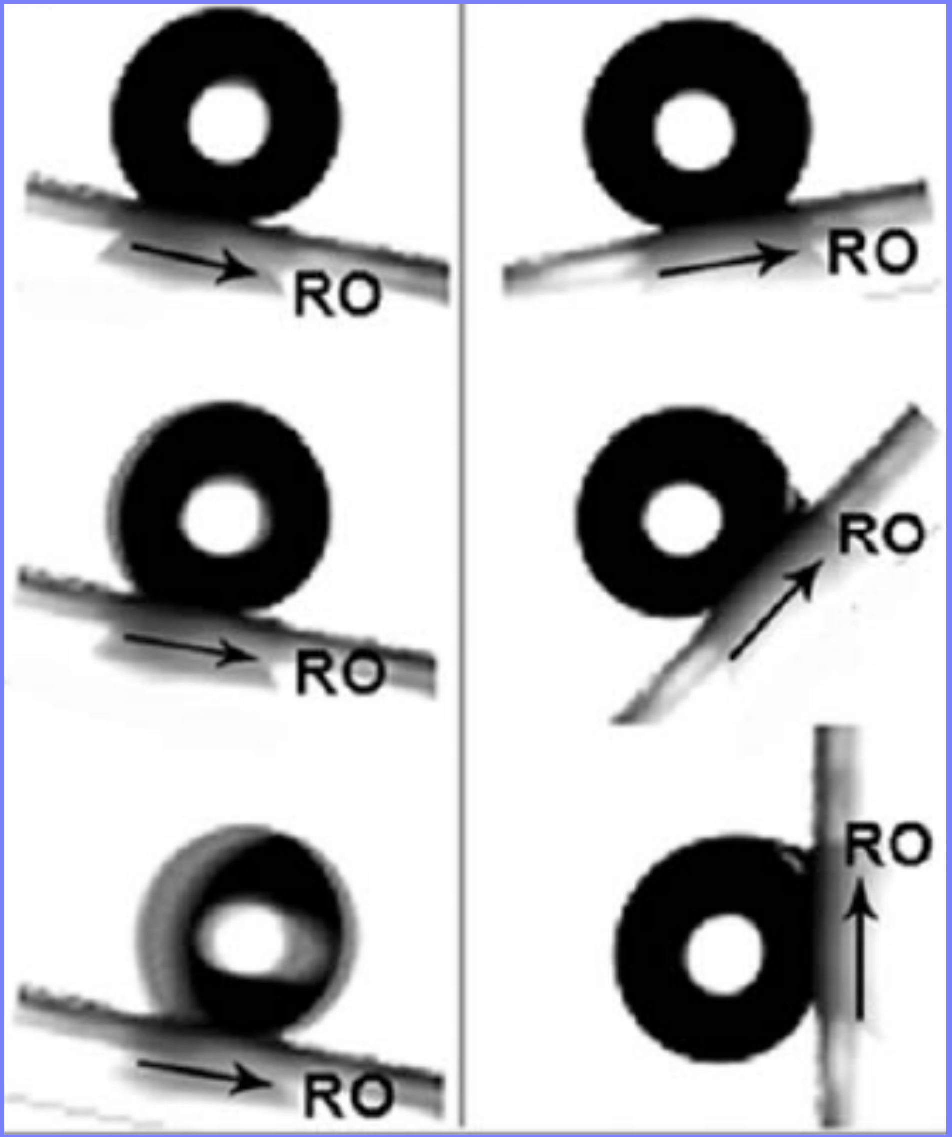


- drops move most easily along nanogrooves
- greatest resistance to motion perpendicular to grooves
- texturing introduces anisotropy in contact line resistance

Unidirectional adhesion

on the butterfly wing

Zheng et al. (2007)



