Materials in Nanotechnology
Bottom up manufacturing
Surface wetting and adhesion

Terence Kuzma
Outline

- Introduction: Definition and Examples
  - Material interface forces
- Contact angle measurement
- Surface modifications and materials tailored to control contact angle
Introduction

• Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces. Wetting deals with the three phases of materials: gas, liquid, and solid.

• Adhesive forces between a liquid and solid cause a liquid drop to spread across the surface. Cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface.
Introduction

The contact angle ($\theta$) is the angle at which the liquid–vapor interface meets the solid–liquid interface. The contact angle is determined by the result between adhesive and cohesive forces. As the tendency of a drop to spread out over a flat, solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability.
Introduction

• The diagram shows the line of contact where three phases meet. In equilibrium, the net force per unit length acting along the boundary line between the three phases must be zero.

• The components of net force in the direction along each of the interfaces are given by:

\[
\begin{align*}
\gamma_{\alpha\theta} + \gamma_{\theta\beta} \cos \theta + \gamma_{\alpha\beta} \cos \alpha &= 0 \\
\gamma_{\alpha\theta} \cos \theta + \gamma_{\theta\beta} + \gamma_{\alpha\beta} \cos \beta &= 0 \\
\gamma_{\alpha\theta} \cos \alpha + \gamma_{\theta\beta} \cos \beta + \gamma_{\alpha\beta} &= 0
\end{align*}
\]

• $\alpha$, $\beta$, and $\theta$ are the angles shown and $\gamma_{ij}$ is the surface energy between the two indicated phases.
Introduction

- These relations can also be expressed by an analog to a triangle known as **Neumann’s triangle**
- Neumann’s triangle is consistent with the geometrical restriction that $\alpha + \beta + \theta = 2\pi$, and applying the law of sines and law of cosines to it produce relations that describe how the interfacial angles depend on the ratios of surface energies.
- This relationship describes how the interfacial angles depend on the ratios of surface energies
Introduction

• If the $\beta$ phase is replaced by a flat rigid surface, then $\beta = \pi$

• The net force equation simplifies to the **Young equation** which relates the surface tensions between the three phases: solid, liquid and gas.

• This equation also applies if the "gas" phase is another liquid, immiscible with the droplet of the first "liquid" phase.

\[ \gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta \]
Young’s Equation

\[ \cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \]

- Contact Angle
- Free energy of solid to gas interface
- Free energy of solid to liquid interface
- Free energy of liquid to gas interface
In Young’s model the interaction between the water droplet and the solid surface is dependent upon the free energy interfaces between the different physical states surrounding the water droplet.
Introduction

• **Low contact angle**, A contact angle less than 90° usually indicates that wetting of the surface is very favorable, and the fluid will spread over a large area of the surface.

• **High contact angle**, Contact angles greater than 90° generally means that wetting of the surface is unfavorable, so the fluid will minimize contact with the surface and form a compact liquid droplet.
Introduction

- **Superhydrophobic surfaces** have contact angles greater than 150°, showing almost no contact between the liquid drop and the surface.
Introduction

The Wetting of Leaf Surfaces and Its Ecological Significances
Huixia Wang1, Hui Shi1 and Yanhui Wang2

<table>
<thead>
<tr>
<th>Contact angle</th>
<th>Degree of wetting</th>
<th>Strength of:</th>
<th>Solid/liquid interactions</th>
<th>Liquid/liquid interactions</th>
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<td>$\theta = 0$</td>
<td>Perfect wetting</td>
<td>strong</td>
<td>weak</td>
<td></td>
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<tr>
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<td>high wettability</td>
<td>strong</td>
<td>strong</td>
<td></td>
</tr>
<tr>
<td>$90^\circ \leq \theta &lt; 180^\circ$</td>
<td>low wettability</td>
<td>weak</td>
<td>weak</td>
<td></td>
</tr>
<tr>
<td>$\theta = 180^\circ$</td>
<td>perfectly non-wetting</td>
<td>weak</td>
<td>strong</td>
<td></td>
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</table>
Introduction

• Understanding and modifying surfaces for adhesion is huge area of research. The application and demands of this area of application is very broad. This series of lectures will define the need and explore typical methods to control adhesion.

