Critical study of contact angle goniometry

Tommi Huhtamäki
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A doctoral thesis completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Science, at a public examination held at the lecture hall M1 of the school on 12 January 2024 at 12 noon.

Aalto University
School of Science
Department of Applied Physics
Soft Matter and Wetting
Abstract

In this thesis contact angle goniometry as a characterization method for solid surface wettability is critically examined. Contact angle goniometry is a powerful and versatile tool for measuring wetting properties, facilitating the study of microscale surface properties by macroscopic an optical method. The apparent ease which with contact angles can be measured have en-sured its position as the golden standard of wetting characterization. Measuring meaningful contact angles and interpreting the data correctly is far from simple, however. Real solid sur-faces exhibit a range of stable contact angles. Collecting meaningful data requires knowledge to recognize the contact angles which can be reproducibly measured, on how to perform the measurements in a reliable manner and on interpretation of the results.

Publication I provides a method for reliable measurement of the receding contact angle. The validity of the method is evaluated both theoretically, and by a wide range of experimental evidence.

Publication II proposes a growth model for the synthesis of silicone nanofilaments - a class of superhydrophobic 1-dimensional polysiloxane nanostructures. Theoretical model for pressure-induced film expansion is provided.

Publication III introduces a protocol for contact angle measurements that can be applied to a wide variety of samples. Instructions on minimizing both systematic and random errors are provided, along with troubleshooting for most common problems encountered.

Publication IV quantifies the error in contact angle measurement caused by misplacement of the baseline - the line between the solid and liquid/gas in the 2D-images analyzed. Special emphasis is given on the error for superhydrophobic surfaces

Publication V expands on publications IV by quantifying the error caused by the optical system used in contact angle goniometry. User error of contact angle measurements is also measured.

Keywords Contact angle, wetting, superhydrophobicity, silicone nanofilaments


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Tiivistelmä

Julkaisu I esittää luotettavan menetelmän vetäytyvän kontaktikulman mitatamiseen. Vastaavuus laskennallisen mallin, teorian ja kokeiden tulosten välillä osoitetaan.

Julkaisu II esittelee uuden kasvumallin silikoninarainofilamenteille, jotka ovat kuitumaisia, superhydrofobisia nanorakenteita. Malli pyrkii ratkaisemaan suyn rakenteiden yksiulotteiselle kasvulle.

Julkaisu III käsittelee kontaktikulmamittauksen protokollaa. Protokolla mahdollistaa luotettavasti toistettavat mittaukset, ja antaa ohjeita mittavirheiden minimoiniseen, sekä tulosten käsittelyn ja tulkintaan.

Julkaisussa IV mitataan, kuinka suuren mittavirheen näytteen ja nesteen välisen rajapinan korkeuden virheellinen määrittäminen aiheuttaa. Erityistä huomiota kiinnitetään virheen ekspontaialiseen kasvuun, kun mitataan kastumattomia pintoja.

Julkaisu V laajentaa julkaisun IV tarkastelua määrittelemällä, kuinka suuret mittavirheet mittauksessa käytetty optinen järjestelmä aiheuttaa.

Avainsanat
Kontaktikulmamittaus, kastumisilmiöt, superhydrofobisuus, silikoninarainofilamentit

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Preface

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Of my co-workers, I must highlight the importance of Dr. Juuso Korhonen. Juuso was my instructor when I started my research as a summer worker. He was a great mentor to the world of scientific research, and I have continued to learn from him and be inspired by the depths of his knowledge to this day.

I also want to thank all the fantastic friends with whom I have had the pleasure and privilege to work with in the SMW research group. This applies also to all the members of the extended "family" of research groups, which have split from Olli’s Molecular Materials, as well as the members of Hyber and Liber Centers of Excellence.

Thanks to my brother, Jouni, for all the good times and friendship over the years, may there be many more to come.

Tärkein kiitos kuuluu äitille ja isälle kaikesta tuesta, turvasta ja rakkaudesta, johon on aina voinut luottaa. Tämä työ on omistettu teille.

Helsinki, 19 December 2023
Tommi Tapani Johannes Huhtamäki
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<td>advancing contact angle</td>
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<tr>
<td>BL</td>
<td>baseline</td>
</tr>
<tr>
<td>CA</td>
<td>contact angle</td>
</tr>
<tr>
<td>CAH</td>
<td>contact angle hysteresis</td>
</tr>
<tr>
<td>CL</td>
<td>contact line</td>
</tr>
<tr>
<td>h-SNF</td>
<td>hollow silicone nanofilament/s</td>
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<tr>
<td>MSCA</td>
<td>most stable contact angle</td>
</tr>
<tr>
<td>MTCS</td>
<td>methyltrichlorosilane</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
</tr>
<tr>
<td>RCA</td>
<td>receding contact angle</td>
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<tr>
<td>SAMs</td>
<td>self-assembled monolayers</td>
</tr>
<tr>
<td>SDAM</td>
<td>scanning droplet adhesion microscope</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy/micrograph</td>
</tr>
<tr>
<td>SHS</td>
<td>superhydrophobic surface/s</td>
</tr>
<tr>
<td>SMF</td>
<td>silicone microfilament/s</td>
</tr>
<tr>
<td>SNF</td>
<td>silicone nanofilament/s</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy/micrograph</td>
</tr>
<tr>
<td>%RH</td>
<td>relative humidity percentage</td>
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</table>
List of symbols

$\alpha$  sliding angle

$\gamma$  liquid surface tension

$\gamma_{SA}$  solid-air interfacial tension

$\gamma_{SL}$  solid-liquid interfacial tension

$\Delta A$  change in area

$\Delta p$  change in pressure

$\delta G$  infinitesimal change in Gibbs free energy

$\delta x$  infinitesimal change in length

$\rho$  density

$\theta$  contact angle

$\theta_A$  advancing contact angle

$\theta_{CB}$  Cassie(-Baxter) contact angle

$\theta_e$  equilibrium contact angle

$\theta_{front}$  lower contact angle of a drop on a tilted surface

$\theta_i$  ideal contact angle

$\theta_R$  receding contact angle

$\theta_{front}$  lower contact angle of a drop on a tilted surface

$\theta_W$  Wenzel contact angle

$\theta_Y, \theta_{Young}$  Young contact angle

$\tau$  line tension

$A$  area

$A_{\text{actual}}$  actual area

$A_{\text{projected}}$  horizontal projection of area

$C$  curvature
Introduction

$D$ diameter

$E$ energy

$F_{LA}$ friction/lateral adhesion force

$f_i$ Cassie fraction of material $i$

$f_{LA}$ liquid-air Cassie fraction

$f_{SL}$ solid-liquid Cassie fraction

$G$ Gibbs free energy

$g$ gravitational constant

$k$ drop shape factor

$L$ contact line length

$l_{ca}$ capillary length

$l_{SA}$ solid-air interface length (2-dimensional system)

$l_{SL}$ solid-liquid interface length (2-dimensional system)

$P, p$ pressure

$R_1, R_2$ principal radii of curvature

$r$ Wenzel roughness factor

$r_b$ radius of solid-liquid interface/drop base radius

$r_f$ roughness ratio in Cassie equation

$S$ spreading parameter

$V_a$ initial droplet volume for receding contact angle measurement

$W$ work of adhesion

$W_a$ approaching work of adhesion

$W_r$ separating (receding) work of adhesion

$x$ length
List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to by their numerals in the text:


Author’s Contribution

**Publication 1:** Reliable measurement of the receding contact angle

Author performed most of the experimentation for the article, including synthesis of silicone nanofilaments, contact angle goniometry and scanning electron microscopy. Author planned and performed the study together with Dr. Juuso Korhonen. Author contributed to the writing process.

**Publication 2:** Hollow polysiloxane nanostructures based on pressure-induced film expansion

Author performed a major part of the experimentation for the, including silicone nanofilament synthesis and contact angle measurement, scanning electron microscopy and transmission electron microscopy. Author contributed to the writing process of the manuscript.

**Publication 3:** Surface-wetting characterization using contact-angle measurements

Author wrote the first draft of the manuscript and contributed to the writing process throughout the entire peer-review process. Author contributed to the development of the measurement protocol, which is the topic of the article.

**Publication 4:** Improving surface-wetting characterization

Author contributed to the planning of the article, performed part of the CA measurements, and contributed to the writing process.

**Publication 5:** Uncertainties in contact angle goniometry

Author contributed to the development of the idea of the article and to the writing process.
1. Introduction

Wetting is ubiquitous and is involved in all facets of our daily lives. It is therefore of paramount interest to science and technology. Wetting is determined by an interplay between adhesive and cohesive forces. Wettability of a material depends on the relative strength between the cohesive forces of a liquid and the adhesive forces between the liquid and a solid. On hydrophilic surfaces, droplets spread over a large area, while on hydrophobic surfaces, drops form a spherical cap. The ability to control wettability of surfaces is important on all fronts of human life, from our daily lives to science and industry (1; 2; 3; 4; 5). Wettability determines how strongly drops adhere to windows (6; 7; 8; 9), how well paint spreads onto a surface, and affects the aggregation of ice on the wings of airplanes (10). Tuning the wettability of a surface is required for many applications, such as inkjet- and 3D-printing, microfluidic devices (11), heat transfer applications (12; 13; 14; 15), fabrication of metal-organic-frameworks (16; 17; 18; 19), etc.

Challenge to control wetting, especially the fabrication of extremely non-wetting (i.e., superhydrophobic) surfaces, largely motivates research on micro- and nanostructured surfaces. Superhydrophobic surfaces (SHS) have potential applications in self-cleaning surfaces (20), fog harvesting (12; 13; 21), reducing hydrodynamic drag (22), enhancing heat transfer (23), gas exchange (24), etc. SHS can be fabricated by for example introducing roughness on a material with low surface free energy. The protrusions of the surface structure make it possible to maintain a layer of air beneath the liquid, leading to the so-called Cassie wetting state (25; 26; 27; 28; 29; 30; 31; 32). This way the contact between the solid and the liquid is minimized, which is required for SHS properties, such as high mobility and low adhesion of droplets on solid surface. If the air layer is lost and the liquid wets the whole surface, the superhydrophobic properties are lost. This wetting state is called the Wenzel state (33).

The control of wettability requires precise and accurate characterization of wetting properties. Contact angle (CA), i.e., the angle of contact between a liquid and a solid as measured on the side of the liquid, remains the golden standard for wetting characterization, 200 years after its discovery (34). The benefits of sessile drop goniometry include relative simplicity and low cost, suitability to use in a wide range of environments, applicability to a wide range of substrates and insensitivity to drop size. The apparent ease of CA measurement is in most cases a misconception, however, and reliable and accurate measurement requires considerable effort and knowledge (35; 36; 37; 38; 39). While valuable
information of surface properties is obtained when measurements are properly performed and interpreted, the technique has severe drawbacks and limitations, all of which are not universally recognized.

The shortcomings of CA characterization are most significant when SHS are characterized. It is often overlooked in the literature that CA measurement errors increase exponentially when approaching the limits of non-wettability. This hinders the development of novel superhydrophobic materials, as interlaboratory comparison of their wetting properties is difficult without standardized techniques and protocols. Development of next-generation SHS requires monitoring the manufacturing process by accurate characterization methods. The inherent errors of CA measurement need to be recognized by the scientific community, and standardized methods and protocols developed to minimize the errors. Furthermore, additional characterization techniques based on direct measurement of the forces involved in wetting will probably be needed.

![Figure 1](image)

**Figure 1.** (a) Water droplets on a lotus leaf: Due to its superhydrophobicity, adhesion is very low between lotus leaf and water. Water forms spherical droplets that roll easily off the leaf surface. (b) Scanning electron micrograph of lotus leaf surface, showing its dual-scale roughness. Microscopic “hills” are covered by nanoscopic “hair”. (c) A water strider, walking on water due to the superhydrophobicity of its legs. Reprinted with permission from (40).

**Motivation**

The focus of this dissertation is the proper use and limits of contact angle goniometry, with emphasis on CA characterization of extremely water-repellent surfaces. Reliable measuring methods and a protocol for repeatable and reproducible CA measurements were produced based on the experience gained during the study. The proper use and limits of CA goniometry, and interpretation of CA data are discussed in the dissertation.
2. Wetting

2.1 Introduction to wetting

Wetting, the process of creating contact between a solid and a liquid, is an area of science where physics, chemistry, and engineering merge. Frequently used materials need to be designed to withstand wet conditions and work properly in humid environments with uncontrollable factors, such as weather, affecting the amount of water in the system. Wetting usually occurs in an environment in which the liquid and solid are surrounded by another fluid, either gas or a second immiscible liquid. The spreading and behavior of the liquid depends on an interplay between the cohesive interactions in the liquid as well as the adhesion between the solid and the liquid. The balance of the adhesive and cohesive forces can be defined by the angle of contact between the liquid and solid, as measured by convention on the liquid side.

This contact angle (CA), along with its many variations, is the main parameter used to characterize the wetting properties of a solid surface. Despite the apparent simplicity of the concept of CA, characterizing the wetting properties by CA measurement is far from simple and unambiguous, both theoretically and experimentally (1; 41; 42).

Figure 2. Wettability of a surface is determined by the balance of interfacial tensions at the contact line (CL). The fundamental relation correlating the contact angle (CA) of a on a solid substrate with the tensions of the three interfaces of the system, namely solid-liquid (\(\gamma_{SL}\)), solid-vapor (\(\gamma_{SV}\)) and liquid-vapor (\(\gamma\)) interfacial tensions, was published by Thomas Young in 1805 (43). Reprinted with permission from (44).


2.2 Surface tension

Surface tension arises from the cohesive interaction between the molecules of a liquid (45). In general, a molecule is likely to have stronger cohesive forces between similar than dissimilar molecules. A molecule on the surface has half of the nearest neighbors replaced by dissimilar molecules. Therefore, while a molecule in the bulk of the liquid is being "pulled" with equal force in all directions, a molecule on the surface is being pulled towards the bulk of the liquid, giving rise to the surface tension.

![Water Droplet on a Solid Surface](image)

Figure 3. Surface tension is caused by the excess energy of the interface, resulting from the unbalanced forces of the molecules on the surface. Molecules in the bulk form strong bonds with the similar molecules surrounding it. Molecules on the surface are missing about half of their nearest neighbouring molecules, which leads to an energetically unfavourable state. Reprinted with permission from (46).

One special property of water that separates it from most liquids is its very high surface tension, resulting in a rubber-like “skin” that resists deformation. Due to this, water exhibits unique behaviour in many circumstances, providing scientists with a continuous source of further research despite the vast efforts already spent. One daily task that demonstrates the properties of water is washing and cleaning: due to the high surface tension, water tends to make poor contact with dirt and stains, especially oily ones. However, increasing the temperature lowers the surface tension, which is intuitively clear when one considers that heating the liquid eventually leads to boiling and evaporation. If all of the liquid evaporates, the interface between the liquid and the gas is destroyed, and surface tension vanishes. Clearly, interfacial tension diminishes as the temperature rises, and, consequently, warm water is used for washing. Likewise, the function of soaps and detergents is to decrease surface tension allowing water to allow better intrusion between the surface and contaminants, and to render fatty stains soluble in water by emulsifying them (41; 45).

The high surface tension of water is due to a very specific polar interaction, called hydrogen bonding. Although the net electric charge of a water molecule is zero, it is not evenly distributed, as the oxygen atom is slightly negatively charged, while the two hydrogen atoms are slightly positively charged. The bonds between the positively charged hydrogen regions of one molecule and the
negatively charged oxygen regions in its neighboring molecules form a highly dynamic network of bonds, with bonds breaking and new ones forming very quickly. The value of surface tension for water at room temperature (20°C) is $\gamma \approx 72.8 \text{ mN/m}$ (47).