Unidirectional adhesion

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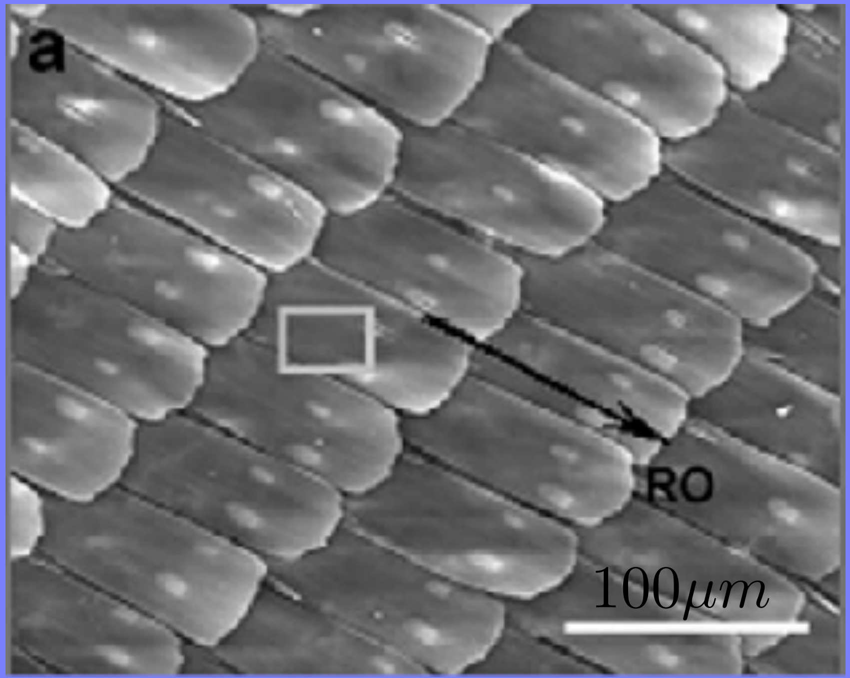
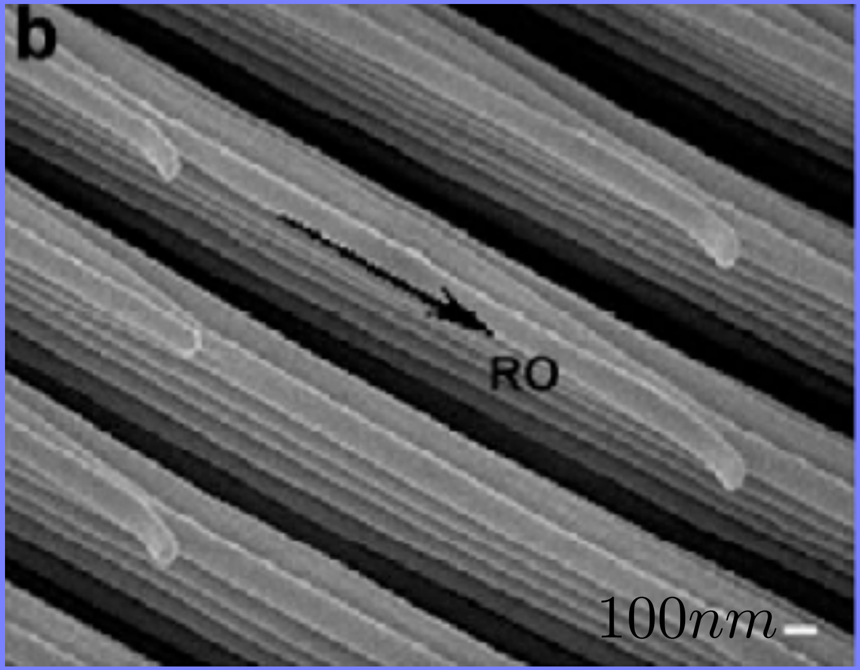