• Some of the first documented research was done in the early 1800’s by Young.

• Understanding adhesion includes chemical affinity, morphology, electrostatics, and characterization coupled with mathematical models to understand the process.

• So we will introduce some base concepts, and add additional concepts to get a full picture of the engineering possibilities.
Timeline of major advances in the area of liquid repellency

The micrograph of the SHS is adapted with permission from REF. 16, American Chemical Society. The micrograph of the lotus leaf is adapted with permission from REF. 17, Springer

Definition and Examples

- Hydrophobicity comes also from the Greek word Hydro(water) and Phobicity (fear) it refers to the physical property of a material that repels a mass of water.
- The evaluation of hydrophobicity is made through water contact angle measurements.
Definition and Examples

- **Hydrophobic**, relating to, or having a lack of affinity for water and resistant to or avoiding wetting

- **Lyophobic**, marked by lack of strong affinity between a dispersed phase and the liquid in which it is dispersed

- **Oleophobic**, having or relating to a lack of strong affinity for oils

https://www.merriam-webster.com
Definition and Examples

- **Hydrophilic**, relating to, or having a strong affinity for water
- **Lyophilic**, marked by strong affinity between a dispersed phase and the liquid in which it is dispersed
- **Oleophilic**, having or relating to strong affinity for oils

[https://www.merriam-webster.com](https://www.merriam-webster.com)
Definition and Examples

• So the adhesion can be influenced by many factors.
  – Surface/liquid chemistry (or other interfaces)
  – Surface morphology
  – Combination of morphology and chemistry as observed in the lotus leaf
  – Other influences such as electrostatic forces such as the VanDer Wals interaction from the hairs on a gecko’s foot
  – Many forces can be simultaneous
Definition and Examples

• The lotus leaf
• Solid/liquid/gas interface
Lotus Leaf

Superhydrophobic! Contact angle > ~150°!

Air layer
Water droplet
Lotus leaf
micrometer-scale structure
Nano-scale structure
Definition and Examples

• Cleaning effect

http://biologyplants.wikispaces.com/Biomimicry+JK
Definition and Examples

- Lotus leaf FESEM image
Definition and Examples

- Lotus leaf FESEM image
Materials in Nanotechnology
Bottom up manufacturing

Surface wetting and adhesion

Part 2

Terence Kuzma
Outline

- Introduction: Definition and Examples
  - Material interface forces
- Contact angle measurement
- Surface modifications and materials tailored to control contact angle
Definition and Examples

- Gecko foot hairs exhibit a form of adhesion due to VanDer Wals forces.
- Solid/solid interface
- The mechanism of adhesion has been a topic of discussion for hundreds of years
Van der Waals’ Forces

• Van der Waals’ forces – attractive forces between two neutral atoms or molecules
• Requires low separation distance
• Theory for macroscopic calculations developed by E. M. Lifshitz in the 1950’s
Van der Waals (Continued)

- Macroscopic interaction energies are calculated by:

\[ U = \frac{\hbar}{32\pi^2d^2} \int_0^\infty d\omega \int_0^\infty dx^2 \left\{ \left( \frac{\varepsilon(i\omega) + 1}{\varepsilon(i\omega) - 1} \right)^2 e^x - 1 \right\}^{-1} \]

- \( \hbar \) – Planck's constant
- \( d \) – separation between media
- \( \omega \) – frequency
- \( x \) – point between the two media
Van der Waals (Continued)

- Between individual atoms, the van der waals’ force is:

\[
F = \frac{\hbar}{16\pi^3 l^3} \int_0^\infty \int_0^\infty \frac{\varepsilon_1(\omega_1)\varepsilon_1(\omega_2)}{\omega_1 + \omega_2} d\omega_1 d\omega_2
\]

- $\hbar$ – Planck's constant
- $l$ – separation distance between the atoms
- $\varepsilon_1$ and $\varepsilon_2$ – dielectric constant of each atom
- $\omega_1$ and $\omega_2$ – frequencies of the atoms
Contact Splitting

