



Historical perspective

Super liquid-repellent layers: The smaller the better



Hans-Jürgen Butt, Doris Vollmer, Periklis Papadopoulos

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

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ABSTRACT

Super liquid-repellent layers need to have a high impalement pressure and high contact angles, in particular a high apparent receding contact angle. Here, we demonstrate that to achieve both, the features constituting the layer should be as small as possible. Therefore, two models for super liquid-repellent layers are theoretically analyzed: A superhydrophobic layer consisting of an array of cylindrical micropillars and a superamphiphobic layer of an array of pillars of spheres. For the cylindrical micropillars a simple expression for the apparent receding contact angle is derived. It is based on a force balance rather than a thermodynamic approach. The model is supported by confocal microscope images of a water drop on an array of hydrophobic cylindrical pillars. The ratio of the width of a pillar w to the center-to-center spacing a is a primary factor in controlling the receding angle. Keeping the ratio w/a constant, the absolute size of surface features should be as small as possible, to maximize the impalement pressure.

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1. Introduction

Super liquid-repellent surfaces show a high apparent contact angle with a liquid, $\Theta^{\text{app}} \geq 150^\circ$, and a low roll-off angle for drops. In the last years the interest in super liquid-repellency has grown enormously since it may open new opportunities both for research and technology. These include self-cleaning, drag reduction [1–4], fog harvesting [5], enhanced heat transfer [6], and gas exchange [2,7]. In microfluidics tiny amounts of liquids can be manipulated with little adhesion and thus little energy dissipation.

To achieve high apparent contact angles the surfaces have to be structured on the nano- and micrometer length scale. This structure

needs to be such that protrusions keep the drop from direct contact with the substrate by capillary forces. A layer of air needs to be maintained underneath a drop over a large part of the apparent contact area, leading to the so-called Cassie or Fakir state. In contrast, when the liquid infuses the surface structure without trapping air we talk about the Wenzel state. In the Wenzel state, super liquid-repellency is not achieved. In addition to the topology also one material property is important for the entrapment of air: The material's contact angle. It is determined by the surface tensions of the liquid, γ_L , the surface tension of the solid, γ_S , and the solid/liquid interfacial tension, γ_{SL} . The material's contact angle, also called microscopic contact angle Θ , is formed on perfectly planar, smooth surfaces. It is given by Young's equation:

$$\gamma_L \cos \Theta = \gamma_S - \gamma_{SL}. \quad (1)$$

E-mail address: butt@mpip-mainz.mpg.de (H.-J. Butt).

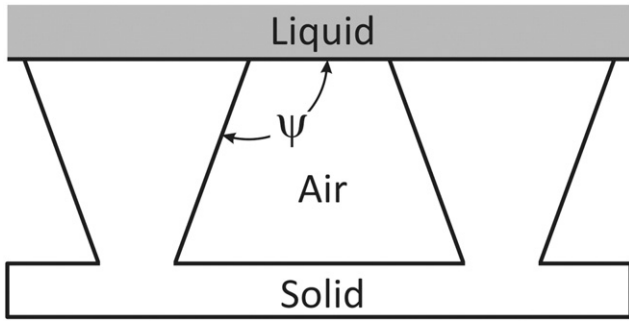


Fig. 1. Schematic of a solid surface with a structure entrapping air underneath a liquid drop when the slope with the horizontal ψ exceeds $180^\circ - \theta$.

A necessary condition for maintaining a layer of air underneath a drop is that the surface structures exceed a slope ψ of $180^\circ - \theta$ (Fig. 1) [8]. Then at zero applied pressure the liquid can form a stable structure with air underneath.

For water as a liquid the entrapment of air is relatively easy to achieve. Many materials such as aliphatic hydrocarbons and perfluoroalkanes form a material's contact angle θ above 90° with water. Therefore, micropillars with vertical walls are sufficient to build a superhydrophobic layer. For non-polar liquids overhanging structures are required [8–12] since θ is below 90° .

On nano- or microstructured surfaces the contact angle depends on the length scale one is looking at. Correspondingly, it is necessary to distinguish the material's contact angles from the apparent (macroscopic) contact angles. The material's contact angle, introduced above is the contact angle formed by the liquid when extrapolating the liquid shape on the 10–1000 nm scale to the contact line. We avoid the 10 nm close to the contact line because interfacial forces between the solid–liquid and liquid/air interface can lead to a change in the shape of the liquid surface [13–15]. The macroscopic scale is the length scale observed by the eye or with a low-resolution microscope. It is larger than the nano- and microstructures forming the super liquid-repellent layer,

thus typically larger than $10 \mu\text{m}$. We also distinguish between the *three phase contact line* (or simply contact line) on the microscopic and the *edge* on the macroscopic length scale [16].