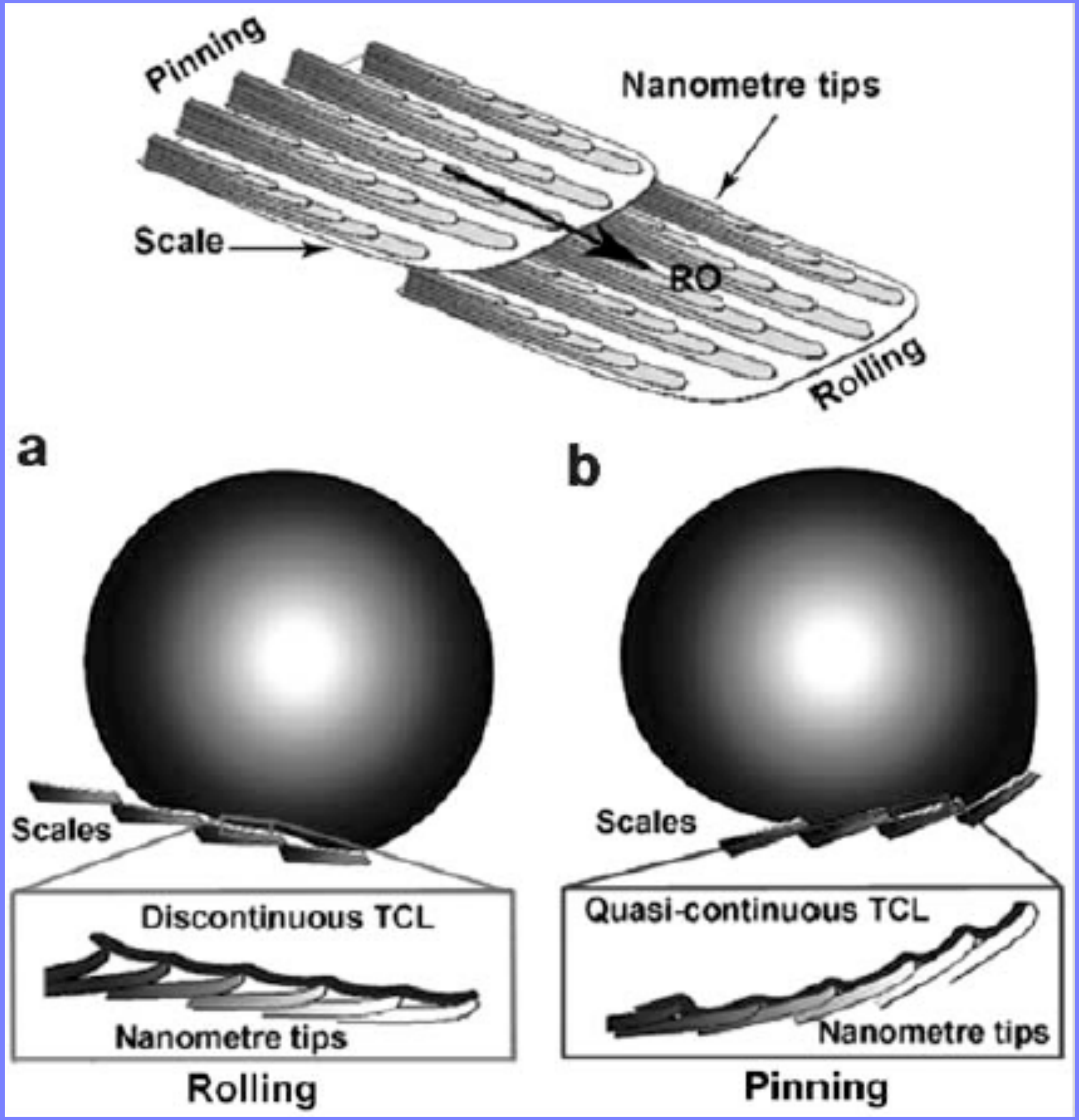
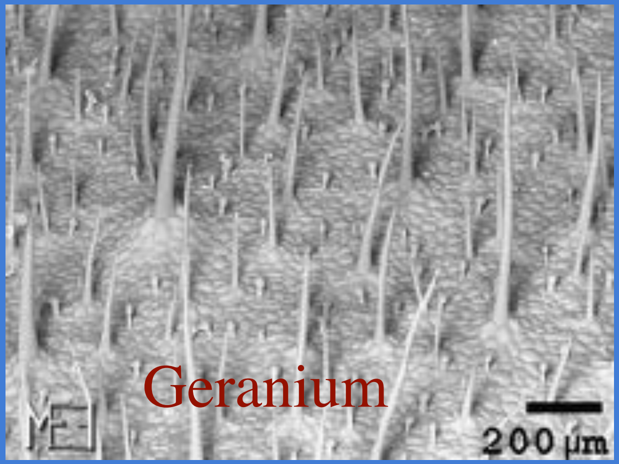
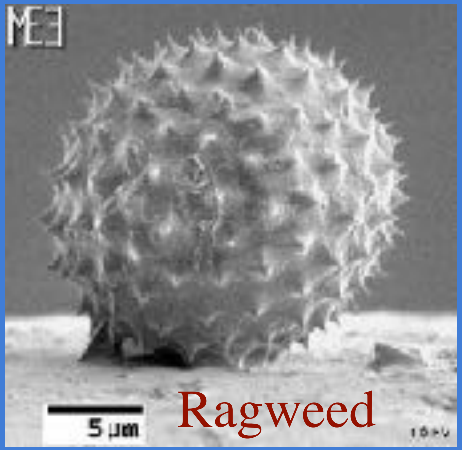