• Contact Splitting – Adhesion will be improved if one surface is split into many small fibrils.
• The force required to separate two surfaces increases based on the number of fibrils:
  \[ F' = \sqrt{nF} \]
• F – Original separation force
• F’ – Separation force with fibrils
• n – number of contacts
Contact Splitting (Continued)

• Five reasons that contact splitting occurs:
  – Strain Energy – Propels separation, must be released for every fibril
  – Conformity – Less energy is required for fibrils than for a smooth surface
  – Ratio of surface area to energy lost from distortions increases for smaller contacts.
  – Uniform stress distribution occurs before fibrils can be removed
  – Limits defect size – reduces damage from a single defect
Definition and Examples

• In 2000 biologists Kellar Autumn of Lewis & Clark College and Robert Full of University of California at Berkeley identified the spatulæ as providing the adhesion forces.

• The sheer abundance and proximity to the surface of these spatulæ make it sufficient for van der Waals forces alone to provide the required adhesive strength.
Definition and Examples

• Gecko foot hairs FESEM pic

Autumn, K, How gecko toes stick. American Scientist 94, 124-132
Definition and Examples

• The feet of a gecko are covered with elastic hairs called setae and the end of these hairs are split into nanoscale structures called spatulae.

• The underside of a gecko toe are covered with uniform ranks of setae, and each setae further divides into hundreds of split ends and flat tips called spatulas. A single seta of the tokay gecko is roughly 110 micrometers long and 4.2 micrometers wide. Each of a seta's branches ends in a thin, triangular spatula connected at its apex. The end is about 0.2 micrometers long and 0.2 micrometers wide.
Definition and Examples

• The adhesion between gecko's foot and the surfaces is exactly the result of the Van der Waals force between each seta and the surface molecules.

• Estimating the total number of about 3,268,800 setae on a tokay gecko's two front feet.

• From the equation for intermolecular potential:

$$\Phi(R, D) = -\frac{\rho_1 \rho_2 \pi^2 \alpha R}{6D}$$

– Where $\rho_1$ and $\rho_2$ are the number of contacts of the two surfaces, $R$ is the radius of each contact and $D$ is the distance between the two surfaces.

https://en.wikipedia.org/wiki/Synthetic_setae
Definition and Examples

• Scientists have recreated geckolike adhesion using silicones, plastics, carbon nanotubes, and other materials.

• Synthetic setae emulate the setae found on the toes of a gecko and scientific research in this area is driven towards the development of dry adhesives.

• Potentially adhesives could have many medical applications, for example tapes that could replace sutures to close a wound and a water resistant adhesive for bandages and drug-delivery patches.
Definition and Examples

- Geckel tape 400 nm wide silicone pillars, coated with a mussel-mimetic polymer
Definition and Examples

• The silicone pillars are fabricated by electron-beam lithography and coated synthetic form of the amino acid that occurs naturally in mussels.

• The material depends on van der Waals forces for its adhesive properties and on the chemical interaction of the surface with the hydroxyl groups in the mussel protein.

• The material improves wet adhesion 15-fold compared with uncoated pillar arrays.

• Tape adheres through 1,000 contact and release cycles, sticking strongly in both wet and dry environments.
Definition and Examples

• One of the first gecko tapes was formed of flexible fibers of polyimide as the synthetic setae structures on the surface of a 5 micron film
• Fibres were 2 micron long, with a diameter of around 500 nm and a periodicity of 1.6 microns
• The tape’s adhesive power increased by almost 1,000 times if they used a soft bonding substrate such as Scotch tape, this allowed more contact
Definition and Examples

Gecko tape, polymer formed by electron beam lithography and dry etching in an oxygen plasma

Materials in Nanotechnology
Bottom up manufacturing
Surface wetting and adhesion
Part 3
Terence Kuzma
Outline

• Introduction: Definition and Examples
  • Material interface forces
• Contact angle measurement
• Surface modifications and materials tailored to control contact angle
Interaction in the liquid phase

• Not only are liquid to surface interactions important, but liquid to liquid interactions can be considered.

• Hydrophobic interactions describe the relations between water and hydrophobes (low water-soluble molecules).