Surface tension affects the behavior of liquids in many ways due to the tendency of physical systems to minimize their total energy. One common phenomenon that follows from energy minimization, which is familiar to most, is the tendency of a drop of oil to immediately spread over the surface of water. Already in 1773, Benjamin Franklin noticed that a teaspoonful of olive oil spread over the area of a quarter of an acre and no more. Continuing the investigation further, in 1890, Rayleigh divided the volume of the teaspoon by the area of spreading to calculate the thickness of the layer, ~1 nm. In this way, he was able to deduce the size of a molecule, due to the oil layer being of molecular thickness. This experiment demonstrates a feasible means of studying dimensions out of the scope of direct observation by recognizing the physical principles of the system.

![Figure 4](image)

Figure 4. a) Clapham pond before a teaspoon of oil is dropped. b) Same location moments after a teaspoon of oil is dropped. Oil spreads and forms a one molecule thick film on top of the water, dampening the ripples of the pond. Reprinted with permission from (48).

For an interface between two phases to be stable, the surface tension pulling surface molecules inwards needs to be balanced by a force of equal magnitude, but in the opposite direction. The force balancing surface tension is a force caused by the so-called Laplace pressure, which is the pressure difference between a drop and the surrounding medium. The pressure difference, $\Delta p$, is given by the Young-Laplace equation (45):

$$\Delta p = \gamma C = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

where $C$ is the curvature of the surface, $\gamma$ is the surface tension of the liquid, and $R_1$ and $R_2$ are the principal radii of curvature. In the case of a sphere, curvature is constant across the surface, and the equation reduces to $\Delta p = \frac{2}{R}$. It follows from Eq. (1) that the Laplace pressure inside a sphere is constant across the volume of the sphere and does not depend on the location. Furthermore, and counterintuitively, pressure inside smaller drops is higher than in larger ones, since the smaller the sphere, the higher the curvature of the interface.
Wetting

In the air, water drops take the form of a perfect sphere, if the effects of gravity and air resistance are ignored. On a solid surface water spreads and, depending on the wetting properties of the solid, forms either lenses or spherical caps, which also is dependent on the surface properties of the solid. Spreading is a process of replacing one fluid by another, in this case, the replacing of gas on the solid surface by water. The extent to which the water spreads is still determined by the basis of energy minimization, there being now three interfacial energies to balance: solid-liquid, solid-vapor, and liquid-vapor. The so-called spreading parameter, \( S \), can be used to weigh the balance of the interactions on the surface (1; 4)

\[
S = \gamma_{SA} - (\gamma - \gamma_{SL})
\]  

(2)

where \( \gamma_{SA} \) and \( \gamma_{SL} \) are the solid-air and solid-liquid interfacial tensions, respectively; and \( \gamma \) is the surface tension of water. The spreading parameter compares the energy of a wet surface against the energy of a dry surface. Based on the value of the spreading factor, three different regimes of wetting can be defined, namely, partial wetting, complete wetting, and complete dewetting.

**Partial Wetting.** If \( \gamma_{SA} < \gamma + \gamma_{SL} \), the spreading parameter is negative. In this partial wetting regime, water wets only part of the surface in the equilibrium state, forming a spherical cap with a finite contact angle between the water and solid. The value of the contact angle depends on the relative strengths of the three interfacial tensions.

**Complete wetting.** If \( \gamma_{SA} > \gamma + \gamma_{SL} \), the spreading parameter is positive and complete wetting occurs. In this regime, water will spread until it covers the whole surface with a uniform layer of nanometer scale thickness.

**Complete dewetting.** From a thermodynamic perspective, complete dewetting may also occur, analogously to complete wetting. In this case, \( S = -2\gamma \), and water beads up to form a perfect sphere to minimize contact with the solid. This regime, in which the solid surface tends to remain completely dry, is not encountered in nature.

![Figure 5](image)

Figure 5. Three wetting states may exist in a three-phase system. In a wetting system, spreading parameter \( S \) can be used to formally divide the states shown above: a) Complete wetting, with formation of a film, contact angle of zero degrees b) Partial wetting, with formation of a spherical cap having a finite contact angle \( \theta \) and c) Complete dewetting, with contact angle 180°. Reprinted with permission from (49).
2.3 Contact angle

2.3.1 Ideal contact angle

When a drop of water is placed on an ideal solid surface, spreading of the drop continues until the line on which all the three phases meet, i.e., contact line (CL), reaches the equilibrium contact angle, $\theta_e$ (50). The equilibrium CA is also known as Young CA, $\theta_Y$. The contact angle is the angle between the liquid and the solid, as measured by convention on the liquid side. The equilibrium contact angle on an ideal solid surface corresponds to the minimum in the Gibbs free energy, $G$, of the system.

Contact angle can be derived based on thermodynamics by free energy approach. For simplicity, one can consider a 2-dimensional wetting system, as it is easier to present, yet equivalent with the three-dimensional case in ideal conditions for an axisymmetric drop. Let us start from a point where a drop brought into contact with an ideal solid has spread until it has reached an equilibrium. Total Gibbs free energy of the system can be written as

$$G = \gamma_{SA} l_{SA} + \gamma_{SL} l_{SL}$$

where $l_{SA}$ and $l_{SL}$ indicate the lengths of solid-air and solid-water interfaces (of a 2-dimensional system), respectively. If the three-phase contact point (contact line in the three-dimensional case) by an infinitesimal step, $\delta x$, the change in energy is

$$\delta G = (\gamma_{SL} - \gamma_{SA}) \delta x + \gamma \cos \theta \ \delta x$$

In equilibrium conditions, an infinitesimal step from the minimum energy does not change the energy of the system, i.e. $\delta G = 0$. Therefore, the right-hand side of the Equation 4 can be rearranged to achieve:

$$\cos \theta_Y = \frac{\gamma_{SL} - \gamma_{SA}}{\gamma}$$

where $\theta_Y$ has been substituted for $\theta$ to highlight that this is the Young contact angle. It represents the equilibrium contact angle for an ideal solid surface (43). An ideal solid is defined as atomically smooth, chemically homogenous, non-reactive towards water and the surrounding atmosphere (no swelling, dissolving, or adsorption). Based on the Young CA, solid materials can be divided into hydrophilic (“water-loving”), $\theta_Y < 90^\circ$ and hydrophobic (“water-fearing”), $\theta_Y > 90^\circ$ (42).
2.3.2 Wenzel and Cassie-Baxter models

Two extreme cases can occur when a drop of water is placed on a rough hydrophobic surface: (i) the drop can maintain full contact with the rough surface beneath it (i.e., the Wenzel state, Figure 6 a), or (ii) pockets of air can remain in the cervices between the solid and the liquid, creating a composite interface with a mix of solid-liquid and solid-air regions beneath the drop (i.e., the Cassie-Baxter state, Figure 6 b). On a hydrophilic surface, water typically exhibits the Wenzel state. Both the Wenzel and the Cassie-Baxter state lead to a configuration with a CA that differs from the intrinsic Young CA of the solid material.

![Figure 6](image)

**Figure 6.** Three possible wetting states of liquid drop on a rough hydrophobic surface: a) Wenzel state, b) Cassie-Baxter state and c) an intermediate state between Wenzel and Cassie-Baxter state. Reprinted with permission from (51).

Wenzel state

Richard Wenzel was the first to notice the connection between roughness and wetting properties while studying textiles to improve their water-repellency. He noticed that the natural tendency of the fabric to either repel or be wetted by water was enhanced by textures on the scale of filaments of yarns (33). Compared to a flat surface, a rough surface “stores” more surface energy, since the
effective surface area is larger. As with Young CA, free-energy minimization approach can be applied to a freely moving contact line on a rough surface, protruding inside the roughness features (see Appendix A and Appendix C). For an infinitesimal displacement of the contact line:

$$\delta G = r (\gamma_{SL} - \gamma_{SA}) \delta x + \gamma \cos \theta_W \delta x$$

where $r$ is a roughness factor suggested by Wenzel, $r = A_{\text{actual}} / A_{\text{projected}}$. By rearrangement and energy minimization, the Wenzel equation is obtained:

$$\cos \theta_W = r \cos \theta_Y$$

Here, $\theta_W$ is the Wenzel CA, $r$ is the Wenzel roughness factor and $\theta_Y$ is the Young angle. The intrinsic wetting properties of a solid are enhanced due to roughness, since the actual area is of course always larger (or equal) than the projected area, $r \geq 1$.

**Cassie-Baxter state**

The Cassie-Baxter state, also known as composite state, was first introduced in 1944 (25). It represents a situation in which air becomes trapped in the roughness features between the liquid and the solid. This leads to part of the contact between solid and liquid being replaced by a contact between liquid and air, as compared to the Wenzel state. Due to air being perfectly hydrophobic, this leads to a notable enhancement of hydrophobicity, resulting in a significantly higher contact angle. The Cassie-Baxter equilibrium contact angle can be written as equal to a weighted average of the contact angle of the solid and contact angle of air ($\theta_{Air} = 180^{\circ}$)

$$\cos \theta_{CB} = f_{SL} \cos \theta_Y + f_{LA} \cos \theta_{Air}$$

$$= f_{SL} \cos \theta_Y + f_{LA}$$

where $f_{ij}$ are the area fractions of interfaces between materials $i$ and $j$. It should be noted that the sum of the area fractions can be above 1 (see Appendix C). The equation can be expanded to a more general form to represent the CA of a chemically heterogeneous surface:

$$\cos \theta_{CB} = \sum_i f_i \cos \theta_i$$

where $f_i$ and $\theta_i$ are the area fraction and CA of each individual material $i$, respectively.

The range of applicability of Wenzel and Cassie-Baxter equations has been a matter of intense debate (28; 29; 42; 51; 52; 53; 54; 55; 56). For the scope of this dissertation, it is sufficient to say that the range of their applicability needs to
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be critically examined for each system, since they are model systems and do not fully describe the complexities of real-life physical systems. Nevertheless, the equations have been shown to correlate with experimental data when properly applied; most importantly, the drop size used to measure $\theta_W$ or $\theta_{CB}$ needs to be several orders of magnitude larger than the characteristic roughness feature size of the surface.

2.4 Contact angles on real surfaces

The most important reason for measuring the contact angle is to try and determine the surface tensions of solid surfaces. Currently, the only way to connect the two is through the Young equation, which only applies to ideal surfaces. Unfortunately, real wetting systems deviate strongly from an ideal system. Wenzel and Cassie models are useful since they consider how two important factors, roughness and chemical heterogeneity, affect the system. Unfortunately, this does not solve the issue regarding the determination of solid surface tension as Cassie and Wenzel CAs are also most stable CAs, whereas measured CAs can be metastable states, and the equilibrium CA is difficult to distinguish (36; 37; 42).

To connect measured contact angles to solid surface tension, one needs to understand what is being measured. Although the solid surface tension is not a directly measurable quantity and cannot be deduced from the measured contact angles by any existing universally applicable theory, acquired CA data provides valuable information when correctly understood. There exists a plethora of different contact angles, which is a source of much misunderstanding and confusion (52). Therefore, it is important to define the ones most relevant to this dissertation.

Contact angles are generally case-dependent variables, not properties of the surface. It is of fundamental importance to specify the CA in question and the experimental methods used when presenting CA data. An especially common misconception that has persisted in the literature for decades is confusing the contact angles of idealized model surfaces in the theory sections with experimentally measured CAs. While ideal contact angles are very useful in data analysis (due to their capability of deducing microscopic information from the data acquired by optical methods), CAs of the models are not directly accessible by experimental methods. Some common misconceptions are explained below (52; 53; 54).

2.4.1 Apparent and actual CA

Apparent contact angles are observed at the macroscopic level. Contact angles at the microscopic level, on the other hand, may significantly differ from the apparent CAs. Young, Wenzel, and Cassie CAs are all apparent contact angles, and should be measured on a scale much larger than the microscopic roughness and chemical inhomogeneity of the solid (42).

Microscopic contact angles are often referred to as actual contact angles. Values of actual contact angles agree relatively well with the theoretical Young angle at the microscopic level, while the contact line meanders to adapt both to the
microscopic roughness as well as the chemical inhomogeneity. On the macroscopic level, as observed by the naked eye, the CL is axisymmetric (assuming that the size of the droplet is 2-3 times the magnitude of the surface heterogeneity/roughness), and the macroscopic apparent CA can deviate significantly from the microscopic actual CA (55; 56; 57).

![Figure 7](image)

**Figure 7.** Picture of a liquid drop on (a) rough and (b) chemically heterogenous solid surface. Actual CA ($\theta_{ac}$) is drawn for both cases, and undulation of $\theta_{ac}$ is apparent on (b). Reprinted with permission from (42).

### 2.4.2 Advancing and receding contact angle

The Young angle is not a measurable quantity for most surfaces by any currently available method. This is due to the various local minima in the Gibbs energy curve: It is not possible to know whether the drop is in the most stable state associated with the Young angle, or in any of the local minima. Contact angle values between the metastable states may vary considerably. The two contact angles that can be reliably measured are the lowest and the highest metastable states, that is, the (apparent) advancing contact angle (ACA) and the (apparent) receding contact angle (RCA). The ACA and the RCA are apparent CAs, observed in the macroscopic level, to distinguish them from the actual CAs measured in the microscopic level.

Contact angle hysteresis is defined as the difference between ACA and RCA. It is an important measure in wetting, and especially so for applications that involve the movement of liquid on solid surfaces as hysteresis is directly connected to the adhesion between a liquid and solid. It would intuitively make sense that the Young angle would be half-way between the ACA and the RCA, but there is no thermodynamic justification for this reasoning. It is often assumed in the literature that a static drop (not moving, expanding, or retracting) would exhibit the global energy minimum of the wetting system, and would characterize the wetting properties of a surface. However, the CA of a freshly deposited drop is typically quite close to the ACA. For a wetting system with a large hysteresis range, this value will then naturally differ significantly from the RCA of the surface. As the RCA dominates the adhesion of the drop, reporting a single static CA can be misleading.
2.4.3 Considerations about static CAs

Various ways exist for measuring the wettability of a surface. A simple method is to measure a so-called static CA by gently depositing a droplet and recording the angle between the solid and the liquid after the drop has stopped spreading, and the wetting system has reached an equilibrium. Static CA does not necessarily represent the energetically most stable CA associated with the Young CA, however, due to existence of several local minima/metastable states on a real solid surface. Each metastable state corresponds to a stable static CA of the surface, and measurement of static CA does not allow distinguishing between them. A static CA does not tell whether a system is in the Wenzel or in the Cassie state. Knowledge of the wetting state is relevant, as the Cassie state is a perquisite for high applications requiring high droplet mobility. In the Wenzel state, on the other hand, RCA may be close to zero even for surfaces with a high ACA or static angle (58). Furthermore, static CA is not able to offer information about the mobility of a droplet on the surface, despite high static CA being beneficial for low adhesion due to reduced solid-liquid contact area. Thus, proper surface characterization requires measuring the advancing and the receding CA.

2.4.4 Dynamic CAs

Dynamic contact angles are not within the scope of this dissertation, but they need to be mentioned as they are often confused with advancing and receding contact angles. ACA and RCA are (meta-)stable contact angles, and they are measured by moving the contact line at such a slow rate that the movement can be approximated to be non-existent. Dynamic contact angles exist outside the range of stable contact angles (CA hysteresis range, see section 2.4.5 below) and are measured as a function of contact line velocity. In other words, for ACA and RCA, the movement of the contact line is practically zero, while dynamic contact angles are measured with finite contact line velocities.

