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Characterization of super liquid-repellent surfaces

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ABSTRACT

Characterization of the wetting properties is a prerequisite for a fundamental understanding and the targeted development of superhydrophobic and superamphiphobic layers. To fabricate super liquid-repellent layers, two requirements need to be met: The surfaces have to be of low energy and their nano- and microstructure needs to be designed in a way that leads to the entrapment of air. The challenge is to design and produce suitable nano- and microstructures to control wetting. Here we describe important methods to quantify wetting properties of super liquid-repellent layers. These properties include the apparent advancing and receding contact angles, the roll-off angle, tensile and lateral adhesion, the impalement pressure, and the observation of drop impact. The most important one is the apparent receding contact angle because it also limits lateral adhesion. The link of these properties to the nano- and microscopic structure of the layer is discussed. Limits, problems, and future challenges are pointed out.

1. Introduction

Using nano- and microstructured surfaces with low surface energy, scientists have learned to reduce the interaction between liquid and a solid surface. Inspired by the water-repellent properties of some plant leaves and wings of insects we begin to understand the physical principles leading to superhydrophobicity. Superhydrophobicity is based on two principles [1,2]: A low surface energy of the solid surface, often achieved by coating the surface with a fluorinated hydrocarbon, and an increased surface roughness, for example by micropatterning. Low surface energy and high surface roughness lead to the entrapment of air when a drop of water is placed on a superhydrophobic layer. Based on these two characteristic properties many methods to fabricate artificial superhydrophobic layers have been developed (e.g. [3–5]). The challenge is still to invent simple, scalable processes leading to optically transparent, mechanically robust and chemically inert layers. Even greater challenges are to make defect-tolerant or even self-healing superhydrophobic layers.

Shortly after the first superhydrophobic surfaces also oil-repellent layers were made [4]. In the meantime the principle of superamphiphobicity is understood [6–8] and used to produce superamphiphobic layers typically by lithography [7,9–11] or by self assembly [4,12–16]. Like for superhydrophobic surfaces one needs to structure the surface in a way that the liquid entraps air. For non-polar liquids, a high roughness is, however, not sufficient. Overhanging structures are required [6,7,10,17,18]. The situation, where air is entrapped underneath the drop, is called “Cassie” or fakir state. The Cassie state is a necessary, but not a sufficient requirement for super liquid repellency. In contrast, when the whole solid surface is covered by the liquid the drop is in the “Wenzel” state.

Being able to fabricate liquid-repellent surfaces may open new possibilities both for research and technology. These include self-cleaning, drag reduction [19–22], fog harvesting [23], heat transfer [24], and gas exchange [20,25]. In microfluidics tiny amounts of liquids can be manipulated with little adhesion and thus little energy dissipation. Therefore, super liquid-repellent surfaces are seen in the broader context which in general aims to control the wetting of surfaces by liquids.

To improve the properties of superhydrophobic and superamphiphobic layers physical methods are required to characterize their wetting properties. The aim of this paper is to describe such methods critically, point out limits, open questions, and encourage the discussion on an appropriate standardization. Standardization is important to facilitate the transfer of scientific results into industrial applications, to compare layers produced in different laboratories and to make a comparison to theory easier. Therefore we first need to identify those wetting properties which are relevant and quantifiable. The suggested properties should be linked to a simple and reliable measurement, which can be established in many laboratories and which leads to reproducible results. Furthermore, the outcome of a measurement should be “robust” and not sensitively depend on secondary parameters, which may be difficult to control.

Here, we only discuss wetting properties. One should, however, be aware that for many applications other properties are decisive, such as mechanical stability, chemical inertness and optical transparency. In particular, mechanical properties play an essential role [26–30] because

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most of the layers with very good wetting properties are not robust enough for e.g. standard scratch tests. Here, developing new mechanical test, which takes into account the nano- and microscale structure of the layer, would be helpful.

2. Terminology

It is useful to first agree on a certain terminology to better organize the vast amount of literature appearing on super liquid-repellency [31]. To our knowledge IUPAC has not defined superhydrophobicity yet. The term comes from the Latin prefix "above", "beyond" (*super*) and the Greek words for "water" (*hydrr*) and "fear" (*phobos*). It is commonly accepted that surfaces, which show a contact angle above 150° and a roll-off angle of a water drop of less than 10° are called *superhydrophobic*. This is not a precise definition. First, one needs to specify, which contact angle is meant, the advancing or receding. Second, the roll-off angle depends on the volume of the drop. Therefore the drop volume needs to be specified. A more accurate definition would be: A layer showing an apparent advancing contact angle of 150° or higher and a roll-off angle of a drop of distilled water of a specific volume.