• Hydrophobes are nonpolar molecules and usually have a long chain of carbons that do not interact with water molecules.
Interaction in the liquid phase

• At the molecular level, the hydrophobic effect is important in driving protein folding, formation of lipid bilayers and micelles, insertion of membrane proteins into the nonpolar lipid environment and protein-small molecule interactions.

• Because of the inherent efficiency of material arrangement due to affinity, it is often be seen in nature
Interaction in the liquid phase

- **Polar molecules**
  - Electrons are not equally shared
  - One part of the molecule is more negatively charged
  - These are naturally hydrophilic to bond to polar water structure

- **Non-polar molecules**
  - Electrons are equally shared
  - Molecules don’t have “poles”
  - These are naturally hydrophobic and avoid interaction with water
Interaction in the liquid phase

• The mixing of fat and water is a good example of this particular interaction.
• The common misconception is that water and fat doesn’t mix because the Van der Waals
• Forces that are acting upon both water and fat molecules are too weak.
• This immiscibility can be used as a patterning technique with block copolymers
Interaction in the liquid phase

Interaction in the liquid phase

The exact process route depends on the properties of the block copolymer being used to create the pattern. This example is for PS-b-PMMA, which self-assembles when heated to about 175 °C (above the \( T_g \) of both blocks, but not totally melted).

- Clean the substrate to remove any contamination.
- Neutralize (randomize) the surface so that both blocks (PS and PMMA) have an equal affinity for the surface. In other words, neither block will preferentially wet or stick to the substrate surface. (More on this later.)
- Dissolve the polymer in a solvent (toluene or PGMEA) to make a dilute solution of the polymer (1 wt% works well).
- Spin coat a thin film (35 nm) of PS-b-PMMA onto the randomized substrate.
- Anneal (heat) the sample in a 175 °C vacuum oven for approximately 24 hours.
- Cool the sample back to rt and verify the self-assembled pattern via FESEM or AFM.
Interaction in the liquid phase

Increasing Length of A →

20:80  Spheres of A
30:70  Cyl of A
50:50  Lamellae
70:30  Cyl of B
80:20  Spheres of B

← Increasing Length of B

Structures form due to phase-separation on the nano-scale

Minimization of surface area between two incompatible phases
Interaction in the liquid phase

Increasing size of PMMA block
Decreasing size of PS block
Overall size (PS + PMMA) remains constant

Light gray: PS
Dark gray: PMMA

Dry Etch Selectivity of Block Copolymers

- Etch resistance depends on chemical composition of the polymer.
- More C = Greater etch resistance
- More O = Less etch resistance
- Relationship holds for the following gases: CF$_4$, Ar, H$_2$, O$_2$.

A measure of the carbon and oxygen content of the polymer
Low energy interactions for biology

• Self assembly through hydrophobic/hydrophillic interaction is seen in nature on many levels
• This method uses little energy and is very robust and predictable
• It is found in cell membranes, proteins and DNA. Naturally these themes are copied by engineers.
Phospholipid Structure

- Choline
- Phosphate
- Fatty Acid

Hydrophilic Head

Hydrophobic Tail
So what is a Phospholipid?

- Natural **self assembly** unit, a classic example of surface interaction
- A phospholipid is a molecule related to fat
- The molecule is comprised of:
  - A **hydrophilic** (water loving) phosphate head
  - Two **hydrophobic** (water fearing) fatty acid (hydrocarbon) tails
- When phospholipids are added to water, they self-assemble.
  - The phosphate head points towards the water, keeping the fatty acid tails away from the water, forming a **bilayer**
  - These bilayers act as cell membranes
Liposomes

• Doxil – passive delivery cancer drug

MPEG-DSPE coating
Aqueous core with entrapped doxorubicin HCL
Liposome bilayer
The Animal Cell

A Tour of the Cell

Interaction in the liquid phase

Lipid bilayers form through the process of self-assembly. The cell membrane consists primarily of a thin layer of amphipathic phospholipids that spontaneously arrange so that the hydrophobic "tail" regions are isolated from the surrounding water while the hydrophilic "head" regions interact with the intracellular (cytosolic) and extracellular faces of the resulting bilayer.
Interaction in the liquid phase