2.4.5 Contact angle hysteresis

The difference between the ACA and the RCA, called contact angle hysteresis (CAH), is considered a measure of the 'stickiness' of a surface, i.e., the resistance to motion experienced by droplets on the surface (59; 60; 61). In nature, we find examples of surfaces utilizing CAH to control the motion and behaviour of water droplets coming to contact or condensing onto the surface. Lotus leaves stay clean and dry due to their negligible roll-off angles (20), butterfly wings (62) and rice leaves (63) exhibit directional wetting properties to guide droplets to desired direction, rose petals combine high CAs and high hysteresis for sticky surface with spherical drops forming on it (64), etc.

The presence of contact angle hysteresis has been known for from at least the time of Rayleigh, who noticed that drops on the same surface (glass) had several different, metastable contact angles (3). This observation was later ignored, and
it became routine for at least some researchers to assume a single, experimentally accessible contact angle. Systematic studies of hysteresis were performed in the latter part of the 20th century by Dettre and Johnson (65; 66; 67).

Thermodynamic hysteresis is a property of the surface originating from its roughness and chemical heterogeneity. Therefore, measurement of the advancing and receding contact angles can be utilized to characterize the quality and homogeneity of the surface. Surface defects are often on the micro- or nanoscale and pinning of the contact line on them can provide information about the type and concentration of defects of surfaces that seem homogenous to the naked eye. Although the CL can pin even to a single defect, the spatial resolution of wetting characterization by CA goniometry is poor, as the CL behaviour on the macroscale is affected by average of the local microscopic features beneath the CL.

To characterize thermodynamic hysteresis, it is necessary to minimize kinetic hysteresis. Kinetic hysteresis consists of time-dependent features making interpretation of the CA data more complex (68; 69; 70). When a drop is deposited on a solid surface, unless it is in the saturated vapor of the probe liquid, molecules of the liquid will evaporate in the gas phase, and subsequently adsorb on the solid surface. The concentration of molecules on the solid surface is a function of distance from the contact line and time. This creates a time-dependent gradient on the interfacial tension, which will affect the advancing contact angle. The amount of the influence will depend on the rate of the motion of the contact line. When the CL is made to recede, a film of liquid is left behind. The film will be thicker the nearer it is to the CL. Maximum film thickness is equal to that of a saturated film. The gradient created by this film differs from that of the diffused film preceding the contact line. Both are functions of time, which leads to time-dependent, kinetic hysteresis.

Time-dependent effects also transpire at the solid-liquid interface. Polymer surfaces, for example, tend to reorganize their structure and reorient their chemical functionalities to minimize the interfacial tension (71). Due to that, the "dry" solid surface an advancing contact line moves over can be very different from the "wet" surface under a receding contact line. The change in the interfacial solid-liquid tension depends on the duration of the contact. Samples, or contaminants on sample surface, may also dissolve into the probe liquid, changing its surface tension and, due to that, the measured contact angles. Liquid may be absorbed into the sample, causing it to swell amongst other possible effects. All these effects need to be considered when designing a measurement protocol to ensure that their effect can be minimized whenever possible.
**Figure 8.** Gibbs energy as a function of geometric CA for a wetting system involving (a) an ideal solid surface and (b) a heterogenous solid surface. a) Gibbs free energy of a wetting system involving an ideal solid surface, water, and gas. There is only a single free-energy minimum due to the homogeneity of the solid. This global energy minimum corresponds to the most stable contact angle, also known as the Young contact angle. b) In a wetting system involving a real solid surface, there exists several local free-energy minima besides the global minimum corresponding to the Young CA. Each local energy minima corresponds to a metastable CA. Due to the energy separating adjacent the free-energy minima, a deposited ‘static’ drop can be in any of the free-energy minima within the hysteresis range. Thus, advancing, and receding CAs are currently the only reproducibly measurable contact angles. Reprinted with permission from (44).

### 2.4.6 Most stable CA (MSCA) and “as is” CA

The most stable contact angle is associated with the global Gibbs energy minimum of a wetting system. A common misuse of contact angles is to simply assume that any static contact angle is the MSCA. Just placing a drop on a surface will not guarantee that it will be in a minimum energy state, the drop can be in any of the local energy minima in the hysteresis range due to energy barriers in between them preventing energy minimization. Contrarily, the “as is” CA, which the drop adapts to when it is just placed on the surface, is quite close to the ACA (42; 45).

The practice of tapping the sample lightly with a finger to move the drop into a global energy minimum, utilizing the vibrations that help overcome energy barriers in between different minima, seems less common now that it was in the past. Although this practice can be helpful if correctly executed, it is impossible to know in which minima the drop is after the tapping, nor to know if the global minimum can even be reached this way (72).

### 2.4.7 Line tension

As was already noted by Gibbs in the 19th century, it may be an oversimplification to use a single value of interfacial tension for the whole interface. Near the contact line, the third phase is close to the interface between the two other phases and may affect the interaction between them. Most significantly, due to
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its high surface energy, the solid may affect the surface tension of water in the vicinity of the contact line. This line tension, as Gibbs called it, has later been quantified for solid-liquid-gas system as \( (42; 73; 74; 75) \)

\[
\cos \theta_i = \cos \theta_Y - \frac{\tau}{r_b \gamma}
\]  

(10)

where \( \theta_i \) is the ideal CA, \( \tau \) is the line tension, \( r_b \) is the radius of the drop base, and \( \gamma \) is the surface tension of the liquid. The magnitude of line tension was a source of intense debate about a decade ago, with even its order being questioned. It has since become clear that line tension only notably affects drops when their curvature is in the nanoscale \( (76) \). Therefore, for drops that are not extremely small, it can be neglected.

2.4.8 Capillary length

Thus far, the analysis of this study has neglected to mention gravity. This can be justified since the systems considered having involved drops of water with a maximum diameter of a couple of millimeters. As scale becomes smaller, volume decreases faster than area, and the interactions related to surfaces become increasingly important in comparison to the bulk, a feature which is at the very heart of nanotechnology. Due to surface effects dominating bulk effects, ants can carry much more than their weight and water striders are able to walk on water, for example.

One can calculate a cut-off length below which interfacial forces begin to dominate over gravity, the so-called capillary length, \( l_{ca} \) \( (45) \):

\[
l_{ca} = \frac{\gamma}{\sqrt{\rho g}}
\]  

(21)

where \( \gamma \) is the surface tension of the liquid, \( \rho \) is the density of the liquid and \( g \) is the gravitational constant. The capillary length of pure water is about 2.7 mm. For droplets with diameters much smaller than the capillary length, gravity can be neglected.
2.5 **Wetting transitions**

A drop on a rough solid surface has two equilibrium drop shapes, the Wenzel state (wetted) and the Cassie state (composite). Depending on the relative surface energies of these two wetting systems, one is more stable than the other. However, a drop can remain in a higher energy state due to energy barriers that need to be overcome to move from one state to the other (77; 78; 79; 80; 81; 82).

**Figure 10.** Reversible wetting transition is facilitated by a dual-scale architecture in the surface roughness. A) Single-level topography (silicon micropillars) only allows irreversible wetting transitions from Cassie to Wenzel state. B) Two-level topography (silicone nano-filaments deposited on silicon micropillars) allows for reversible transitions between micro-Cassie and nano-Cassie state. The dual-scale roughness is encountered in all known functional surface bio-interfaces. There is a wide range of different shapes of the roughness asperities vary, while the size of the asperities varies to a lesser degree. Reprinted with permission from (81).
In a wetting transition, the wetting state of the system changes from one configuration to another. Traditionally, it has been thought that only Cassie to Wenzel transitions can occur spontaneously (the energy barrier in between being overcome by vibrations, pressure build-up in the drop due to evaporation, or such), while reverse transition to Cassie state was not possible. Reversible wetting transitions between two wetting states have been demonstrated for example by Verho et al. in 2012 (81). Reversible transitions can occur on surfaces with dual-scale roughness, with transitions happening between the so-called micro-Cassie and nano-Cassie states.

2.6 Superhydrophobicity

Wetting phenomena and superhydrophobic surfaces found in nature have inspired scientists and engineers to develop applications with desirable properties for industrial needs as well as for the needs of our daily lives. Understanding the theoretical foundations of wetting and surface phenomena is required for designing surfaces with needed functionalities. However, for the behaviour of water on surfaces with extreme wetting properties, both the theoretical and the practical understanding is still developing. The theoretical principles, fabrication, applications, and challenges of SHS have been reviewed by many research groups during the last two decades (83; 84; 85; 86; 87; 88; 89; 90; 91; 92). On SHS, surface roughness affects the solid-liquid interactions significantly. Thus, effect of topology facilitates tailoring surface structures that provide desired functional surfaces. Due to the wide range of fields interested in extreme non-wetting behaviour, it has been studied from different angles with varying emphasis. From the industrial perspective, emphasis has also been placed on cost-effective, reliable, and scalable methods to produce SHS with robust water-repellent, chemical, physical and mechanical properties. Another approach is to study the fundamental relationships between surface design and dimensions, and the corresponding wetting properties, adhesion, and droplet mobility.

First SHS were described more than 50 years ago, although the underlying mechanisms and interplay between surface chemistry and microscopic surface structure were not yet understood (66). Ground-breaking work on the field was performed by Barthlott & Neinhuis from the later 1970s to 1990s, and the seminal paper on the effect of surface structure for superhydrophobicity and the Lotus effect was published by in 1997 (20). Their research laid the foundations of the field and ignited the explosion of interest on artificial SHS in academia and industry (93). Natural SHS that have inspired artificial biomimetic SHS can be found in for example the infamous lotus leaf (20; 94), body parts of insects such as the Namib desert beetle (21; 95), legs of the water strider (96; 97; 98; 99), eye of a mosquito (100), etc.

The properties of SHS depend on the Cassie state of droplets, rather than the more typical Wenzel state (93; 101; 102; 103). A stable Cassie state achieved with an interplay of surface chemistry and surface structure. Due to the relatively high surface tension of water, requirements for the surface structure are far less stringent than for surface that are non-wetting towards liquids with low surface
tensions, such as oils. With sophisticated surface designs, like re-entrant or overhang structures, superhydrophobicity can be attained with even moderately hydrophilic surface chemistry (104; 105; 106). The high CA and low hysteresis, and therefore low droplet adhesion, is caused by the low solid-liquid contact fraction, which is often below 10% of the total area below the droplet (3).

Perhaps the most striking property of a SHS is the self-cleaning lotus effect (102). It is a common misconception that the Lotus effect, the superhydrophobic self-cleaning effect of the lotus leaf, requires a hydrophobic surface chemistry, coupled with a hierarchically rough surface. Yet, the Cheng et al. have demonstrated the waxy surface of the lotus leaf to be moderately hydrophilic, with a CA of 74° (107). Water has also been observed to condense onto a lotus leaf at high humidity (108; 109), which also suggests the wax of the leaf is hydrophilic. The entire lotus leaf is covered with wax tubules. Thus, a re-entrant structure is formed on the liquid-vapor interface, reducing the solid area fraction further. The multi-scale roughness of the surface structure contributes by enhancing the CA, reducing the CA hysteresis, and improving wetting stability (107; 110; 111).

Combining multi-scale roughness and hydrophobic surface chemistry leads to the formation of air pockets on multiple size scales. This reduces the liquid-vapor interfacial area significantly, thereby leading to lower CAH and droplet adhesion. As a result, the self-cleaning properties of the surface are improved (112). These conclusions are supported by the Gibbs free energy approach. Furthermore, multiscale roughness can reduce the height of features needed for reaching the desired level of water-repellency (113; 114), making the surface less susceptible to mechanical damage. In general, the microscale roughness can better resist damage than the fragile nanoscale roughness. Additionally, even if some of the surface features are worn or flattened, the multiscale nature of the undamaged portion will be able to retain the Cassie state. Single-scale nanoroughness, on the other hand, is easily worn off by mechanical abrasion, while single-scale microroughness will easily lose the Cassie state after being partially damaged.

The role of the multi-scale roughness has been studied experimentally and analytically by various research groups (112; 113; 115; 116; 117; 118; 119; 120). Among other approaches, the free energy approach has also been used to analytically study the effect of the multi-scale roughness (118; 119). When a drop of water condenses on a micro-rough surface, it has been shown to be in the Wenzel state (118). On a surface with dual-scale roughness, however, a condensed drop can transition from the Wenzel to the Cassie-Baxter state by external energy input. Adding a third scale of roughness further increases the wetting stability of a SHS (119). The second and third scale of roughness improve the wetting stability, increasing the resistance for a catastrophic wetting transition significantly.
3. Contact angle measurement

3.1 Introduction

CA measurement has received tremendous interest from both science and industry, the most important reason being that Young contact angle remains the only way to assess solid surface tension experimentally. The surface tension of a solid is closely related to its adhesive properties, allowing direct definition of polymer properties, such as ease of coating, oleophobicity, or hydrophilicity, which play an important role in many industrial processes, including painting, oil recovery, lubrication, liquid coating, printing, and spray quenching.

When performed and understood correctly, CA measurements can reveal important and detailed information about interfaces. However, interpretation of CA data is not as easy and straightforward as performing the measurements. Proper measurement of meaningful CAs requires carefully developed, well-controlled measurement protocols and some operator experience.

3.2 ACA and RCA measurement

Proper characterization of wetting properties requires measurement of the advancing and the receding CAs, which are the only unique CAs which can currently be reliably measured. Advancing CA is measured by slowly adding liquid to a drop deposited on a solid surface and analysing the angle of contact from the recorded images. Analogously, receding CA is measured by slowly removing liquid to a drop deposited on a solid surface and analysing the angle of contact from the recorded images. Distinguishing ACA and RCA from the other CAs in the CA measurement data can be challenging, however. Performing CA measurements in a way that allows for the measurement of ACA/RCA also requires some knowledge of the theory, and user experience.
Some points originating from the theoretical considerations of CAs should be kept in mind when performing CA measurements. The drop size, for example, needs to be sufficiently large compared to the average size of heterogeneity of the surface. This is important since the drop becomes more axisymmetric when it is sufficiently large, which ensures that the obtained results are meaningful and represent the ACA and the RCA. Drop sizes of 2-3 magnitude larger than the average wavelength of heterogeneity are typically considered sufficiently large (42). Furthermore, large drop size decreases the dependency of the measured ACA/RCA on the size of the drop. For ACA, the CA should remain almost constant while the drop size is increased during an experiment, provided that the solid is isotropic. For RCA measurement, large initial drop size ensures that RCA is reached before start of the measurement (see Publication I for more details (121)). Too small initial drop volume can be recognized from the data due to CL pinning: if RCA is not reached before the beginning of the measurement, baseline (BL) will not start to recede immediately when liquid is withdrawn from the droplet. Instead, BL width will remain constant, and value of measured CA will decrease. This value is not equal to the RCA (estimated stage where RCA is reached is marked in the CA data presented in with a dashed black line).
Contact angle measurement

Figure 12. Results from RCA measurements performed with (a) too small initial drop volume, and (b) sufficiently large initial drop volume. The green curve shows measured CA, while the blue curve shows the baseline width. The estimated volume at which the RCA is reached is marked by the dashed vertical line. Reprinted with permission from (44).

