Multiphase Flow and Heat Transfer

Contact Angle

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Contact Angle Hysteresis

CAH = \theta_a - \theta_r

The immersion and removal sequence illustrating advancing and receding contact angles
Three Different Contact Angles

1. Static contact angle
2. Receding contact angle
3. Advancing contact angle

For a real surface

$$\theta_{\text{rec}} < \theta_{\text{stat}} < \theta_{\text{adv}}$$
Contact Angle Hysteresis

Generally acknowledged to be a consequence of three factors:

1. Surface inhomogeneity
2. Surface roughness
3. Impurities on the surface

For an idealized solid surface that is perfectly smooth, clean and homogeneous in composition, \( \theta_a = \theta_r \).
Applications of Contact Angle Hysteresis

- Coating processes (dynamic hysteresis)
- Digital microfluidics and evaporation of droplets leading to the well-known coffee stain
- Immersion lithography
- Fiber coatings
- Ink-jet printing

Lithography works on the principle that grease and water repel each other. There is no carving involved. The artist draws on a stone with a greasy crayon (hydrophobic) and then covers the stone with a thin film of water. The oily ink (rolled over the surface) will stick to the greasy image but not to the water-covered areas.
Applications of Contact Angle Hysteresis

- In some cases, hysteresis is a problem (immersion lithography) while in others it is essential (dip-coating).
- Determining and controlling contact angle hysteresis are critical for the operation of these industrially relevant systems.
Effects of surface inhomogeneity and roughness on the apparent contact angle for advancing and receding liquid fronts.
Liquid Droplet to Resist Downward Motion

(a) Liquid
   Solid

(b) Liquid
   Solid

Contact Angle
CAH can allow a liquid slug in a small vertical tube to resist downward motion.

\[
P_1 - P_2 = \frac{2\sigma}{r_{\text{top}}}
\]

\[
P_4 - P_3 = \frac{2\sigma}{r_{\text{bottom}}}
\]

\[
P_4 - P_1 = \rho_g g L
\]

\[
P_3 - P_2 = \rho_l g L
\]

\[
2\sigma \left( \frac{1}{r_{\text{top}}} - \frac{1}{r_{\text{bottom}}} \right) = (\rho_l - \rho_g) g L
\]

The length of a slug depends on CAH.
Coffee Stain Effect

- Coffee stain phenomenon - real undesired nuisance and a limiting physical factor in: inkjet printing of circuits, OLED displays, or drying of paint, and so on.
- For optimal efficiency the molecules should be distributed homogeneously, but in practice predominant at rim.

Illustration of coffee stain formation in Panel (a) and a microscope image of a coffee stain formed by fluorescently labeled 5 µm particles in Panel (b)
Coffee Stain Effect - Electrowetting

- Suppressed by applying electrowetting (EW) with an alternating voltage. Electric force that disturbs the force balance at contact line.

- EW with AC frequency alternatively increases and decreases the apparent contact angle essentially depinning the contact line, i.e., not allowing it to get struck to intrinsic roughness features on the surface.

Suppression of Coffee stain effect using electro wetting
Drop Allowed to Evaporate

As the drop evaporates

(a) Without EW leading to a pronounced coffee stain effect
(b) Treated with EW – leading to almost homogeneous residue
Hydrophilic and Hydrophobic Surfaces

- **Hydrophillic - water loving!**
  - When the solid has a high affinity for water
  - $\theta < 90^\circ$, water spreads
  - High surface energy eg., glass, metals
  - Superhydrophillic, $\theta < 5^\circ$

- **Hydrophobic - water repelling!**
  - $\theta > 90^\circ$, Water does not spread
  - A spherical cap resting on the substrate with $\theta$
  - Low energy e.g. teflon
  - Superhydrophobic, $\theta > 150^\circ$
Effect of Surface Roughness

\[ \theta_E = \text{Equilibrium contact angle of an ideal surface} \]
\[ \theta^* = \text{Apparent contact angle of a rough surface} \]

Two models:
- Wenzel state
- Cassie-Baxter state
In this state

- There are no air bubbles,
- Droplet is in good contact with the surface.
- Pinned droplet.

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

\[
r = \frac{\text{Real surface area} \ (A_{3D})}{\text{Projected surface area} \ (A_{2D})}
\]

\[\therefore \text{there are no real surfaces, } r > 1\]
Consequences of the Wenzel Equation

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

\[\vdash \text{there are no real surfaces, } r > 1\]

\[\implies \cos \theta^* > \cos \theta_E\]

**Hydrophilic:** \(\theta_E < 90^\circ\)

Say, \(\theta_E = 45^\circ\) and \(r = 1.2\),

Then \(\theta^* = 32^\circ\)

\(\theta^* < \theta_E\)

**Hydrophobic:** \(\theta_E > 90^\circ\)

Say, \(\theta_E = 135^\circ\) and \(r = 1.2\),

Then \(\theta^* = 148^\circ\)

\(\theta^* < \theta_E\)

Roughness makes a hydrophilic surface more hydrophilic

and a hydrophobic surface more hydrophobic.
Cassie-Baxter State

In this state

- Water sits on top tiny air bubbles
- Heterogeneous surface
- Adhesive force (water-solid) is extremely low
- Water droplets roll-off
- Self cleaning
- Generally for highly rough surfaces
Cassie-Baxter State

A special case:

\[ \cos \theta^* = -1 + \Phi_s (\cos \theta_E + 1) \]

\( \Phi_s \) - Ratio of solid in contact with liquid (0 \( \rightarrow \) 1)

If no solid is in contact,

\[ \Phi_s \rightarrow 0 \]
\[ \cos \theta^* \rightarrow -1 \]
\[ \theta^* \rightarrow 180^\circ \]
Petal Effect vs Lotus Effect

Water droplets on Lotus

Water droplets on Rose Petal

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