Interaction in the liquid phase

- Proteins are a major class of biomolecules that can directly connect biology to nanotechnology.
- Our bodies are 20% protein: this allows us to think, feel, move, and function.
- Proteins come in many shapes and sizes, giving them many functions:
  - Catalysis of chemical reactions within cells
  - Cellular gatekeepers
  - Immune system monitoring by recognition of foreign cells
  - Structural support to cells and tissues
- Compare to DNA: 1 structure and 1 function
Interaction in the liquid phase

• Proteins are built from 22 types of Amino Acids ~1 nm in size (e.g. tryptophan).
• DNA gives the protein information on how to assemble from the amino acid building blocks.
• Proteins have highly variable structures and can change their shapes in response to their surroundings in order to provide a signal.
• Proteins can provide binding sites for chemical reactions to occur.
• Proteins can identify cells. This is important for cancer, because tumors may have identifying proteins.
• Proteins also identify materials such as catheters
Amino Acid Hydrophilicity

Hydrophobic (normally buried inside the protein core):
Amino Acid Hydrophilicity

Polar (usually participate in hydrogen bonds as proton donors or acceptors):

https://en.wikipedia.org/wiki/Amino_acid
Amino Acid Hydrophilicity

Charged (side chains often make salt bridges):

https://en.wikipedia.org/wiki/Amino_acid
Amino Acid Hydrophilicity

Special cases:

https://en.wikipedia.org/wiki/Amino_acid
### Hydrophobicity Scale for Amino Acids

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Ile, Val</td>
<td>Cys</td>
<td>Gly, Leu, Ile Val, Ala</td>
<td>Cys, Ile Val, Ala</td>
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<tr>
<td>Leu</td>
<td>Phe, Ile Val</td>
<td>Phe</td>
<td>Phe</td>
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<tr>
<td></td>
<td>Leu, Met, Trp</td>
<td>Cys</td>
<td>Met</td>
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<tr>
<td></td>
<td></td>
<td>His</td>
<td></td>
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<td></td>
<td></td>
<td>Tyr</td>
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<td>Gly</td>
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<td>Trp</td>
<td>His, Ser</td>
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<td>Lys</td>
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<td>Glu, His Asp</td>
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<td>Asn, Gln</td>
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<tr>
<td>Arg</td>
<td>Lys</td>
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</table>
Interaction in the liquid phase

Linear Amino Acid Strand

Bumps in Funnel represent energy barriers, and the folding will take the path of least resistance to its final native state.

Native 3D conformation

https://en.wikibooks.org/wiki/Structural_Biochemistry/Proteins/Protein_Folding

https://en.wikipedia.org/wiki/Protein_structure#Amino_acid_residues
Interaction in the liquid phase
Interaction in the liquid phase

- The cell’s membrane (lipid bilayer) has many receptors which receive chemical signals from other cells and the extracellular matrix.
- A ligand is a molecule that binds with a receptor in order to induce a cellular response.
  - Ligand can be a neurotransmitter, hormone, pharmaceutical drug, toxin, proteins on another cells membrane, etc.
- Proteins on the cell membrane serves as a marker identifying one cell to another or a specific environment within the body.
- Cell response will vary depending on the type of cell and the signal (ligand) received.
- For cell adhesion such as bone cells to prosthetic, new cells must see specific markers such as proteins.
Wetting/proteins/cell growth

Functions of Plasma Membrane Proteins

- **Outside**
  - Selective transport channel

- **Plasma membrane**
  - Enzyme

- **Inside**
  - Cell surface identity marker
  - Cell adhesion
  - Cell surface receptor
  - Attachment to the cytoskeleton

Wetting/proteins/cell growth
Wetting/proteins/cell growth
Wetting/proteins/cell growth

Theofilos Koutouzis
University of Florida, College of Dentistry, Department of Periodontology
Wetting/proteins/cell growth

- Wetting and controlled growth is critical to procedures such as total knee replacement. Note that some areas readily wet, and will have rapid cellular growth (bone adhesion). Other areas such as the “cartilage” high molecular weight polyethylene, will not have cell growth.
Materials in Nanotechnology
Bottom up manufacturing

Surface wetting and adhesion

Part 4

Terence Kuzma
Outline

• Introduction: Definition and Examples
• Contact angle measurement
• Surface modifications and materials tailored to control contact angle
Contact angle