Figure 13. An example of receding contact angle data measured on a silicon substrate coated with silicone nanofilaments. a) Too small initial volume of drop was used in the measurement shown in red; therefore, the drop has not reached the receding CA at the beginning of the measurement. The CAs that are not deemed RCA have been removed from the curves on the right (b). For the measurements shown in other colours (black, green, yellow, and blue), the initial drop volume was sufficiently large, and only data points for which fitting failed have been removed on the right. Reprinted with permission from (44).

When a droplet is deposited on a solid surface, it is typically in a metastable state with a corresponding CA close to but below the ACA. When volume of the drop is increased, CA usually increases while the CL stays pinned until the ACA is reached. After this, further increase of volume results in advancing of CL while the CA remains constant at ACA, provided that the solid is isotropic. Deviations from constant ACA give therefore information about the heterogeneity of the solid.

Upon starting an RCA measurement, the initially deposited droplet is again in a metastable state with a corresponding CA close to ACA. When the volume of the droplet is decreased, the CL remains pinned while the CA changes through the whole hysteresis range until reaching the RCA at the opposite end of the range. Required initial drop size thus depends on the hysteresis of the solid.
3.3 CA measurement error

CA measurements suffer from practical limitations, as to some degree do all characterization methods. CA goniometry depends heavily on operator influence, for example. It was demonstrated in Publication IV that results obtained by independent experienced scientist can vary up to 10° even with the same setup, especially for CAs exceeding 150°, which renders interlaboratory comparison practically impossible for SHS (122). All CA measurements are based on optical imaging of the probe droplet, followed by image analysis to determine the droplet profile from the images (123; 124; 125; 126; 127). The inaccuracies in the results originate mainly from the optical distortions in images of the droplet, especially near the CL region. The distortions are affected by imaging conditions and parameters, such as camera resolution and magnification, room lighting, contrast, etc.

3.3.1 Optical errors

The optics used in CA goniometry are a source of systematic errors that are to some extent unavoidable. Tiny deviations from horizontal level in the imaging direction or tilt of the sample may lead to significant errors. Results depend strongly on the details of the measurement procedure and camera parameters, such as the magnification, contrast, or whether the baseline is determined manually or by the vendor-provided software. Optical distortions are largest in the

---

Figure 14. Minimum initial drop volume needed in RCA measurements for the CA to reach the receding phase before the measurement is started. The drop volume is determined by the CA hysteresis, which needs to be estimated before the measurements, or iterated based on previous runs of measurements. Reprinted with permission from (44).
vicinity of the BL. The edge of the droplet is diffuse, and heavily pixelated when a high-resolution camera is utilized. Diffuse edge and pixelation cause an unavoidable systematic error in measured values of CA ranging from approximately 1° to above 10° since determination of the BL location becomes subjective (122). An automatic baseline placement function is often provided by the goniometer software, but for SHS, it will often fail, too. This is due to the short width of the baseline and sagging of the drop edge which can block the camera view of the baseline. Improvements have been proposed to experimental procedures (Publication III (44), Publication I (121)) and analysis methods (125; 126; 127), yet the problems remain largely unresolved.

![Figure 15](image)

**Figure 15.** Ambiguity in drop edge detection as demonstrated with (a) a steel ball mimicking a liquid drop on a SHS, and (b) a water droplet ($V = 8.8 \text{ ml}$) on a SHS. Reprinted with permission from (128).

### 3.3.2 Error caused by baseline misplacement

Just one pixel displacement of the baseline can cause substantial errors in the CA values, especially for highly hydrophobic surfaces. In Publication III, it was demonstrated experimentally and by simulations (122) that error increases substantially for increasing CA. The uncertainty range of the experiments and simulations matched each other relatively well, corresponding to ~1° for CAs less than 120°, ~2° for CAs of ~150°, and ~5° for CAs of ~162°. Small systematic errors caused by baseline misplacement have previously been reported also for other types of surfaces (129).

Since CAH is calculated by subtraction, propagation of errors makes uncertainty even more pronounced, up to $\sqrt{2}$ times greater than for single values of CA. For reflective surfaces, reflected image of the drop (below the droplet in the recorded image) can help baseline determination. On the other hand, for macroscopically rough surface (e.g., woven textiles), BL is irregular, and visibility may be blocked by features of the solid surface. Thus, determination of CA becomes difficult.
Figure 16. Error caused by 1-pixel misplacement of the baseline as a function of CA. Error grows exponentially as CA approaches 180°. a) Photograph of a sessile droplet, with a close-up of the CL region. b) Sketch of a sessile droplet, with baseline locations drawn in the close-up. c) Error in CA as a function of CA. For more details, see Publication IV (122).

Errors caused by baseline displacement were systematically studied in Publication V (128) by simulating one-pixel baseline shift from the theoretical location of the interface. The results are shown in Figure 17, where error in CA is plotted as a function of CA for different pixel dimensions. The pixel dimensions imitate different camera resolutions, demonstrating the importance of high-resolution images. It can be seen from Figure 17 that error from BL misplacement increases exponentially as CA approaches 180°.
3.3.3 Effect of drop size on CA

The size of the drop is absent from the Young equation. Yet, the results of CA measurements are sensitive to the drop size. Different drop sizes cause different types of measurement errors, and the appropriate size that minimizes the overall deviation from the theoretical CA is a balance between the various sources of errors. For example, the size ratio between the needle tip and the drop diameter affects how much the needle distorts the drop shape, which may cause fitting errors. Thus, it is recommended that the diameter of the drop is at least five times the diameter of the needle tip. The base area of the drop should also be much larger than the average size of the chemical or topographical heterogeneity of the surface. Marmur recommended that the base area of the drop should be preferably 100–1,000 times larger than the typical length scale of heterogeneity to avoid significant distortion of the CL (42). The difficulty with this condition is that the actual length scale of the heterogeneity is often unknown. Therefore, relatively large drops are used to ensure that the condition is fulfilled.

The CA is properly defined only for axisymmetric droplets. For CA the results and interpretation of CA measurements to be meaningful, the droplets used in the measurements must be large enough to be axisymmetric, as larger drops tend towards axisymmetry. Additionally, smaller drops are more susceptible to evaporation, and optical errors caused by light scattering and diffraction. Furthermore, difficulty in baseline location determination causes larger errors for smaller droplets.
3.3.4 Curve fitting

Droplet profile is determined by curve fitting, utilizing the gradient in contrast between the liquid and the gas phase in the recorded images. Manufacturer-provided software includes automatic fitting feature, usually offering several possible fitting methods to choose from. BL location must be determined before curve fitting can be performed. This can be done either manually by the operator, or automatically by the software. Manual determination is recommended, as automatic determination often fails. The CA is then determined automatically by the manufacturer provided software from the contact point between the BL and the fitted curve. The accuracy of the fitting depends on the quality of the data. Thus, strict measuring protocol is required to ensure that incorrect procedures are avoided, as considerable errors may result from them.

Algorithms

Several mathematical methods can be used for curve fitting. Available algorithms include but are not limited to the following:

- Young-Laplace,
- circle,
- elliptical,
- polynomial,
- tangential,
- B-spline snakes, etc.

The method of choice varies depending on the type of the sample, the size of the droplet, etc. Different algorithms provide different value for the same image of a wetting system. The Young-Laplace method (also called axisymmetric drop-shape analysis, ADSA) is the only curve-fitting method with a physical basis, and thus recommended for most cases (130). The method fits the drop shape in the recorded image to a theoretical drop profile based on the Young-Laplace equation:

\[ \Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  \hspace{1cm} (12)

Young-Laplace method is recommended method of choice in most circumstances, as it is the only method with a physical basis, and because of its excellent reproducibility and precision (130). The method assumes axisymmetry and will therefore lead to large errors for nonaxisymmetric drops, e.g., when characterizing very hydrophilic or macroscopically rough surfaces. However, CAs are ill-defined in the absence of axisymmetry in any case.
3.3.5 CA errors on superhydrophobic surfaces

For SHS, the existing algorithms based on edge detection introduce significant error due to the blurred area around the baseline (122; 128). The contact points where the droplet profile intersects with the solid surface are difficult to precisely determine due to the blurring, and the errors from this effect can consequently be significant. Experimental errors with a commercial goniometer software match the analytically and numerically calculated errors relatively well. The quantified errors demonstrate how the error increase with increasing CA, ranging from 0.5° for contact angles below 150° to 8° for contact angles close to 180°. Additional source of error is the uncertainty in the drop edge detection, which was not included here. Thus, actual errors in CA measurements may be larger than the error shown in Figure 17.

3.4 Characterization of SHS wettability

With a history of more than 200 years, CA goniometry is still considered the gold standard in wetting characterization, and is routinely used for characterizing SHS, also. Measured CA can vary depending on the experimental methods,
and on how the droplet is deposited on the solid surface. The measurement is based on the apparent profile of the drop, and therefore susceptible to the inherent inaccuracies and systematic errors of the optics systems and fitting procedure used. Measurements on SHS are especially error prone due to the extremely high CAs (52). Save for a few reports (e.g., (123; 124; 126; 127)), the inherent inaccuracy of CA measurements is often overlooked by its users. For development of next-generation SHS and applications utilizing the desirable properties, it is mandatory for the scientific community to recognize and solve the issues concerning characterization of SHS.

The need for coatings with increasingly high quality, manufacturing process must be monitored by characterization techniques that can quantify the wettability and adhesion with high precision (123). CA goniometry is the conventional method for characterizing wettability of various surfaces (132). The frictional forces of next-generation SHS may be lower than possible to characterize by CA measurement. The need for coatings with increasingly high quality, manufacturing process must be monitored by characterization techniques that can quantify the wettability and adhesion with high precision (123). Thus, there is a need to measure the forces directly. Various techniques have been developed for direct measurement of the frictional forces between a liquid drop and a solid surface, including tilt-stage (132; 133; 134; 135), oscillating droplet tribometer (136), force-calibrated elastic cantilevers (7; 137; 138; 139; 140), tensile adhesion measurement with a microelectromechanical balance (141; 142; 143; 144), scanning droplet adhesion microscope (SDAM) (145), etc. Also, the high mobility of droplets makes adhesion characterization challenging. The adhesion and retention forces are at the limits of resolution of the characterization techniques, and droplets roll off the surfaces with the slightest inclination. Assuming circular CL shape, the friction force \( F_{LA} \), also referred to as the lateral adhesion force, can be calculated as (7; 133; 146):

\[
F_{LA} = \frac{24}{\pi^3} \gamma D (\cos \theta_r - \cos \theta_a)
\]  

(13)

where \( D \) is the diameter of the CL and \( \gamma \) is the surface tension. As the ACA and the RCA approach each other with increasing hydrophobicity of the surface, relative errors in lateral adhesion force measured by CA goniometry increase due to the limited accuracy of image analysis.

### 3.5 Equipment

Contact angle goniometry, which is also known as the sessile drop method, is often favored due to its relative simplicity and low cost. It is performed by direct optical imaging of drops on the sample surface, followed by image analysis using vendor-provided software to obtain the contact angle data.
The drop sizes vary between a couple of microliters to some tens of microliters; the diameters of the contact area between the drop and the sample is typically in the millimetric scale. Therefore, the samples need not be uniform, and effects due to the edges of the sample can be avoided. Furthermore, only one side of the sample needs to be measured in an experiment, meaning that the sample can be one-sided. This is in contrast with the Wilhelmy plate and many other methods, which averages the results over the whole sample perimeter at once (147). In the Wilhelmy plate for rough samples, the perimeter length may be difficult to reliably measure, which renders it challenging to deduce the contact angle from the measured strength.

A goniometer consists of a horizontal stage to mount a solid or liquid sample, a motor-driven syringe connected to a needle with tubing to form a liquid drop, an illumination source, and a camera to record images of the drop. The use of relatively high magnifications enables a detailed examination of the intersection profile. The resolution of the recorded images in the contact line region can be of crucial importance in minimizing the errors of measurements (122; 128).

It is important to store the used liquids in properly closed and sealed containers to prevent contamination. A different set of syringe, needle, and tubing should be used for each probe liquid; otherwise, cross-contamination is likely to occur. It is of importance that the syringe-tubing-needle system is leak-tight, as leaking air can result in a loss of volume control when manipulating the amount of liquid during measurement.
Figure 19. A photograph of a contact angle goniometer (top, Copyright by Biolin Scientific Oy) and a sketch of a contact angle goniometer set-up (bottom, reprinted with permission from (44)).
3.6 Measurement protocol for ACA and RCA

A protocol with steps for measuring ACA and RCA are provided here. For the full measurement protocol with details about equipment set-up and tips on troubleshooting challenging parts of the procedure, see Publication III (44).

Advancing contact angle measurement

1 Prepare and clean the sample.

2 Prepare the goniometer syringe and tubing. Fill the syringe with more water, if necessary, and check the tightness of the water tubing. If other probe liquids are used with the same goniometer, use a different needle and tubing for each probe liquid.

3 Dispense ~20–100 µl of water into a spare cup or a piece of paper to remove possible air bubbles or impurities in the needle tip.

4 Place the sample on the sample stage. Check that the stage is horizontal (no tilt in any direction).

5 Dispense a 2-µL drop of water to ensure that it freely hangs on the tip of the needle. Lower the needle to allow the drop to feature on the lower part of the computer screen. Position the needle so that it is in the middle of the screen, pointing directly downward.

6 Raise the sample stage so that the drop comes into contact with the sample, until the tip of the needle is about halfway inside the drop and is in the middle of the drop from the perspective of the camera (see Figure 19) for the needle position from the camera perspective). Dispense 1 µL of water at a flow rate of 0.05 µL/s to ensure that the overall size of the drop is 3 µL. The low flow rate is necessary to avoid dynamic effects. Wait for 30 s to ascertain that the system is in equilibrium.

7 Start recording the video. Continue quickly to the next step (Step 8).

8 Dispense 8 µL of water at a flow rate of 0.05 µL/s.

9 Stop the video. The recorded images are used for analyzing the ACA (see the Analysis section).

Receding contact angle measurement

10 Estimate the recommended starting droplet volume for RCA measurement ($V_a$) (see
for instructions on ways to determine $V_a$). If you have no approximation of the receding angle of the sample, perform a measurement to determine the contact angle at which the baseline starts to move.

11 Deposit a drop with a volume larger than $V_a$ onto the sample. The flow rate can be high at this stage, for example, 2 µL/s.

12 Adjust the height of the stage to ensure that the needle is close to the sample surface without touching it.

13 Remove water from the drop at a flow rate of 2 µL/s until it is ~13 µL in size. Adjust the position of the needle again, if needed.

14 Remove 2 µL at 0.05 µL/s. The low flow rate is used to avoid dynamic effects.

15 Wait for 30 s to ensure that the system is in equilibrium.

16 Start recording the video. Continue quickly to the next step (Step 17).

17 Withdraw water at a flow rate of 0.05 µL/s until the droplet is completely removed.

18 Stop recording the video after the water removal. The recorded images are used for analyzing the RCAs (see the Analysis section).

19 Lower the sample stage to avoid contact between the needle and the sample. Clear any possibly remaining water off the sample with a stream of pressurized gas or a lint-free paper tissue. Move either the stage or the sample so that the next measurements of ACA and RCA will be in a different location, raise the stage back near the needle and start again from Step 5. If the size of the sample does not allow measurements on different locations, repeat the measurement on the same location.

**Analysis**

20 Expand the window showing the first recorded image of the droplet to ensure that you can distinguish the interface between the droplet and the sample surface as well as possible.

21 Use the manual baseline option and place the baseline on this interface. If there is any tilt on the surface, tilt the baseline until it is in the correct position on both sides of the drop.