Plants are bumpy: isotropic roughness provides water-repellency

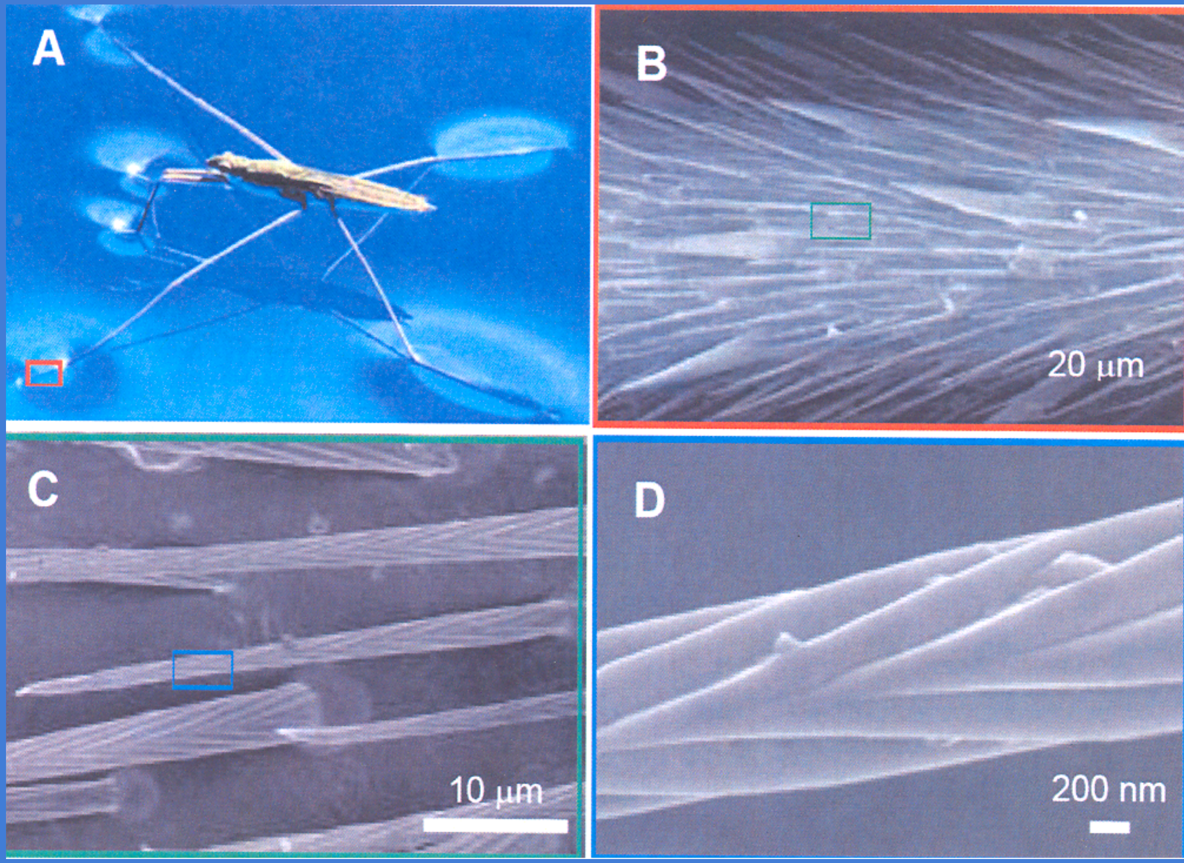




Water-walking bugs are hairy

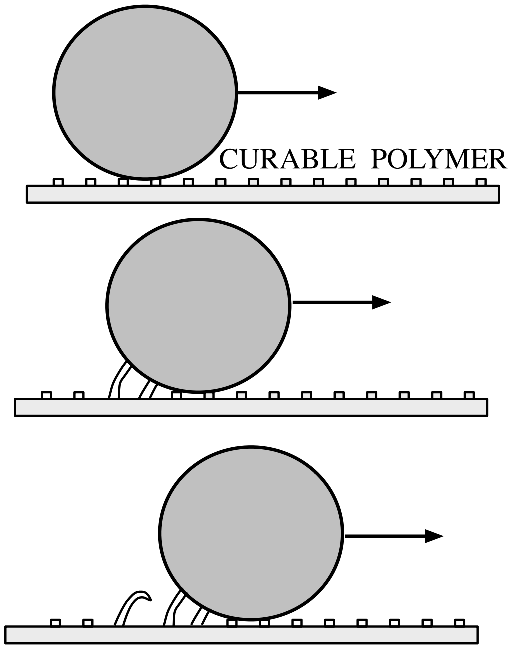
- roughness provides water-repellency