• When an interface exists between a liquid and a solid, the angle between the surface of the liquid and the outline of the contact surface is described as the contact angle $\theta$ (lower case theta). The contact angle (wetting angle) is a measure of the wettability of a solid by a liquid.
Contact angle

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</table>

The images a, b, c, and d illustrate different contact angles and their corresponding wetting degrees.
Surface free energy

- According to Young's equation, there is a relationship between the contact angle $\theta$, the surface tension of the liquid $\sigma_l$, the interfacial tension $\sigma_{sl}$ between liquid and solid and the surface free energy $\sigma_s$ of the solid:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos \theta$$

https://www.kruss.de/services/education-theory/glossary/contact-angle/
Surface free energy

Young's equation is used to describe the interactions between the forces of cohesion and adhesion and measure what is referred to as surface energy.

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]

- \( \theta \) is the contact angle
- \( \gamma_{sl} \) is the solid/liquid interfacial free energy
- \( \gamma_{sv} \) is the solid surface free energy
- \( \gamma_{lv} \) is the liquid surface free energy
Surface treatment

- Hydrophilic coatings wet the surface very easily, and maintain the wetness for longer time. Thus, using hydrophilic coatings eliminates the need for additional lubricants.
- Almost all natural materials are hydrophilic in nature.
Surface treatment

List of coatings/interfaces

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solid surface energy (mN/m)</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile butadiene styrene (ABS)</td>
<td>38.5</td>
<td>80.9</td>
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<tr>
<td>Epoxies</td>
<td>44.5</td>
<td>76.3</td>
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<tr>
<td>Fluorinated ethylene propylene (FEP)</td>
<td>19.1</td>
<td>108.5</td>
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<tr>
<td>Nylon 6</td>
<td>43.9</td>
<td>62.6</td>
</tr>
<tr>
<td>Paraffin</td>
<td>24.8</td>
<td>108.9</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>29.3</td>
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<tr>
<td>Polycarbonate (PC)</td>
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<td>Polydimethylsiloxane (PDMS)</td>
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<td>Polyethylene (PE)</td>
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<td>Polyethylene oxide (PEO)</td>
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<tr>
<td>Polyvinyl chloride (PVC)</td>
<td>37.9</td>
<td>85.6</td>
</tr>
</tbody>
</table>
Surface condition/morphology

Young

Wenzel

Cassie

$\cos \theta = \frac{\gamma_{sv} - \gamma_{il}}{\gamma_{lv}}$  Young’s Equation

$\gamma = $ surface tension

$s, l, v = $ solid, liquid, & vapor phases

$\theta = $ equilibrium contact angle of a liquid droplet on a flat solid surface

$\cos \theta^* = r \cos \theta$  Wenzel Model

$r = $ surface roughness = the ratio of the actual to the apparent surface area of the substrate

$\theta^* = $ apparent contact angle on a textured surface

$\cos \theta^* = -1 + \phi_s (1 + \cos \theta)$  Cassie Model

$\phi_s = $ fraction of solid-liquid contact

www.me.umn.edu/~lixxx099/EFRI_CAES/Research/texturing.htm
Surface condition/morphology

• When depositing a water drop on a “rough” surface at least two types of wetting can be identified. These are known as the Wenzel situation or Cassie or Fakir State.
Wenzel state

• The second and simplest picture is the so-called Wenzel state. The liquid is able to interact with the morphology and the liquid seeps into the contours. (Wenzel 1936).
Wenzel state

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

where \( \theta^* \) is the apparent angle which corresponds to the stable equilibrium state (i.e. minimum free energy state for the system). The roughness ratio, \( r \), is a measure of how surface roughness affects a homogeneous surface. The roughness ratio is defined as the ratio of true area of the solid surface to the apparent area.
Wenzel’s Equation

\[ \cos \theta_W^* = r \cos \theta_Y \]

- Young’s Contact Angle
- Roughness ratio
- Wenzel Contact Angle

\[ r = \frac{\text{true surface area}}{\text{ideal surface area}} \]
Wenzel’s Model