22 Analyze all the recorded images.
23 After the analysis is complete, check from the images of a different-sized drop that the baseline was placed in the correct position.

24 Check the fitting error of the analyzed images by comparing the fitted curves to the actual drop profile. Remove the data points with clearly visible fitting errors (Figure 13).

25 Plot the average of the contact angles on the left- and right-hand sides of the drop as a function of the drop volume (Figure 13).

26 Plot the baseline length as a function of the drop volume.

27 If all the above tests were passed, calculate an average of the contact-angle value obtained from each image in a measurement.

28 Calculate the ACA and the RCA values of a sample as an average of five or more measurements each. Report both the advancing- and the receding-angle averages, and the standard deviations of the measurements.

Results

The resulting CA values are calculated as averages of the datapoints gathered during the measurement. An example of the gathered data is shown in Figure 13.

CA data interpretation

Contact angles are very sensitive to factors, such as surface geometry, roughness, defect concentration, contamination, and deformation. This allows for detection of microscale properties using a macroscopic method. Even nanometric defects can be detected using the CA measurement. The sensitivity renders the compiling of contact angle data difficult: the method is also very sensitive to the measurement methodology, and even when measurements are done identically, variations in properties between samples of same material can yield a wide variation in contact angles. Therefore, handbook collections of contact angle data for different materials to serve as the reference source are rare.

Contact angle measurement is essential when fundamentally characterizing wetting systems in science and can be used to study various wetting and dewetting phenomena. Theoretically, CA shows the balance between adhesion between the drop and the surface, and the cohesive interactions inside the drop. CAs provide information on features, such as surface chemistry, homogeneity, ease of coating for a substrate, and the quality of a coated surface. Some surface properties can be quantifiably characterized with CA measurements, while for others only qualitative information is gained.
Solid surface tension. The most common use for CA goniometry is to characterize solid surface tension. The only way to access solid surface tension is through Young equation, which renders this problematic as the Young angle is a property of an ideal surface. The real-surface counterpart of the Young angle, which is the most stable CA, is cumbersome to measure experimentally. Despite some articles suggesting methods how to measure MSCA by either utilizing vibrations (148) or on an inclined plane (149), no matured technique for routinely characterizing MSCA exists. Solid surface tension can also be estimated via (semi-) empirical equations, utilizing measured values of ACA and RCA (50).

Adhesion. One of the surface properties associated with contact angles is adhesion. According to the literature, it is related to the sliding angle, contact angle hysteresis \( \theta_a - \theta_r \) (144) and the difference between the cosines of RCA and ACA \( \cos \theta_r - \cos \theta_a \) (150). It has been demonstrated that static CA does not correlate well with adhesion (144), which is not surprising considering the random nature of the droplet deposition process.

Shedding and sliding of droplets from SHS are governed by adhesive and frictional forces, which relate to CAs in the following manner (see Appendix D for details):

\[
F \sim \cos \theta_r - \cos \theta_a
\]  

(14)

For low CAH, even a small error in the placement of the BL leads to significant relative errors in CAH and the corresponding adhesion force. For a surface with an RCA of 170°, one pixel error in the location of the BL can cause at least a 300% error in CAH and adhesion force. This demonstrates that CAH can be impractical for characterizing adhesive properties of SHS, as errors will remain high when approaching the upper CA limit even with improved imaging and fitting algorithms. Thus, force measurements appear currently to offer more potential in characterizing next-generation SHS. Traditional force-based measurements, like the classic Wilhelmy plate, suffer from drawbacks that make them unsuitable for this purpose. Wilhelmy plate, for example, has strict requirements for the sample geometry and does not give information about local wetting properties (147). Some recently developed techniques allow for detection of miniscule forces between droplets and surface. Droplet friction, for example, can be quantified by measuring the deflection of a thin capillary inserted in a droplet (147). Oscillating droplet tribometer can measure droplet friction forces down to 10 nN by inducing and tracking the back-and-forth motion of a magnetic water droplet (136). Scanning droplet adhesion microscope can produce spatial maps of local wetting properties, measuring adhesion forces down to 5 nN level (145).

Drop mobility. Difference between cosines of RCA and ACA \( \cos \theta_r - \cos \theta_a \) is expected to correlate with drop mobility (150). Studying interactions between imaging materials and print surface, Samuel et al. (144) found that advancing
CA correlates well with wetting force, while receding CA was found to be a good measurement for adhesion.
4. Silicone nanofilaments

Silicones, also known as polisiloxanes, currently comprise one of the most important family of materials; these different silicone-based materials are in use in nearly all areas of human life. Silicones are characterized by a chain or network of alternating silicon and oxygen atoms, known as the siloxane chain. The length of the chain as well as the organic side-groups attached to the silicon atoms vary, allowing for a range of properties in different silicone materials. First synthesized in the beginning of the 20th century by Kipping, the silicone industry did not begin gaining ground until the industrial-scale synthesis of methylchlorosilane, an important silicone precursor, was discovered by both Richard Muller and Eugene G. Rochow, albeit independently of each other (151).

The extraordinary combination of several desirable properties, such as good thermal and environmental stability, biocompatibility, non-toxicity, water-repellency, low chemical reactivity, and flexibility, combined with their low price, renders silicones a very widely used material in nearly all areas of daily lives (152). Furthermore, other engaging properties include their very high stability even under very harsh conditions; resistance to oxidation; they are hydrophobic, biocompatible, and non-degradable; and possess excellent thermal and dielectric properties. Many of the mechanical properties stem from the flexibility of the siloxane chain, which is the most flexible polymer chain known to surface science, whereas others stem from the properties of the organic residues attached to the siloxane chain. The combination of desirable properties with very few negative ones is the reason silicones are used in such a plethora of applications, including sealants, resins, elastomers, gels, oils, electrical insulators, fire-stops, antifoaming agents, and hydraulic media. Their inertness to environmental and health issues allows for medical use, as well as their use in personal care, such as skin and hair care products.

Despite being heavily used, very little has been known about silicones at the nanoscale. Silicone nanoparticles have been known for more than 50 years (153), and self-assembled monolayers (SAMs) from silane precursors have been used for surface modification since the 1980s (154). 1-dimensional silicone nanofilaments were only discovered this century and offer a new and exciting kind
of nanomaterial with many desirable properties and range of potential applications. Silane SAMs and SNF have the same precursors in common and share some of the complexities and difficulties in their synthesis.

4.1 Silicone chemistry

Silanes can be mono-, di-, or tri-functional depending on the number of hydrolysable side-groups that are attached to the silicone atom. Water cleaves the bonds of hydrolysable groups forming reactive hydroxyl groups (OH) and creating molecular hydrogen, hydrochloric acid, or alcohol as a by-product. Monofunctional groups can form only dimers or monolayers, whereas the others can polymerize and create more complex structures (155; 156; 157).

Weather silane precursors form SAMs or multi-layered coatings (silicone) depends on the reaction conditions used in the synthesis. Polymerization of one of the most common silane precursors, methyltrichlorosilane, proceeds in the following manner:

1. Water hydrolyses the chlorine groups, leading to the formation of methyltrisilanol and hydrochloric acid.
2. Hydroxyl groups in the silanol condense with one another, or with hydroxyl groups on a substrate surface, forming polymethylsilsesquioxane and water.

The reaction steps, assuming complete hydrolysis and condensation for simplicity, are shown below in Eq. 15 and Eq. 16. The sequence of all possible hydrolysis
and condensation reactions is not known, we can only deduce the likely sequence from the start and end products.

\[
\text{MeSiCl}_3 + 3n\text{H}_2\text{O} \rightarrow n\text{MeSi(OH)}_3 + 3n\text{HCl} \tag{15}
\]

\[
n\text{MeSi(OH)}_3 \rightarrow [\text{MeSiO}_3]_n + \frac{3n}{2}\text{H}_2\text{O} \tag{16}
\]

In dry reaction conditions, hydrolysis can only occur in the surface-bound trace water layer, which exists on most surfaces. Consequently, only a monolayer of silane is deposited, forming a SAMs coating. In addition, monofunctional silanes can only form monolayers, even in humid reaction conditions.

**Silane SAMs**

Self-assembled monolayers from organosilane precursors have been utilized since 1980s, since the pioneering work of Sagiv et al. (154), for modification of inorganic surfaces. They offer great benefits owing to their excellent properties, including hydrophobicity and stability under extreme conditions. Organic-inorganic hybrids are a class of materials that can be designed to have specific properties and functionalities by combining the properties of organic and inorganic components. Unique materials with designed nanoscale morphology and tailored chemistry can be created with properties that fit the application. The details of the reaction process have been studied to a great extent. Several reaction products can be formed when a hydroxyl-containing surface is exposed to reactive silanes, depending on the reaction conditions. Furthermore, depending on the chain length and size of the organic residue, silanes will favor either a monolayer formation or vertical polymerization, thus leading to a multilayer or bulk growth. Monolayer formation is usually preferred for most applications; therefore, synthesis is performed under strict control of the amount of water.

The deposition of silanes and silicones involves hydrolysis, physical adsorption and surface condensation through covalent bonds, hydrogen bonds, and van der Waals forces. Silanols of hydrolysed silane interact with the substrate surface, hydrophilic groups being essential surface groups for condensation of silanes in most cases. Thus, it is commonplace to activate the surfaces to maximize the reactivity prior to the SAMs deposition.

The molecularly thin layer of silane is less than 2 nm thick. Thus, it does not affect the morphology or the shape of surface structures. Condensation of a monolayer varies from several minutes up to several hours in duration, depending on various factors, such as the silane concentration and temperature. Complete condensation of silanols into a covalent siloxane network requires aging of the surfaces in air for few days or annealing at 100-120 °C for a few hours (159; 160).
For a given organosilane precursor, the properties of a deposited layer depend on the reaction conditions, such as water content and temperature. Many studies focused on improving the properties of the films by studying the hydrolysis of organosilanes and the self-assembly mechanism. Step-by-step, the knowledge has accumulated as other processes were proven while others ruled out, resulting in a hydrolysis-physical-adsorption-surface condensation sequence being ultimately established.

4.2 Silicone nanofilaments

Silicone nanofilaments (SNF) can be utilized to render a wide variety of materials superhydrophobic, superhydrophilic, superoleophobic or superamphiphobic (161; 162; 163; 164; 165; 166; 167; 168; 169). The synthesis can be performed in gas or solvent phase (161; 170), exposing the substrate to a trifunctional silane precursor, typically MTCS (171; 172; 173). The gas or solvent phase must contain a well-controlled amount of water within a certain optimum window, which facilitates slow hydrolysis of MTCS, thus allowing the synthesis to be diffusion-limited (174). For the solvent phase, one of a variety of non-polar solvents (e.g., toluene on n-hexane) can be used (171; 172; 173; 175). The consensus in early studies on SNF was that the substrate surface must contain hydroxyl groups (161; 172; 174). Surfaces are typically activated with oxygen plasma treatment, basic surfactant solutions or piranha solution. Hydrolyzed or partially hydrolysed MTCS moieties will react with the hydroxyl groups on an activated surface, inducing the formation of polysiloxane (silicone) nanofibers, i.e., SNF. Steric hindrances prevent more than two of the three hydroxyl groups of reacting with the surface. The polysiloxane crosslinks during the polymerization, eventually leading to the formation of SNF. HCl gas forms as a by-product of the MTCS hydrolysis (174; 176). One benefit of SNF is the wide variety of substrate materials which can be rendered superhydrophobic, including silicon, glass, cotton, various metals, and ceramics (161; 170; 175; 177; 178; 179). Besides MTCS, other silanes can be used as precursors for SNF, including other organosilanes, such as vinyltrichlorosilane (174; 176) and a mixture of tetraethoxysilane/tetrachlorosilane with an organosilane (180; 181). Properties of both the individual filaments and the SNF coating depend on many controllable and uncontrollable reaction parameters (151; 171; 172; 182; 183). The controllable parameters include silane concentration, water concentration, temperature, reaction length, substrate material, substrate activation, etc.

4.2.1 SNF Synthesis

SNF can be synthesized in either the gas phase or in solvent. The gas phase offers some benefits, including the coating of arbitrarily shaped objects, easier control of impurities and water concentration, and a lack of problems caused by handling the waste solvents. As the SNF synthesized in our group are almost
exclusively done in the gas phase, the discussion here will focus on gas phase synthesis. Synthesis in solvent is very similar in theory, with the exception that diffusion of the reactants is expected to be slower due to the viscosity of the medium.

It is generally agreed that proper cleaning and activation of the surface is needed (151; 160; 161; 162; 172; 176; 184). In some cases, such as coating glass, the activation step can be omitted due to a sufficiently high native hydroxyl density of the surface. The activation can be performed by oxygen plasma, a combination of UV/ozone, or by using a piranha solution. All these methods have the added benefit that they also remove organic contamination from the surface: treatment with piranha solution directly removes it, while the other methods oxidize the organic contaminants, rendering them easily rinsed away from the surface with water. When drying the activated sample, it is important that the water leaves the substrate surface as a continuous film, otherwise, inhomogeneous SNF coating will result in the synthesis.

The reaction conditions are expected to affect the properties of the coating, therefore allowing tailoring of the properties to suit the application in mind. The main reaction controllable reaction parameters are water concentration, silane concentration, and the length of the reaction. The properties that can be tuned accordingly include the wetting properties, coating thickness, and morphology.

**Effect of reaction conditions**

SNF synthesis was studied both experimentally and from the literature for this dissertation to gain insights into the growth mechanism of the filaments. The mechanism of formation is of interest for two reasons: (i) basic scientific interest, as no other amorphous soft material forms unidirectional nanostructures through self-assembly, and (ii) for further optimization of the synthesis process. The properties of SNF-coated surfaces, such as their hydrophobicity, surface morphology, coating thickness, and optical properties, depend on the coating conditions. This allows for an optimization of the prepared coatings to suit the application in mind, and to examine the kinetics of the reaction by observing the changes in the resulting coatings caused by variation of the reaction parameters. Four different SNF synthesis reactors were assembled and optimized during the research carried out for this dissertation: Three atmospheric pressure gas-phase reactors and a vacuum reactor. The assemblies of the atmospheric reactors evolved over time, due to improvements made based on the user experience gained. Two reactors and their typical synthesis protocols are introduced in the Experimental section: last version of the atmospheric reactor, and the vacuum reactor.

The primary parameters that affect SNF synthesis are relative humidity, silane concentration, catalyst concentration, temperature, pressure, gas/liquid phase, absolute substrate area, substrate material, and substrate pre-treatment. In addition to these controllable parameters, there are many uncontrollable parameters which are significant. Surface chemistry is very sensitive to imperfections,
contamination, irregularities, and surface topography. Any differences in storage conditions, details in handling and performing substrate pre-treatment, or differences in the specifics of the reactor and other equipment may lead to differences in the results gained.

The details of all the complexities of silane chemistry are difficult to completely understand, and may lead to irreproducible and seemingly contrary results, as has been observed for the formation of monolayers of alkoxy silane. The chemistry of SNF growth on surfaces is closely related to the chemistry of silane monolayer formation and can be expected to be similarly complex. Consequently, deviations in the obtained results can follow from small differences in the individual coating protocols.

Variables for which one has little or no control on include impurities, irregularities, imperfections, and surface structures. Other issues that may also have an effect include differences in the individual pieces of laboratory equipment, time between different steps of the synthesis protocol, individual handling of the substrate, and laboratory atmosphere.

Reaction parameters.

A short overview of the important reaction parameters and their role in the reaction is given below.