- driving leg exhibits unidirectional adhesion
- anisotropic roughness facilitates **propulsion**

(Prakash & Bush 2011)

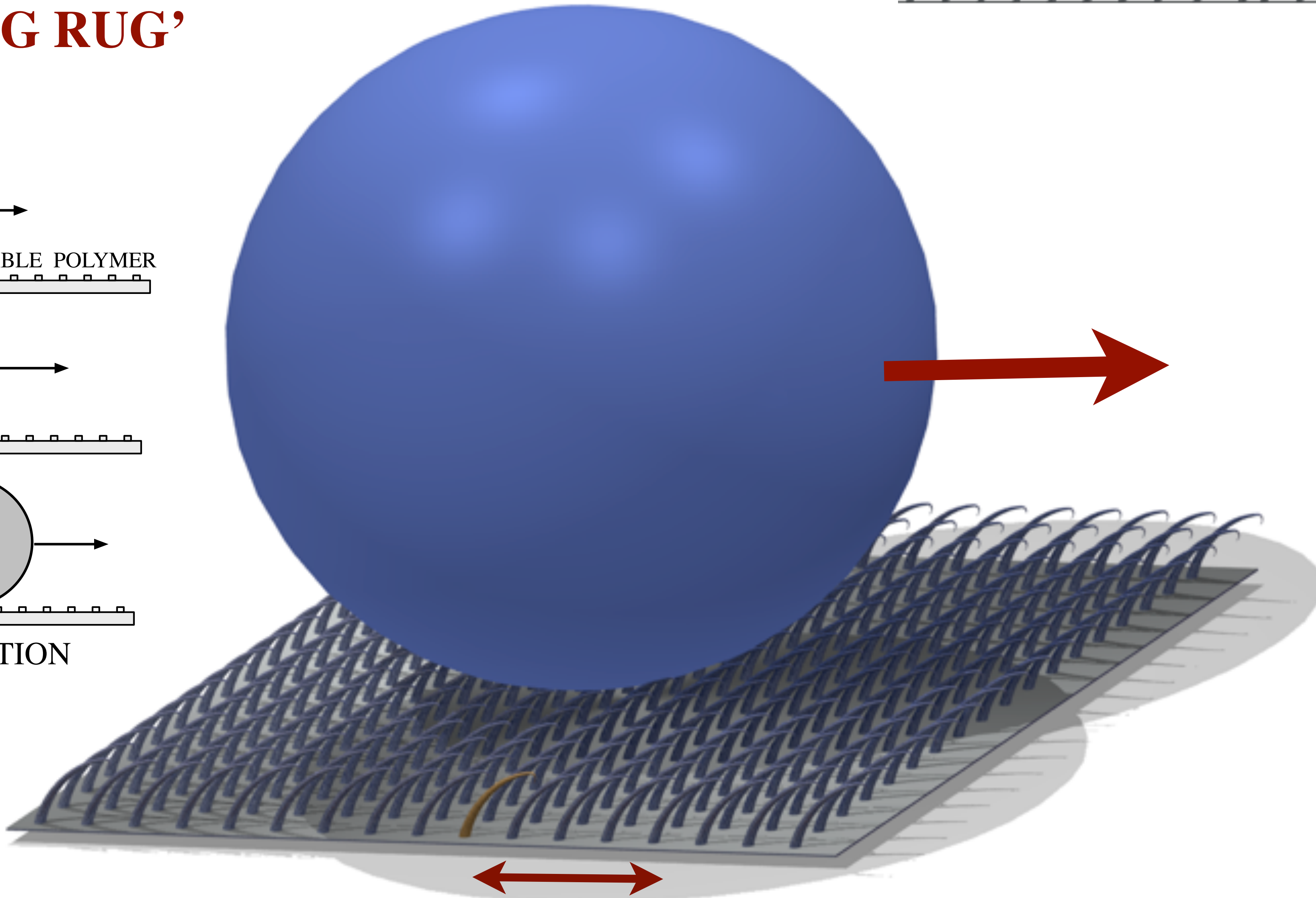


Biomimetic unidirectional surface

`THE BUG RUG'