A fundamental task is to link the material's apparent contact angles. The contact angle for superhydrophobic surfaces is often calculated with the Cassie–Baxter-equation [17]:

$$\cos\theta^{\text{app}} = \phi(\cos\theta + 1) - 1. \tag{2}$$

Here, ϕ is the area fraction of solid/liquid interface to the total projected surface area. For example, for a sessile water drop on top of a square array of cylindrical, hydrophobic pillars with radius R and spacing a the area fraction is $\phi = \pi R^2/a^2$ (Fig. 2). θ^{app} is an average between the material's contact angle on the solid surface and the angle with air (180°) weighted by their respective proportions. Eq. (2) shows that one should expect the same contact angle for equal ratios of R/a . Inserting $\phi = \pi R^2/a^2$ and rearranging for R leads to

$$R = \frac{a}{\sqrt{\pi}} \sqrt{\frac{\cos\theta^{\text{app}} + 1}{\cos\theta + 1}}. \tag{3}$$

For a given material's contact angle θ and a desired apparent contact angle θ^{app} the pillar radius increases linearly with the pillar spacing.

The Cassie–Baxter equation is derived assuming thermodynamic equilibrium. However, liquid drops are often not in global thermodynamic equilibrium and their shape is determined by pinning of the edge [8,18–26]. They are in a metastable state and not in a global energy minimum. Therefore, on real surfaces the contact angle for an advancing liquid front is larger than the one for a receding liquid. We distinguish between material's advancing θ_a and material's receding contact angles θ_r . On the macroscopic length scale we discriminate between *apparent* advancing and *apparent* receding contact angles, denoted by θ_a^{app} and θ_r^{app} , respectively. θ_r^{app} is also called a depinning contact angle.

Since liquid drops are usually not in thermodynamic equilibrium, in particular not on microstructured surfaces, Eq. (2) is not applicable to calculate θ_r^{app} or θ_a^{app} for super liquid-repellent layers. Choi et al. introduced a differential parameter to extend the applicability of the Cassie–Baxter

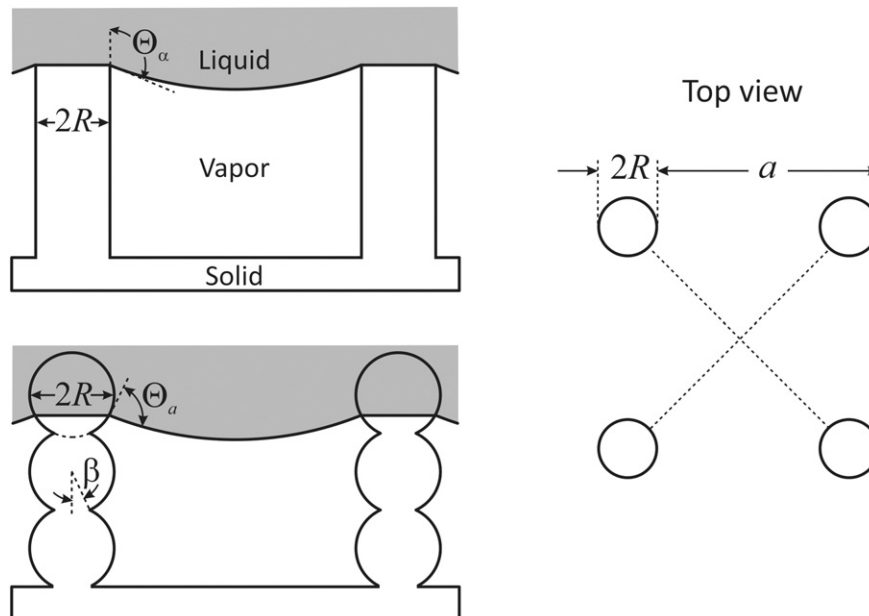


Fig. 2. Schematic of square array of micropillars from side and top view. Top: Cylindrical pillars; bottom: pillars of sintered spheres. The liquid is suspended on top in the Cassie state.

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