Water. Water is obviously a major factor in SNF synthesis. While its key role in facilitating SNF growth is well-established (151), the details of the reaction kinetics are not as clear, resulting in the exact role of water being uncertain and raising some questions, such as: Is the absolute amount of water in the reaction the limiting factor, or rather the relative humidity of the reaction volume? What is the relative importance of water in the gas phase, and of the surface adsorbed water layer? Generally, it has been clear that high water concentrations lead to formation of surface structures with larger diameters, and that the growth of SNF is facilitated by a relatively clear-cut, mid-range water concentration.

Recently, the relations between the different water-related parameters were systematically studied by Olveira et al. (183). They reported on the ways that different shapes of surface morphologies were synthesized, as well as their sizes and concentrations adjusted by varying the absolute amount of water, relative humidity, and temperature of the reaction. Based on their findings, relative humidity appears to be the key parameter determining the final shape of surface structures in SNF synthesis. An absolute amount of water is not critical, but rather the amount of water in relation to the saturation value of gaseous water. This indicates that the synthesis is not based on a simple gas-phase or gas-solid interphase reaction, but rather depends on the condensation of water on the solid surface.

Based on the experiments conducted by the author of this thesis, an optimum in relative humidity for our reactors has been located between 25-35 % relative humidity (%RH). Variation in the morphology in this range is minor, the type of defects being the most characteristic feature indicating whether low or high
humidity conditions were used. In dry conditions, with only trace water present, a thin film forms on the substrate surface. If the humidity is increased to a level of roughly above 10 %RH, small spherical structures can be observed on the surface. Further increase in the humidity leads to elongated structures instead of spherical one, the diameter of which corresponds quite well to that of the earlier spheres. When relative humidity is above the optimal range for SNF synthesis, a rough, thick film was observed on SEM examination of the substrate surfaces, along with spherical particles with larger dimensions.

**Silane.** Optimum silane concentrations for SNF synthesis have also been reported by many researchers (151; 183). According to the literature, the effect of silane concentration can be summed up in the following way:

- Low silane concentration leads to formation of a thin film.
- Small increase in the concentration results in formation of small spheres and short filaments.
- Optimum concentration results in the growth a thick SNF coating.
- Above the optimum concentration spherical particles and agglomerates with more random topography are formed, along with a SNF coating.

It is not known if higher silane concentration leads to longer and thicker filaments as a limiting factor, or whether the high concentration just accelerates the growth of the filaments due to kinetic effects. Low silane concentrations can also yield long filaments if extended reaction durations are used.

**Time.** It has been reported that the length of the filaments rapidly increases in the beginning of the reaction, but that the growth rate levels off at elongated reaction times. This seems feasible considering that the concentration of the reactants reduces as the reaction continues. Slower diffusion processes are assumed to dominate the kinetics as the reaction progresses, especially if the reactor is not equipped with a blower to facilitate convection. Longer reaction times lead to longer filaments, thicker SNF coatings and, consequently, higher water-repellency. This is partly due to the increased roughness and porous nature of a thick SNF coating, which facilitates a stable trapped air layer. Continuing the reaction even after the growth of the filaments has completed may still improve water-repellency of the coating due to reaction of hitherto unreacted hydroxyl groups in the filaments.

**Pre-treatment.** A long-held consensus in the SNF research was that a sufficiently high concentration of surface hydroxyl groups must be available to facilitate SNF growth. Therefore, a cleaning procedure is needed, and if native hydroxyl groups were not present in a sufficiently high density, a subsequent activation step to create artificial hydroxyls would follow. It has recently been demonstrated that surface hydroxyls are not a necessity, as SNF were grown onto surfaces without hydroxyls (185). However, this does not eliminate the need for a clean and activated surface for uniform SNF coatings, and is more relevant when the growth method is considered.

**Post-treatment.** Hydroxyls act as hydrophilic pinning points if they appear in the final product, lowering especially the receding contact angle, thereby increasing CA hysteresis. The unreacted hydroxyl groups can be terminated by
post-treatment of the sample by annealing or radiative heating (159). Consequently, the water-repellency of an SNF coating may improve by exposure to the reaction atmosphere, even after the reactive moieties have been consumed.

4.2.2 Proposed growth model for SNF

The growth mechanism of SNF is not fully understood, due to the inherent complexity of silicone chemistry and self-assembly. Several growth mechanisms have been proposed in the literature, offering variety of approaches (151; 174; 176; 186). Rollings & Veinot proposed a diffusion-limited mechanism for gas phase synthesis. It was suggested that hydrolysed silanes reacting with the surface hydroxyl groups form small islands that act as seeds from which the SNF growth starts (174; 176). The islands extend into the gas phase, where incoming hydrolysed silane moieties are more likely to react with the top of the islands, than to diffuse into the valleys between the islands. The growth of the islands is therefore one-dimensional, directed away from the surface. As a result, one-dimensional structures, the SNF, are eventually formed. To the benefit of this model, an explanation for the uniaxial beginning of growth is offered. However, none of the growth models proposed before the work on this thesis started was deemed to satisfactorily explain the break of symmetry leading to 1-dimensional filaments with high aspect ratios.

Growth process. The physicochemical model proposed in Publication II (186) was based on the experimental evidence that SNFs occasionally exhibit a hollow core (hollow SNF, denoted \textit{h-SNF} here). Using a SNF synthesis process similar to what has been described earlier in the literature (157; 160; 161; 162; 174; 176; 178; 179; 187), the reaction product depends strongly on the amount of water in the reaction. With increasing amount of water, the reaction product transforms from a thin film with low water content to a SNF coating with medium water content, and on to a thick, rough film with high water content. The growth model described aims to specifically explain the phase during which the deposited film transforms into nanofilaments. Detailed transmission electron microscope (TEM) analysis showed that the SNF were occasionally exhibit a hollow core yet appeared similar under SEM examination to the SNF previously reported in the literature. Despite the hollow nature, the \textit{h-SNF} reported by Korhonen et al. differed from the polysiloxane nanotubes previously reported by Seeger’s group (188). The growth model is based on chemical condensation reactions occurring within the newly formed polysiloxane film, pressure build-up due to the reactions and a uniaxial elongation process of the cavities resulting from the excess pressure created by the reactions. It was suggested that all the filaments go through this kind of elongation growth process, most of them collapsing into a solid tube structure when the excess pressure is removed as the reactants are consumed and chemical reactions stop. The study applies the growth process to silicone macrofilaments (here denoted \textit{SMF}, see Appendix E
for more information about SMF formation), which show strikingly similar appearance to SNF despite the difference in length scale of several magnitudes.

Figure 21. TEM micrographs showing hollow features in SNF. (a) and (b) show cross-sectional transmission electron micrographs of the h-SNFs, colour is added to (a) for emphasis. (c) h-SNF detached from silicon surface, exhibiting hollow core. (d) and (e) are representative SEM micrographs of SNF. (f) TEM micrograph of pearl-necklace type SNF structure. Reprinted with permission from (186).
Figure 22. SNF growth model proposed in Publication II (186). (a) A flat polysiloxane film was initially assumed to form on the substrate surface. (b) Gaseous reaction by-products (HCl, H₂O) are envisioned to migrate preferentially into defects inside the silicone film, forming bubbles inside of it. (c) The bubbles elongate in the direction away from the substrate surface, as the polysiloxane is less crosslinked there due to forming later, thus giving rise to uniaxial elongation or the cavities. (d) As an end-product, a hollow SNF is formed. In the right column, SEM micrographs of a SNF coating at different stages of development. Reprinted with permission from (186).

4.3 Experimental section

Materials and methods

Materials: Methyltrichlorosilane (MTCS, CH₃SiCl₃) (99%) was purchased from Sigma-Aldrich and used without further purification. Purified water was provided by a Millipore Milli-Q system (> 20 MΩm⁻¹, Milli-Q, Millipore, U.S.A.). 100 mm diameter Si <100> test grade wafers were purchased from University Wafer (South Boston, U.S.A.).

Preparations. Typically used substrates were pieces cut from 100 mm diameter test grade Si <100> wafers. Wafers were cut in four equal sized pieces by making a small scratch on the surface of the wafer with a diamond pen and applying a gentle mechanical shear stress to the wafer by hand (protective gloves were used to prevent contaminating the substrates).
Silicone nanofilaments

**Cleaning.** Substrates were ultrasonicated in 10% Deconex 11 Universal solution for 30 minutes, applying 40°C heating (Borer Chemie, Switzerland). Milli-Q water was used in the solution. Substrates were rinsed with copious amounts of Milli-Q water and dried under a stream of pressurized nitrogen.

**Activation.** Further surface activation was performed by plasma treatment (Diener Pico 100 W oxygen plasma) for 5 minutes to increase the surface hydroxyl coverage. After the plasma treatment, rinsing with copious amounts of Milli-Q water is again performed, as plasma mainly oxidizes organic contaminants (with 100W power, removal is very slow); oxidized contaminants are readily removed from the surface by a stream of water.

**Precursor.** MTCS and the needles and syringes were stored in a glove box with an inert nitrogen atmosphere (< 1 ppm oxygen). The syringe was pumped 10 times in the inert atmosphere to remove possibly remaining humidity from it. A needle was inserted in the syringe and the desired amount of MTCS was withdrawn into it as estimated by the volume scale in the syringe.

**Water.** Purified water (Milli-Q) was used as a reactant in the SNF synthesis. The way water was delivered into the reaction depended on the reactor type:

a. Vacuum reactor: A pre-destined amount of water was pipetted into a test tube, which was then connected to the vacuum reactor. Opening a stop-valve allowed water to evaporate into the reactor, with the help of external heating by a hot air blower. The inlet was again closed, and the system was left to equilibrate for typically 15 minutes.

b. Atmospheric pressure reactor: The reactor was flushed with a mixture of dry and humidified nitrogen. The details of this process evolved with the experiences gained through the years of use, three different phases being distinct: (i) the gas was first humidified by flowing through a bubbler filled with purified water; (ii) due to previous problems with equilibration, a heat bath was added around the bubbler to avoid cooling of the water due to evaporation during flushing and the drop in relative humidity caused by it; and (iii) to avoid liquid drops of water being carried to the reactor by the flow of nitrogen, an empty bubbler was added to the gas line between the bubbler filled with water and the reactor.

Maintaining the cleanliness of the bubbler water as well as all the dishes and tubing in the wet line is of critical importance. Contamination causing a failure in SNF synthesis is very likely to enter the reaction during the liquid phase, and water is a very likely source of contamination when problems are encountered.

**Note about rinsing and drying.** The synthesis is extremely sensitive to the steps in which substrate is in contact with water, even in the pre-treatment. Any contamination affecting the results will most likely enter through the liquid phase, from any step during which liquids are used. The complexity of the synthesis is well demonstrated by how the trail of a drop separating from the water film will exhibit different color compared to the rest of the sample after the SNF coating, implying different thickness of coating along the trail.

Two things need to be considered when contact is made between water and the substrate:
(1) Contamination: When the substrate is rinsed under a stream of purified water, it is important to hold the substrate in such a way that any water touching the tweezers - or any other element - does not touch the surface after that. Contamination from tweezers or gloves can be transferred on the substrate by water. Moreover, when the substrate is picked up from the Deconex solution, some liquid will be trapped between the tweezers and the substrate. Care needs to be taken to wash this without spreading this trapped liquid onto other areas of the substrate.

(2) Drying: When the substrate is dried after plasma activation, water needs to leave the surface as a continuous film. Drying by evaporation, for example, will lead to inhomogeneous coating. Moreover, if drops of water separate from the film and re-enter the dry surface, the path on the surface of which this separate drop travels will differ in the thickness of its coating compared to other areas. The differences in thickness are often visible to the naked eye, as the colour of the coating along the path of the drop once moved is different from the rest of the surface.

The issue with drying is mainly encountered after plasma activation, as the water sticks very tightly to the activated and highly hydrophilic surface. After ultrasonication in Deconex solution, water only partially wets the silicon surface. As it does not form a film, film-wise removal is naturally not necessary to achieve a homogenous coating.

**Reactor set-ups**

**Vacuum reactor.** The in-house built c. 5 l reactor was composed from a glass container closed with a lid, with the two parts pressed against each other by a collar. The joint was sealed with an O-ring coated by a fluoropolymer and silicone-based high vacuum grease. Vacuum grease was wiped off with paper and replaced for each synthesis reaction. Inlet stopcocks were made from PTFE (polytetrafluoroethylene, *i.e.*, “Teflon”). Tubing used to connect different parts were made of either PTFE or silicone, which were found to be sufficiently inert, although silicone hardened with time and had to be regularly replaced. Vacuum and exhaust tubing were either PVC (polyvinyl chloride) or stainless steel. Sealing of inlet connections was performed using PTFE collars and high vacuum grease. Thus, the materials directly in contact with the reaction were limited to glass, PTFE, and a trace amount of high-vacuum grease.
Atmospheric reactor. In-house built from borosilicate glassware ordered from VWR. An in-going gas-line was connected through a PTFE-stopcock to the base-part of the reactor and directed to the bottom of the reactor with silicone tubing to ensure a maximum mixing of gas inside the reactor. A ceramic plate was placed on a groove of the reactor wall, about mid-height of the base in height to act as a support for a custom-made glass tower, which was used as an evaporation cup for the silane. The ceramic plate also worked as a support for a PTFE block used as a substrate holder. The outlet for the gas was in the cap of the lid. When the reactor was sealed, the inlet stopcock was closed, and the outlet was shut by placing a septum secured with parafilm between the lid and the cap. Silane was injected through the septum onto the top of the glass tower inside the reactor.

The gas line consisted of an incoming high-pressure nitrogen line (nitrogen 2.5, i.e., 99.5 % nitrogen), the pressure of which was lowered with a pressure-reducer to around +1.5-2 bar. The gas line was then divided into separate dry and wet lines. The dry line was equipped with a flowmeter and connected via steel and silicone tubing to a mixing bottle, in which the dry and wet gases would be mixed. For the wet line, equipped with an identical flowmeter, the path to the mixing bottle contained a bubbler filled with purified water and an empty bubbler to remove any liquid water possibly carried with the flow. The bubbler containing the purified water was sank in a heat bath set a couple of degrees above
the room temperature to ensure a constant temperature of water throughout the flushing. The mixing bottle was connected to a glass vessel equipped with the probe of a hygrometer. This was used to monitor the humidity of the reaction; the location of the %RH measurement was carried out "upstream" in the in-going gas-line to avoid any damage to the probe caused by harmful reaction products of the SNF reaction.

**Protocol for SNF synthesis in vacuum reactor**

1. Rinse the substrate with purified water.  
2. Ultrasonicate the substrate for 30 minutes with 40°C heating in 10% Deconex solution.  
3. Rinse the substrate with purified water.  
4. Dry the substrate with pressurized nitrogen.  
5. Activate the substrate for 5 min in 100 W oxygen plasma.  
6. Rinse the substrate with purified water.  
7. Dry the substrate with pressurized nitrogen (CRITICAL).  
8. Transfer the substrate into the reactor.  
9. Seal the reactor lid with vacuum grease and close the reactor.  
10. Pump the reactor into a vacuum.  
11. Wait for 30 minutes.  
12. Close the vacuum line.  
13. Connect a test-tube with a pre-destined amount of water to the water line.  
14. Open the water line and let the water evaporate into the reactor (apply heating to speed up evaporation, if needed).  
15. Close the water line.  
16. Equilibrate for 15 minutes.  
17. Connect a PTFE vessel with pre-destined amount of MTCS into the silane-line.  
18. Open the silane line.  
19. Wait overnight.  
20. Flush the reactor with nitrogen for c. 15 min.  
21. Stop the flushing.  
22. Open the reactor and remove substrate.