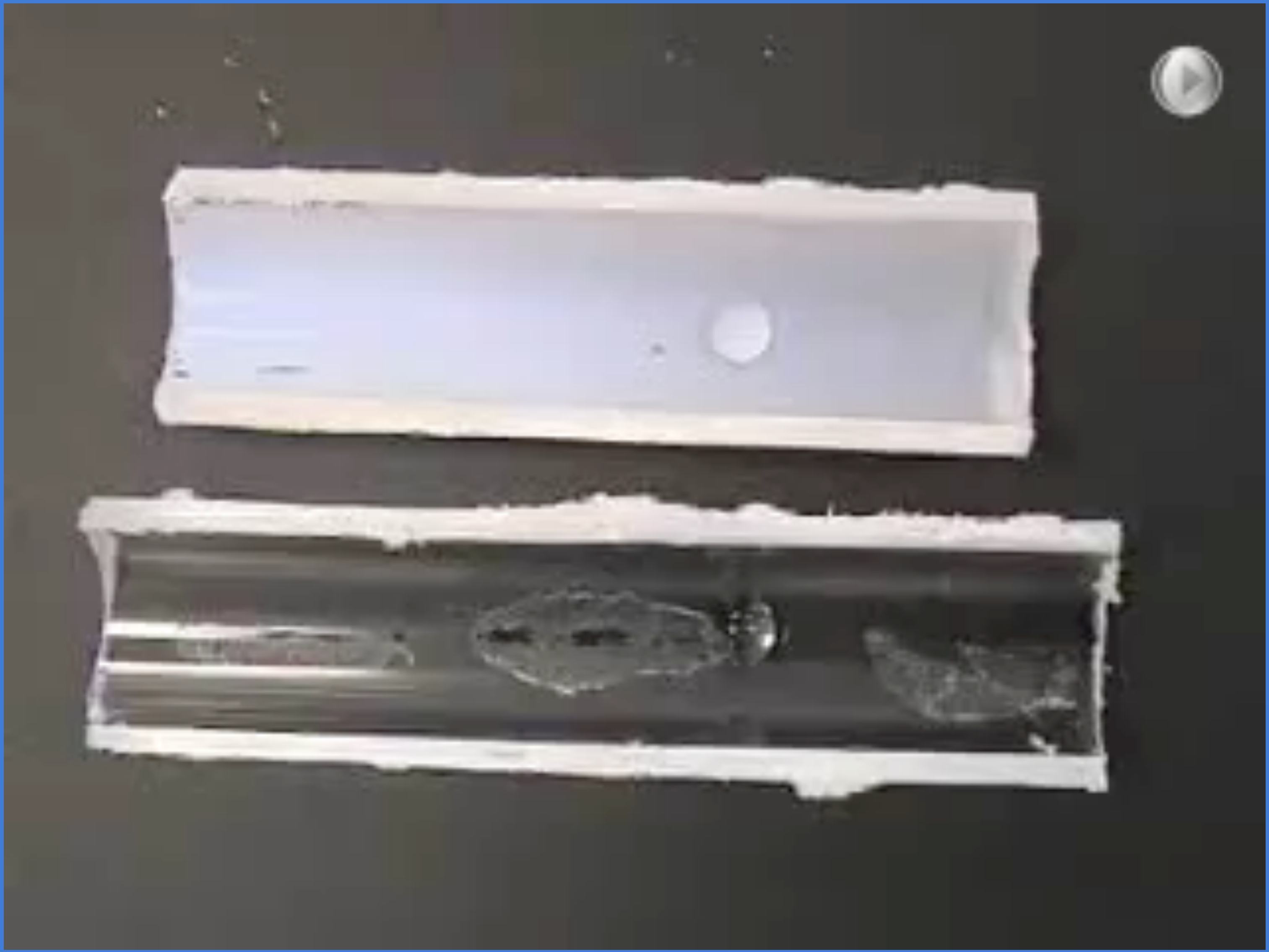


FABRICATION

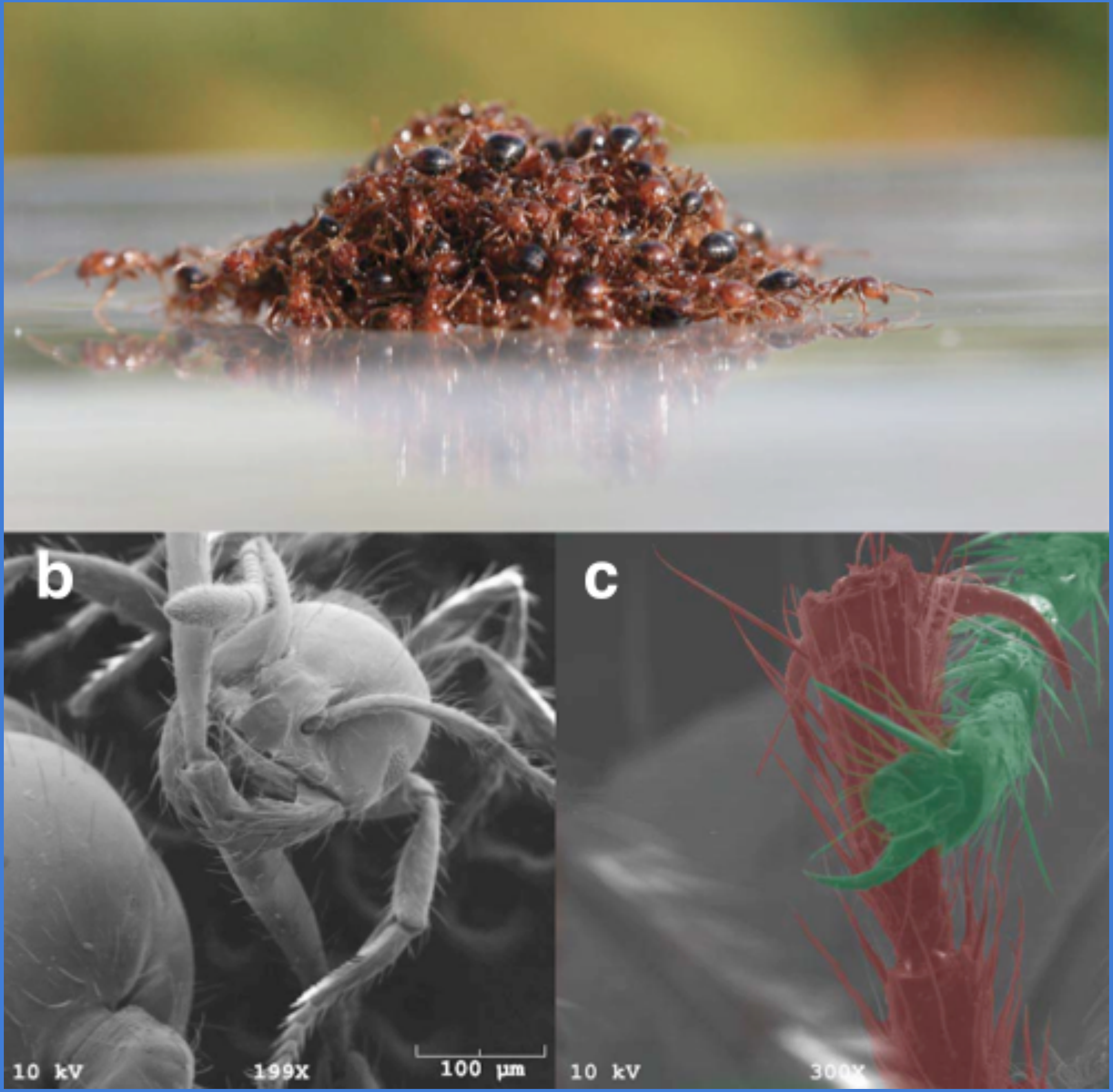


- permits drop motion in only one direction
- applications in directional draining, microfluidics

Vibration-induced motion on a directional surface



The ant raft: a self-assembling superhydrophobic surface



Mlot et al. (2011)