Contact angle hysteresis,
The wetting of textured solids

John W. M. Bush

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Fluid-Solid Contact: WETTING

Equilibrium contact angle $\theta_e$

Energy differential: 
\[ dW = dx \left( \sigma_{SG} - \sigma_{SL} \right) - dx \sigma \cos \theta_e \]

Young’s relation:
\[ \sigma \cos \theta_e = \sigma_{SL} - \sigma_{SG} \]

Hydrophobic surface

Hydrophilic surface

$\theta_e > \pi/2$ $\theta_e < \pi/2$
Total wetting on a flat solid
Partial wetting on a flat solid
<table>
<thead>
<tr>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
</tr>
<tr>
<td>Plexiglas</td>
</tr>
<tr>
<td>Wax</td>
</tr>
</tbody>
</table>

Partial wetting
methylnaphtalene  \( \gamma = 20 \text{ mN/m} \)

water  \( \gamma = 73 \text{ mN/m} \)

mercury  \( \gamma = 500 \text{ mN/m} \)
<table>
<thead>
<tr>
<th>Fluorinated Oil</th>
</tr>
</thead>
<tbody>
<tr>
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$\theta_e > \pi/2$  $\theta_e < \pi/2$

Hydrophobic surface  Hydrophilic surface
The raindrop paradox
Contact angle hysteresis

Static contact angle is not uniquely $\theta_e$

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

- lateral chemical force must overcome contact force
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 \( \theta_e \), 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

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

Feng et al. (2004)
Contact angle hysteresis

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The wetting of textured solids

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Wetting of a rough hydrophobic surface: Wenzel vs. Cassie

**Wenzel state**

\[ \cos \theta^* = -1 + \frac{f_s}{\delta} \cos \theta \]

where \( f_s \) is exposed/planar area

**Cassie state**

\[ \cos \theta^* = r \cos \theta \]

where \( r \) is total/planar area

\[ dW = r \, dx \left( \sigma_{SG} - \sigma_{SL} \right) - dx \sigma \cos \theta^* \]

\[ \theta^* \text{ INCREASES, but } \Delta \theta \text{ INCREASES} \]

\[ \Delta \theta \text{ DECREASES} \]
Wetting of a rough hydrophobic surface: Wenzel vs. Cassie

Wenzel state
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dW = r \, dx \, (\sigma_{SG} - \sigma_{SL}) - dx \, \sigma \cos \theta^* \]
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\cos \theta^* = r \cos \theta
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Cassie state
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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
A perfectly hydrophobic surface

\[ \theta = \theta_A = \theta_R = 180^\circ \]

"The Lichao surface"

Gao & McCarthy (2006)
Wetting of a rough hydrophobic surface: Wenzel vs. Cassie

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Water-repellency: requires the maintenance of a Cassie state

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

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

Zheng et al. (2007)
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'

- 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)