Rinse the substrate with purified water to remove possibly remaining by-products from the surface.

**Protocol for SNF synthesis in atmospheric reactor**

1. Rinse the substrate with purified water.  
2. Ultrasonicate the substrate for 30 minutes with 40°C heating in 10% Deconex solution.  
3. (During sonication) Start a pre-flush to the reactor and adjust the flow of dry and wet line to reach the desired %RH.  
4. Flush the reactor with pressurized nitrogen using a pressure gun.  
5. Clean the reactor from the vacuum grease of the previous synthesis using lint-free paper.  
6. Adjust the flow of nitrogen if %RH has not remained stable.
7. After the ultrasonication has finished, rinse the substrate with purified water.
8. Dry the substrate with pressurized nitrogen.
9. Activate the substrate for 5 min in 100 W oxygen plasma.
10. Rinse the substrate with purified water.
11. Dry substrate with pressurized nitrogen (CRITICAL).
12. Transfer the substrate into the reactor and place it onto a PTFE holder on the ceramic plate.
13. Seal the lid of the reactor with vacuum grease and place the lid on top of the reactor base.
14. Move the lid back and forth slightly without opening the reactor until the vacuum grease between the lid and the base turns transparent.
15. Check that the %RH remains stable, adjust if necessary.
16. Flush for 1 h after the %RH level has stabilized.
17. During the flushing (step 16.) measure a predestined amount of MTCS into a syringe equipped with a needle inside a glovebox.
18. Stop the flushing (step 16.) and seal the reactor.
19. Inject the silane through the septum into the evaporation vessel inside the reactor.
20. Wait overnight.
21. Open the reactor and let reaction by-products mix with air and dilute.
22. Remove the substrate from the reactor.
23. Rinse the substrate with purified water to remove possible remaining by-products from the surface.
5. Conclusions

SHS find use in self-cleaning surfaces, fog harvesting, reducing hydrodynamic drag, enhancing heat transfer, gas exchange, etc. Understanding the theoretical foundations of wetting and surface phenomena is required for designing surfaces with desired functionalities. Knowledge of the behaviour of droplets on surfaces with extreme wetting properties is still developing, however.

After a history of 200 years, contact angle goniometry remains the gold standard for wetting characterization. The details of superhydrophobic phenomena are complex, however, and a single parameter like CA does not sufficiently describe all their intricacies. The present thesis focuses on the challenges of wetting characterization by contact angle goniometry, especially CA measurement on SHS. Proper characterization of surface wettability by CA goniometry requires knowledge of the ACA and the RCA. While the ACA is usually straightforward to measure, measuring the RCA can be challenging. Publication I demonstrated a method to measure the RCA reliably on surfaces with a wide variety of contact angle hysteresis, using the needle-in-drop method. Initial volume of the drop was found to be the key parameter facilitating successful RCA measurement, especially for surfaces with high CAH.

Superhydrophobicity depends on two factors: low surface energy and surface structure on the nano- and microscale. Although superhydrophobicity can be achieved by nanoscale roughness alone, all natural and most artificial SHS utilize hierarchical structure by combining nano- and microscale roughness. The combination of proper surface chemistry and hierarchical roughness leads to minimal contact area between the solid and the liquid, which is required for superhydrophobicity.

SNF are a novel class of nanomaterials, which fulfil both requirements for superhydrophobicity in one fabrication step. Publication II demonstrated that SNF can have a hollow interior, instead of the previously assumed uniform solid core. Based on this and additional supporting experimental evidence, a novel growth model was proposed, suggesting that growth of SNF occurs as a pressure induced local film deformation process.

Save for a few reports in the literature, the inherent inaccuracies of CA measurements are typically overlooked. As outlined in Chapter 3, the optical system used in CA goniometry produces systematic errors that become increasingly pronounced for CAs above 150°. Publications IV and V draw attention to the significant errors in CA measurements, especially when characterizing ex-
tremely water-repellent surfaces. The details of the optical system, image processing and fitting procedure have a significant effect on the value of measured CA. Additionally, despite the apparent simplicity of the method, reliable measurement of CAs on SHS relies on the skill and experience of the operator. Results of identical measurements performed by different users, all experienced and skilful scientists, were shown to vary up to 5-10°.

The factors characterizing superhydrophobicity can be translated to two objectives: i) minimizing CAH and maximizing CA. Current quantitative definition for a SHS is typically a CA above 150° and CAH below ~10°. These limits for CA and CAH are admittedly arbitrary, but commonly used in the scientific community. Perhaps the most striking characteristic of non-wettable surfaces is the high mobility of droplets on them, and ease at which liquid is removed from them. Mobility of droplets, which is an important parameter for many SHS applications, correlates with the CAH. It is obvious that the magnitude of unavoidable systematic and random errors mentioned above make evaluation of droplet mobility on SHS based on CA measurements extremely difficult. Thus, accurate comparison of superhydrophobic surfaces between laboratories becomes next to impossible. This can hinder the development of SHS.

The research outlined in the present thesis demonstrates the limitations and challenges of CA goniometry, especially when characterizing superhydrophobic surfaces. Fundamental understanding and ability to design next-generation SHS will likely require better standardization of characterization methods and protocols. For the development of next-generation SHS, force-based characterization methods may be required. Force measurements can also further our theoretical understanding of contact angles, which would facilitate development of better measurement methods in the future.
Appendix A

Surface energy and surface tension

The terms surface energy and surface tension are often used interchangeably in the literature, in a strict thermodynamical sense they are not identical concepts (190). In this thesis, surface energy is the term preferred for solids, while surface tension is used for liquids. Surface energy and surface tension of a liquid can be considered equal, as a liquid surface can freely adopt the minimum energy confirmation. For solids the relationship between surface energy and surface tension is less straightforward, as inner stresses can prevent the material from adopting the shape which would minimize surface energy.

Cutting bulk material requires work to break the bonds between the molecules. the amount of work required is proportional to the cut area. The amount of energy, $E$, stored in the interface can be written as

$$E = \gamma A$$

where $\gamma$ is the surface energy (constant, units J/m$^2$) and $A$ is the interfacial area. Thermodynamically, surface energy can be defined as the increase of Gibbs free energy, $\delta G$, per surface area, $\delta A$:

$$\gamma = \frac{\delta G}{\delta A}$$

Surface energy is caused by a higher energy state of molecules on the surface as compared to the molecules in the bulk. Molecules in the bulk are surrounded by other similar molecules and therefore have strong bonds with all their neighbours. Molecules on the surface have fewer neighbours of the same kind, which is energetically less favourable. Magnitude of surface energy depends on several factors, such as chemistry, roughness, surface charge and temperature of the interface.

Like surface energy, surface tension can be thought to equal the work, $dW$, required to create new area of the interface, $dA$:

$$\gamma = \frac{dW}{dA}$$
Surface tension gives liquid interfaces their rubber sheet-like nature. A molecule in the bulk is being “pulled” with equal force into every direction due to the intermolecular bonds it has with its neighbours, resulting in a net force of zero. Molecules on the surface have half of their nearest neighbours missing, and consequently, are affected by a net force directed towards the bulk. The net force affecting the surface molecules creates pressure, \textit{i.e.}, the \textit{Laplace pressure}. The value of surface tension depends on the strength of the intermolecular interactions. Polar molecules have typically strong intermolecular interactions, while non-polar molecules form bonds by weaker van der Waals-interactions.

Surface tension of liquids is usually between $20 \times 10^{-3}$ and $80 \times 10^{-3}$ N/m (5). Surface tension of water at room temperature (20°C) is roughly $72.8 \times 10^{-3}$ N/m (47). For fluorinated liquids, surface tension can be as low as $12 \times 10^{-3}$ N/m (47). Liquid surface tension is straightforward to measure, and several measurement techniques are readily available, for example sessile or pendant drop, du Nouy-ring (191), Wilhelmy plate (5; 47). Measuring solid surface tension is on the contrary not straightforward, due to the difficulty of separating the energy needed to deform the surface from the energy needed to create new surface. Thus, the solid surface tension is typically characterized indirectly, by for example CA goniometry. Several models exist for solid surface tension characterization based on CAs, typically involving CA measurement by several probe liquids with varying surface tension (42).
Appendix B

Young-Laplace derivation

Thermodynamics dictates that all spontaneous changes of state decrease the Gibbs free energy of the system. Decrease in the Gibbs free energy of a liquid drop of constant volume is accompanied by a decrease in the surface area of a liquid due to the excess energy associated with a surface. The excess surface energy leads to surface tension, which causes a pressure difference, $\Delta P$, between a liquid drop and the surrounding medium. Let us consider a small section of the surface of a drop of liquid. Axes $x$ and $y$ are oriented along the principal radii of curvature of the surface. If the surface is dilated by an infinitesimal amount, $\delta z$, the local radii of curvature change from $R_i$ to

$$R_i + \delta z = (1 + \frac{\delta z}{R_i})R_i$$  \hspace{1cm} (20)

The change in area ($A = \delta x \delta y$) can be written as

$$A + \delta A = \left(1 + \frac{\delta z}{R_i}\right) \delta x \left(1 + \frac{\delta z}{R_2}\right) \delta y$$

$$\approx \left(1 + \frac{\delta z}{R_1} + \frac{\delta z}{R_2}\right)A$$ \hspace{1cm} (21)

The corresponding change in drop volume is $\delta V = A \delta z$. An infinitesimal displacement from the equilibrium position does not change the Gibbs free energy, $G$. Thus,

$$\delta G = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) A \delta z - \Delta P \delta V = 0$$ \hspace{1cm} (22)

where $\delta V = A \delta z$ is the infinitesimal change in the drop volume caused by the displacement of the interface, $\delta z$. By re-arranging, we get the Young-Laplace equation:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \gamma C$$ \hspace{1cm} (23)

where we the notation $C = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ for local curvature has been used.
Appendix C

Principles of energy minimization

Young originally derived the contact angle from the local force balance on contact line where the three phases co-exist. The derivation is straightforward for an ideal surface, but for a rough surface this is not necessarily the case. Superhydrophobic surfaces, for example, are commonly continuous but nondifferentiable. It is therefore not possible to define the physical slope of the surface at every location, making it difficult to apply the force balance approach.

The concept of surface free energy was unknown to Young, since it had not been invented yet. To the best of our knowledge, Gauss was the first to introduce the concept by proposing that the existence of attractive forces leads to a term in the potential energy proportional to the surface area of the liquid. This causes the tendency for liquids to always contract and exercise a tension (31). Boltzmann demonstrated that a liquid can be deformed without changing the total surface area, which means that there is no change in the potential energy. However, should there be a change in the total surface area, there must be an accompanying change in the potential energy proportional to it (31).

The classical equations for CAs can be derived from the thermodynamic principles of a drop-resting-on-solid wetting system. The derivation utilizes the energy minimization approach, as the equilibrium CAs are associated with the global energy minimum of the wetting system. For a wetting system with a drop of liquid resting on an ideal solid surface, the equilibrium state of an interface is governed by two equations: the Young equation, which determines the local equilibrium CA on the contact line between the three phases, and the Young-Laplace equation, which determines the equilibrium shape of the liquid-vapor interface.

Assumptions

Certain assumptions can be made to simplify the calculations for free energy minimization of a wetting system. First, the volume of a drop resting on a solid surface is assumed constant. The condition of constant volume is not required but makes the calculations easier. For an ideal surface (i.e., flat, rigid, homogeneous, chemically inert, and insoluble), the only independent variable of the Gibbs energy is then the contact angle, $\theta$. Rough surfaces require two independent variables: the contact angle, $\theta$, and the ratio of solid contact, $f$. It has been questioned whether a strictly thermodynamic treatment of heterogeneous wetting has been questioned (150; 192; 193). Due to energy barriers separating the
local energy minima, the system may be unable to reach the global energy minimum. It is therefore assumed that the contact line can move freely on the solid surface to allow the system to find its minimum energy configuration.

The size of the drop is assumed to be within the following limits (27; 194; 195):

- The drop is much smaller than the capillary length, thus surface tension dominates over gravity.
- Drop is large compared to the average size of roughness asperity.
- The volume of liquid in the asperities is negligible with respect to the total liquid volume.
- The drop is large enough to allow for line tension effects to be ignored.
- The drop is large enough to consider the liquid-air interface below the drop is flat.

Given the assumptions above, the shape of the drop can be regarded hemispherical and the contact line circular. The drop is thus axisymmetric, and contact angle between the solid and the drop, $\theta$, is well-defined. Due to axisymmetry, a 2-dimensional system can be considered instead of a 3-dimensional one.

![Figure 24. Contact angle and surface free energy. Solid black line represents liquid-vapor interface in the original position, dotted line between blue and white regions the liquid-vapor interface after CL movement. CA $\theta$ remains unchanged by movement of the CL (see Assumptions section above). As the CL advances along the surface by a small distance, $\Delta A$, LV interface also increases by the amount of $\Delta A \cos \theta$. Reprinted with permission from (196).](image-url)

For the 2-dimensional system, it is further assumed that:

1. A liquid front exists and is of a straight line. The movement of the liquid front and hence interfacial area changes determine the free energy change of the entire system.

2. Gravity is negligible. On a horizontal solid surface, this assumption is reasonable as the gravity centre of the liquid drop will not change significantly because of the liquid front movement. This assumption has been used in most of the previous models (65; 66; 197).

3. There is no effect of line tension as this is a two-dimensional model and the three-phase contact line is a straight line. In fact, even if the sessile drop is three-dimensional, the line tension is extremely small and thus can be neglected for a macroscopic drop (198).
(4) The Young equation is locally valid. This assumption is essentially correct and has been obtained as a result by the model of Li and Neumann (199). It is also proved to be correct by Wolansky and Marmur (56) if line tension can be ignored.

(5) The solid surface itself is non-deformable and rigid and there is no liquid film existing in front of the three-phase contact line.