- Water droplet is sitting within the grooves of the surface. In the Wenzel model there is increased contact between the water and the solid the surface.
The third figure implies the creation of a liquid–vapour interface below the drop, on a fraction of surface of the order of $1-\phi_S$, considering these interfaces as flat (the drop is large compared with the pillars, implying a negligible curvature of the liquid–vapour interface at the scale of pillars).
Cassie state-Fakir state
Cassie state-Fakir state

\[ \cos \theta^* = r_f f \cos \theta_Y + f - 1 \]

Here the \( r_f \) is the roughness ratio of the wet surface area and \( f \) is the fraction of solid surface area wet by the liquid. It is important to realize that when \( f = 1 \) and \( r_f = r \), the Cassie-Baxter equations becomes the Wenzel equation. On the other hand, when there are many different fractions of surface roughness, each fraction of the total surface area is denoted by \( f_i \).

A summation of all \( f_i \) equals 1 or the total surface.

\[ \gamma \cos \theta^* = \sum_{n=1}^{N} f_i (\gamma_i, sv - \gamma_i, sl) \]
Surface condition

• Liquid conforming to the solid surface (Wenzel situation)
• Liquid sitting on the top of the posts (Cassie or fakir state)
Surface condition

\[ \Lambda_c = \frac{-\rho g V^{1/3} \left( \frac{1 - \cos(\theta_a)}{\sin(\theta_a)} \right) \left( 3 + \left( \frac{1 - \cos(\theta_a)}{\sin(\theta_a)} \right)^2 \right)^{2/3}}{(36\pi)^{1/3} \gamma \cos(\theta_{a,0} + w - 90)} \]

where

- \( \rho \) = density of the liquid droplet
- \( g \) = acceleration due to gravity
- \( V \) = volume of the liquid droplet
- \( \theta_a \) = advancing apparent contact angle
- \( \theta_{a,0} \) = advancing contact angle of a smooth substrate
- \( \gamma \) = surface tension of the liquid
- \( w \) = tower wall angle

Surface condition

To calculate updated advancing and receding contact angles in the Cassie-Baxter state, the following equations can be used:

\[
\theta_a = \lambda_p (\theta_{a,0} + w) + (1 - \lambda_p) \theta_{air} \\
\theta_r = \lambda_p \theta_{r,0} + (1 - \lambda_p) \theta_{air}
\]

With also the Wenzel state:

\[
\theta_a = \lambda_p (\theta_{a,0} + w) + (1 - \lambda_p) \theta_{a,0} \\
\theta_r = \lambda_p (\theta_{r,0} - w) + (1 - \lambda_p) \theta_{r,0}
\]

Where

- \( \lambda_p \) = linear fraction of contact line on the asperities
- \( \theta_{r,0} \) = receding contact angle of a smooth substrate
- \( \theta_{air} \) = contact angle between liquid and air (typically assumed to be 180°)
Characterization

• A tensiometer is a device for measuring the surface tension of a liquid and/or the interfacial tension between two liquids. There are different types of tensiometers with different measuring methods for particular measuring ranges and problems:
  • Force sensor tensiometer, bubble pressure tensiometer

https://www.kruss.de/services/education-theory/glossary/tensiometer/
Contact Angle

Instruments that analyze contact angels are either referred to as:

Tensiometers
Contact Angel Analyzers
Geniometer
Contact Angle

The tangent angle formed between a liquid drop and its supporting surface is relative to the forces at the liquid/solid or liquid/liquid interface. This angle is representative of surface bonding energy.
Contact Angle Tools

Kruss DSA 10 Contact Angle Analyzer

Cahn Radian DCA Analyzer

SensaDyne Bubble Tensiometer
Characterization

• A bubble pressure tensiometer is an instrument for determining the dynamic surface tension. The maximum internal pressure of a gas bubble which is formed in a liquid by means of a capillary is measured.

• According to the Young-Laplace equation, the internal pressure $p$ of a spherical gas bubble (Laplace pressure) depends on the radius of curvature $r$ and the surface tension $\sigma$. 
Outline

• Introduction: Definition and Examples
  • Material interface forces
• Contact angle measurement
• Surface modifications and materials tailored to control contact angle