If the layers is super oil-repellent, it is called *superoleophobic* (*oleum*: Latin for oil) [7]. If the layer repels both, water and oil frequently the term *superamphiphobic* (*amphi*: Greek prefix for "on both sides", referring to water and oil) is used. In this case a drop of a polar and non-polar liquid forms a contact angle of 150° and higher and a roll-off angle lower than 10° for a drop of specific volume. The liquid needs to be specified. Sometimes the adjective *superomniphobic* (from Latin *omnis* "all") is used. As to our knowledge no surface repels perfluorinated alkanes we avoid that term.

With respect to cleaning water, filters have been coated with oil-repellent surfaces. In this case the oil is under water. We talk about under water superoleophobicity. The medium surrounding the oil drop is in this case water rather than air or a gas [32].

In the following we use the term super liquid-repellent layer rather than surface to indicate that it necessarily has a certain extension in the direction normal to the mean surface.

The term "*Lotus effect*" was to our knowledge first used in 1992 [33] to describe the effect of self-cleaning on plant leaves. The anticontaminant effect of the particular structure of leaves was even pointed out much before. In general, the term *Lotus effect* is used for the self-cleaning effect on superhydrophobic layers that are structured on the 0.1 to 100 μm length scale, and as a results show a low adhesion to contamination in the form of particles. The contact area between the particles and the superhydrophobic layer is strongly reduced so that contamination is easily rinsed off by water. Self-cleaning and superhydrophobicity sometimes but not always coincide. They are two different phenomena.

3. Contact angles

Currently the most widely used parameter to characterize super liquid-repellent surfaces is the contact angle. A high apparent contact angle implies a strong liquid repellency.

3.1. Microscopic and macroscopic contact angles

All super-liquid repellent surfaces are structured on the nano- or micrometer length scale. Therefore, it is necessary to distinguish between the microscopic contact angles determined by the materials and the macroscopic, apparent contact angles of the layer. We term the contact angle measured on a smooth, homogeneous planar surface of a certain material, the material contact angle Θ. This is the contact angle formed by the liquid when extrapolating the liquid shape on the 10 nm–1 μm scale to the interface. We neglect the effect of interfacial forces, which may influence the shape of the liquid interface on the 10 nm scale close to the contact line [34,35]. On an ideal smooth, inert surface the material contact angle can be described by Young's equation [36]:

$$\gamma \cos\Theta = \gamma_{SV} - \gamma_{SL}. \tag{1}$$

Here, γ, γ_{SV}, and γ_{SL} are the interfacial tensions of the liquid/vapor, solid/vapor, and solid/liquid interfaces, respectively.

It is well known that on real surfaces the contact angle for an advancing liquid is larger than the one for a receding liquid. The advancing contact angle is observed when, for example, the volume of a sessile drop is slowly increased, just before the contact line starts to advance. The receding contact angle is measured when the volume of a sessile drop is decreased just before the contact line recedes. Therefore we distinguish between advancing Θ_a and receding material contact angles Θ_r.

The microscopic material contact angle needs to be distinguished from the macroscopic, apparent contact angle Θ^{app} (Fig. 1). It is the apparent contact angle which is measured by the sessile drop method. The macroscopic scale, that is the length scale observed by eye or with a low-resolution microscope, is much larger than the nano- and microstructures forming the super liquid-repellent layer. Typically it is larger than 10 μm. In addition to the material properties of the surfaces, Θ^{app} is determined by the nano- and microstructure of the underlying pattern. Again, the apparent advancing contact angle Θ_a^{app} is higher than the apparent receding contact angle Θ_r^{app}. The difference, $\Delta\Theta^{app} = \Theta_a^{app} - \Theta_r^{app}$, is called apparent contact angle hysteresis. We also distinguish between the three-phase contact line (TPCL), or simply contact line, on the microscopic and the edge of the drop on the macroscopic length scale.

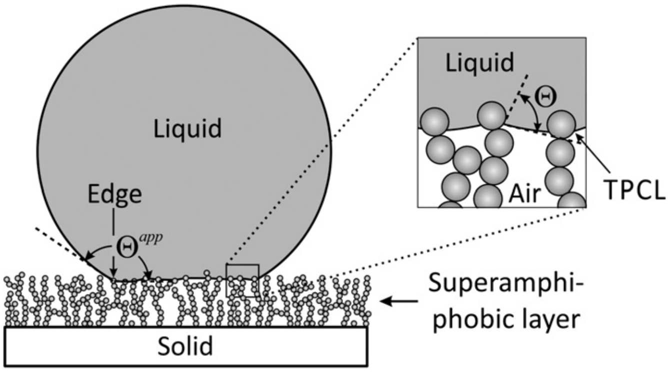

Fig. 1. Schematic of a sessile liquid drop on a superamphiphobic surface made of highly porous aggregates of nanospheres. The schematic illustrates the difference between the materials contact angle Θ and the apparent contact angle Θ^{app}. The term "edge" is used to distinguish the apparent contact line and the microscopic three-phase contact line (TPCL).