**Young equation**

Based on the assumptions presented in the previous section, the total Gibbs free energy of a wetting system is the sum of the interfacial energies involved. Interfacial energy can be calculated as a product of energy per unit area of the interface and the corresponding interfacial area. Hence, the total Gibbs free energy, $G_{\text{tot}}$ can be written as:

$$G_{\text{tot}} = \sum \gamma_{ij} A_{ij} = \gamma_{\text{SL}} A_{\text{SL}} + \gamma_{\text{SV}} A_{\text{SV}} + \gamma_{\text{LV}} A_{\text{LV}}$$  \hspace{1cm} (24)

where $\gamma_{ij}$ is the interfacial tension and $A_{ij}$ the interfacial area between phases $i$ and $j$. An increase in solid-liquid (SL) contact area by an infinitesimal step, $\Delta A_{\text{SL}}$, for a drop resting on a solid surface is balanced by a decrease of equal magnitude in solid-vapor (SV) interface, $\Delta A_{\text{SV}}$:

$$\Delta A = \Delta A_{\text{SL}} = -\Delta A_{\text{SV}}$$  \hspace{1cm} (25)

The change of liquid-vapor interfacial area, $\Delta A_{\text{LV}}$, for an increase of contact area by an infinitesimal step, $\Delta A$, can be deduced by simple trigonometry to be $\Delta A_{\text{LV}} = \cos \theta \Delta A$. Changes in the CA caused by infinitesimal movement of the CL are of second order, and therefore ignored here. Change in the Gibbs energy of the system, $\Delta G$, due to small perturbation near the equilibrium can now be written as:

$$\Delta G = (\gamma_{\text{SL}} - \gamma_{\text{SV}}) \Delta A + \gamma \cos \theta \Delta A$$  \hspace{1cm} (26)

In the vicinity of an equilibrium, small variations in the contact line location do not affect the total energy of the system. The change of Gibbs energy, $\Delta G$ corresponding to movement of the contact line by an infinitesimal step, $\Delta A$, is therefore:

$$\Delta G = 0 = (\gamma_{\text{SL}} - \gamma_{\text{SV}}) \Delta A + \gamma \cos \theta \Delta A$$  \hspace{1cm} (27)

Re-arranging
\[
\gamma \cos \theta \Delta A = (\gamma_{SV} - \gamma_{SL})\Delta A
\]  
(28)

Dividing both sides by \(\gamma \Delta A\) yields the Young equation

\[
\cos \theta = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma}
\]  
(29)

**Wenzel equation derivation**

The surface energy approach can be used in both above cases. In the Wenzel state the solid-liquid interfacial area is increased by a factor \(r\), which is the ratio between the actual solid area beneath the drop divided by the projected area, \(r = \frac{A_{\text{actual}}}{A_{\text{projected}}}\). For a movement of the contact line by an infinitesimal step, \(dx\), the corresponding change in the free energy is therefore:

\[
(y_{SL} - y_{SV})r \Delta A + \gamma \cos \theta \Delta A = 0
\]  
(30)

Recombining

\[
\gamma \cos \theta \Delta A = (\gamma_{SV} - \gamma_{SL})r \Delta A
\]  
(31)

Dividing both sides by \(\gamma \Delta A\) yields

\[
\cos \theta_W = \frac{r(y_{SV} - y_{SL})}{\gamma}
\]  
(32)

In combination with Young equation, the Wenzel equation is obtained in the following form:

\[
\cos \theta_W = r \cos \theta_Y
\]  
(33)

**Cassie-Baxter equation derivation**

Assuming the average properties of the materials and their area fractions to be global constants, they are independent of the location of the contact line, and therefore do not change when the contact line advances or recedes. Near an equilibrium the change in the Gibbs energy for a small perturbation is zero, and can be expressed as

\[
\Delta G = (y_{SL}^A - y_{SV}^A)\Delta A_A + (y_{SL}^B - y_{SV}^B)\Delta A_B + \gamma \cos \theta \Delta A = 0
\]  
(34)

Recombining the terms, we get

\[
\gamma \cos \theta \Delta A = (y_{SV}^A - y_{SL}^A)\Delta A_A + (y_{SV}^B - y_{SL}^B)\Delta A_B
\]  
(35)
Here, $\gamma_{SV}^i$ and $\gamma_{SL}^i$ are the interfacial tensions, and $\Delta A_i$ are the changes in the wetted areas of the individual materials, $i$. Dividing both sides by $\Delta A \gamma$, and recognizing that the CA of the drop is the Cassie-Baxter CA, we can write:

$$\cos \theta_{CB} = \frac{(\gamma_{SV}^A - \gamma_{SL}^A) \Delta A_A}{\gamma} + \frac{(\gamma_{SV}^B - \gamma_{SL}^B) \Delta A_B}{\gamma}$$

(36)

Substituting the Young CAs, $\theta_i$, for each material $i$, $(\gamma_{SV}^i - \gamma_{SL}^i) = \cos \theta_i$, we get:

$$\cos \theta_{CB} = \cos \theta_A \frac{\Delta A_A}{\Delta A} + \cos \theta_B \frac{\Delta A_B}{\Delta A}$$

(37)

Cassie fractions, $f_i$, for each individual material, $i$, can be defined as $f_i = \frac{\Delta A_i}{\Delta A_A + \Delta A_B}$. Therefore, the Cassie-Baxter equation can be re-written as:

$$\cos \theta_{CB} = \cos \theta_A f_A + \cos \theta_B f_B$$

(38)

For a flat solid, sum of the solid fractions equals unity, $f_A + f_B = 1$. Thus, $\frac{\Delta A_A}{\Delta A} = f_A$ and $\frac{\Delta A_B}{\Delta A} = 1 - f_A$. Substituting these expressions, the Cassie-Baxter equation can be written in the form

$$\cos \theta_{CB} = f_A \cos \theta_A + (1 - f_A) \cos \theta_B$$

(39)

where $\theta_{CB}$ is the Cassie-Baxter apparent CA, $\theta_A$ is the Young CA for material A, $\theta_B$ is the Young CA for material B and $f_A$ is the solid fraction of material A. For a rough surface, the sum of the solid fractions is above unity, and the simplification above cannot be made. The equation can be generalized for several materials as

$$\cos \theta_{CB} = \frac{\sum_{i=1}^{n} f_i (\gamma_{SV}^i - \gamma_{SL}^i)}{\gamma} = \sum_{i=1}^{n} f_i \cos \theta_i$$

(40)

### Composite surface

On superhydrophobic surface, a drop often contacts only the tops of the roughness features. The resulting composite surface amplifies the water-repellency of the surface, as air is perfectly hydrophobic. Cassie-Baxter equation can also be applied to a case in which water bridges over the roughness features, with pockets of air remaining below the drop. A simple example is a case of a drop resting on a solid surface consisting of flat-topped, microscale pillars. The surface is assumed to have low surface energy, and the size of pillars suitable for facilitating an air-trapping scenario.
Here, the drop rests on a chemically heterogeneous surface with domains of
type A consisting of the solid material, and domains of type B consisting of air.
Air is perfectly, so $\theta_{\text{air}} = \theta_B = 180^\circ$ and $\cos \theta_B = -1$. Cassie-Baxter can be written as:

$$\cos \theta_{\text{CB}} = \cos \theta_A f_A + \cos \theta_B (1 - f_A) = \cos \theta_A f_A - 1(1 - f_A)$$
$$= f_A(\cos \theta_A + 1) - 1$$  \hspace{1cm} (41)

Here, $\theta_A$ is the Young CA of the solid and $f_A$ the Cassie solid fraction.

**Cassie-Baxter equation with roughness**

Interfaces of a wetting system described by the Cassie-Baxter are often assumed
flat in the literature. Real solid surfaces are rarely flat, however, and including
a roughness ratio gives rise to another form of the Cassie-Baxter equation.
Based on the drop size assumptions stated above, the liquid-vapor surface can
be considered flat. Let us examine a wetting system consisting of a pillared solid
substrate like the example in the previous section, but this time rough instead
of flat-topped pillars. Let $r_f$ be the roughness factor of the pillar tops and $f$ the
solid area fraction. The change in Gibbs’ energy for small change in wetting area
is now

$$\Delta G = (\gamma_{SL} - \gamma_{SV}) f r_f \Delta A + \gamma (1 - f) \Delta A + \gamma \cos \theta \Delta A = 0$$
$$\gamma \cos \theta \Delta A = (\gamma_{SV} - \gamma_{SL}) f r_f \Delta A - \gamma (1 - f) \Delta A$$  \hspace{1cm} (42)

Dividing both sides by $\gamma \Delta A$ yields:

$$\cos \theta = r_f \frac{\gamma_{SV} - \gamma_{SL}}{\gamma} + f - 1$$  \hspace{1cm} (43)

Using the Young equation, and recognising that the CA in the previous equation
is the Cassie-Baxter CA, we get:

$$\cos \theta_{\text{CB}} = r_f \cos \theta_Y + f - 1$$  \hspace{1cm} (44)

In the case of homogeneous wetting, contact between drop and solid surface is
complete, so $f = 1$ and $r_f = r$. The above equation then reduces back to the
Wenzel equation, $\cos \theta_{\text{W}} = r \cos \theta_Y$. 


Appendix D

Young-Dupré/Work of adhesion

Specific energy (per unit area of the solid substrate) required to disconnect a drop from a solid surface, $W_{ad}$, can be written as

$$W_{ad} = \gamma_{SA} + \gamma - \gamma_{SL}$$  \hspace{1cm} (45)

Combining this with the Young equation, written in the form $\gamma_{SA} - \gamma_{SL} = \gamma \cos \theta_Y$ gives

$$W_{ad} = \gamma (1 + \cos \theta_Y)$$  \hspace{1cm} (46)

where $W_{ad}$ is the energy of adhesion and $\theta_Y$ is the Young angle. The above equation is called the Young-Dupré equation. The equation can be used to estimate the idealized work of adhesion. However, it is not clear how the idealized work of adhesion relates to the adhesion force, as the Young-Dupré equation implies that the drop preserves its shape when detached from the solid surface, which is obviously not true.

Young-Dupré equation combines the concept of work of adhesion with Young equation. The work of adhesion is defined as the reversible work per unit are required to separate a solid and a liquid (under constant pressure and temperature) to an infinite distance, thus creating new solid-vapor and liquid-vapor interfaces and destroying a solid-liquid interface.

$$-\Delta G^a_{SL} = W^a_{SL} = \gamma_{SV} + \gamma - \gamma_{SL}$$  \hspace{1cm} (47)

Here, $-\Delta G^a_{SL}$ is the Gibbs free energy of solid-liquid interface. Combining Eq. 47 with Young equation, the Young-Dupré equation, which relates contact angle to the work of adhesion and Gibbs free energy, is obtained:

$$-\Delta G^a_{SL} = W^a_{SL} = \gamma (1 + \cos \theta_Y)$$  \hspace{1cm} (48)

Work of adhesion is high for small CA values, and vice versa. A substantial amount of energy must therefore be spent to overcome adhesive forces and separate a liquid from a superhydrophilic solid. When $\theta$ approaches $180^\circ$, $W^a_{SL}$ approaches zero, which indicates that no work is needed to separate liquid from perfectly hydrophobic surface. It should be noted, however, that idealized work of adhesion is used in this derivation: it is assumed that the liquid does not
change shape when detaching from the surface, no surface reconstruction takes place on the solid surface, the solid surface does not exhibit CA hysteresis, the process is reversible with no adhesion hysteresis, etc. In real world, work of adhesion is not reversible, and more energy is required to detach a drop of liquid from a solid than is released when the drop attaches to the surface.

**Sliding angle/ Lateral adhesion**

A drop resting on a tilted surface is at an equilibrium. Gravitational forces pulling the drop down are balanced by the lateral adhesion caused by (frictional capillary forces) CAH force acting on the CL. The CAH force originates from difference in Laplace pressure along the CL, which can be observed from the difference in CA on the front and rear edge of the drop. Gravitational pull increases as a function of the angle of tilt. At a critical angle of tilt, the gravitational force overcomes the lateral adhesion resisting the motion (13). This angle is called the *sliding/roll-off angle*, and it can be used as a parameter for wetting characterization, as it measures the strength of lateral adhesion between the drop and the solid surface. Besides surface properties, the sliding angle depends on the size of the drop, however. For proper surface characterization, drops of well-defined size should be used: 5 or 10 μL drops are typically used.

Lateral adhesion is caused by CA hysteresis along the drop perimeter. The lower the sliding/roll-off angle, the lower the lateral adhesion between liquid and the solid. The gravitational force affecting the drop can be written as:

$$ F_g = mg \sin \alpha \quad (48) $$

where $m$ is the mass of the drop, $g$ is the gravitational constant and $\alpha$ is the angle of tilt. The maximum lateral adhesion force can be estimated from the balance of the forces that exists just before the drop starts to move on the tilted surface. The lateral adhesion force, $F_{LA}$, is proportional to the difference in the contact angles on the rear and the front side of the drop, the contact line length and the surface tension of the liquid, and can be written as (133; 200):

$$ F_{LA} = k L \gamma (\cos \theta_{\text{rear}} - \cos \theta_{\text{front}}) \quad (49) $$

Here, $L$ is the contact line length, $\gamma$ is the surface tension of the liquid, and $k$ is a constant that depends on the shape of the drop: values ranging between $k = \frac{4}{\pi}$ and $k = 2$ have been reported in the literature (146; 200). $\theta_{\text{rear}}$ and $\theta_{\text{front}}$ are the contact angle at the top and the bottom part of the drop, respectively. The relationship above indicates that to minimize the lateral adhesion, small CAH (small $\cos \theta_{\text{rear}} - \cos \theta_{\text{front}}$) and high CA (i.e., short CL length) are needed. Just before the drop starts to move, maximum lateral adhesion is equal to the gravitational force at the critical angle of tilt, $\alpha$: 

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\[ mg \sin \alpha = kL \gamma (\cos \theta_r - \cos \theta_a) \]  
\hspace{1cm} (50)

Re-arranging:

\[ \sin \alpha = \frac{kL \gamma (\cos \theta_r - \cos \theta_a)}{mg} \]  
\hspace{1cm} (51)

The critical angle, \( \alpha \), depends on the mass of the drop: the larger the drop, the lower the critical angle. Therefore, the size of the drop used to measure the sliding angle needs to be reported with the results to allow for cross-laboratory comparison. Drops of 5 and 10 \( \mu \)l are typically used in the measurements.

The CA at the front edge of a drop on an inclined plane, \( \theta_{\text{front}} \), is often equated with the ACA, while the CA at the rear edge, \( \theta_{\text{rear}} \), is equated with the RCA. Due to the complex 3-dimensional geometry of the drop, the ACA is not always reached at the same time at the leading edge of the drop as the RCA is reached at the trailing edge. Thus, \( \theta_{\text{front}} \), and \( \theta_{\text{rear}} \) do not necessarily equal the ACA and the RCA, respectively, as measured on a level plane (201). However, it has been experimentally demonstrated that \( \theta_a = \theta_{\text{front}} \), and \( \theta_r = \theta_{\text{rear}} \) for a wide variety of surfaces and tilt angles (146).

**Tensile adhesion**

Tensile adhesion can be measured with a microelectronic balance. Small droplet (typically 5 \( \mu \)L) hanging freely on a ring, a plate or end of a capillary is made to contact and withdrawn from a solid surface that is characterized. The so-called snap-in force, which correlates with the ACA, is measured when the drop is lowered to make contact with the surface. The so-called pull-off force, which correlates with the RCA, is measured as the drop is slowly detached from the surface.

Contrary to the Young-Dupré equation, in a more realistic case work of adhesion cannot be considered reversible, as more energy is dissolved when separating a drop from a surface than when bringing it to contact with a surface. This gives rise to adhesion hysteresis:

\[ \Delta W = W_r - W_a > 0 \]  
\hspace{1cm} (51)

\[ W_r = \gamma (1 + \cos \theta_R) \]  
\hspace{1cm} (52)

\[ W_a = \gamma (1 + \cos \theta_A) \]  
\hspace{1cm} (53)

where \( \Delta W \) is the adhesion hysteresis, \( W_r \) and \( W_a \) are the separating (receding) and the approaching (advancing) work of adhesion, respectively, \( \gamma \) is the surface tension, and \( \theta_A \) and \( \theta_R \) are the advancing and the receding CA, respectively. The separating work of adhesion, \( W_r \), should correlate well with the pull-off force
(202; 203). For SHS, pull-off force has been experimentally demonstrated to correlate well with the sliding angle, and CA hysteresis (144).
Appendix E

Silicone macrofilaments

Silicone macrofilaments (SMF) form when MTCS is added dropwise to a water bath. The growth sequence is described in (186).

Figure 25. Silicone macrofilament growth in a sequence of schematic illustrations (upper row, (a)-(d)), and in a sequence of photographs (lower row, (a)-(e)) A detailed photograph of SMF is shown in column (e) on the upper row. Reprinted with permission from (186).
References


References


80. Wetting transition of water droplets on superhydrophobic patterned surfaces. 


References


References


