Superamphiphobic Particles: How Small Can We Go?

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Water and oil repellent coatings—so-called superamphiphobic coatings—greatly reduce the interaction between a liquid and a solid. So far, only flat or weakly curved superhydrophobic and superamphiphobic surfaces have been designed. This raises the question of whether highly curved structures or microspheres are feasible. Therefore, we coated microspheres with a superamphiphobic layer and measured the force between the spheres and a liquid. A qualitatively different dependence of the adhesion force on the applied load for superamphiphobic and smooth spheres is detected. Furthermore, we demonstrate both experimentally and theoretically that superamphiphobicity fails below a critical particle radius, depending on topological details and type of liquid. Therefore, this study sets a fundamental physical limit to the application of superamphiphobic layers for small objects with high curvature.

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The self-cleaning property of many superhydrophobic surfaces fascinates laymen and scientists alike [1,2]. Motivated by the desire for a fundamental understanding of the physical origin of water repellency, a variety of techniques have been developed to fabricate and characterize superhydrophobic surfaces ([3–7] and references therein). Superamphiphobic layers extend the liquid-repellent properties to nonpolar liquids. Such layers exhibit an apparent advancing contact angle of greater than 150° and roll-off angles below 10° for aqueous solutions and nonpolar liquids [8–11]. Essential for superhydrophobicity and superamphiphobicity are microscopic pockets of air that are trapped beneath the liquid [12–15]. Superhydrophobic layers combine low surface energy materials having contact angles > 90° with rough surface topography. Since no materials exist that form contact angles > 90° with oils, superamphiphobicity requires overhanging structures or convex curvatures to keep the liquid in a metastable position with air entrapped underneath [11,16–18]. Therefore, the robustness of superamphiphobic layers against wetting depends on details of the topography and in particular on the shape of the overhangs or protrusions.

Macroscopic spheres of millimeter to centimeter radius were successfully coated with a superhydrophobic layer [19,20]. However—to the best of our knowledge—all natural and artificial superhydrophobic as well as all artificial superamphiphobic surfaces are flat or only weakly curved on a millimeter scale. This raises the fundamental question of whether highly curved objects can be coated with superamphiphobic layers, still keeping their liquid repellency.

We recently introduced a method to fabricate superamphiphobic layers from candle soot [9]. Here we extend this work and coat microparticles of well-defined radii [Figs. 1(a),1(b)]. The particles are brought into contact with a liquid surface. The force to detach the coated particle from the interface, the so-called adhesion force, is measured with a resolution better than 1 nN by means of the colloidal probe technique [21].

The aim of this study is threefold. First, we demonstrate the potential of colloidal probe experiments to characterize superamphiphobic surfaces. Second, we explore the fundamental
aspects of the interaction of superamphiphobic microspheres with fluid interfaces and discuss the differences in adhesion between superamphiphobic and smooth microspheres. Third, we identify limits of liquid repellency caused by the curvature of a superamphiphobic layer, in this case imposed by the curvature of the microspheres.

On superamphiphobic layers it is important to distinguish between microscopic and macroscopic length scales and contact angles. The macroscopic length scale is defined by the radius $R$ of the microsphere including the superamphiphobic layer [Figs. 1(c),1(d)]. It can be viewed as the radius of an envelope around all nanoparticles. The microscopic length scale is defined by the radius of the coated soot particles $r$, where two or three nanoparticles may aggregate into small clusters.

Scanning electron microscope (SEM) images showed that the silica-coated soot particles have an outer radius of $r = 55 \pm 70$ nm and the outmost nanoparticles have a lateral distance of typically $0.5 \pm 1$ μm [Figs. 1(a),1(b)]. To characterize the layer we distinguish between the apparent contact angle $\Theta$ on the macroscopic and the material’s contact angle $\vartheta$ on the microscopic length scale. On a perfectly smooth, homogeneous surface such as in Fig. 1(c), both contact angles coincide. Macroscopic advancing and receding contact angles were measured in the sessile drop configuration on flat superamphiphobic surfaces (Table I).

Using an atomic force microscope (Nanowizard 3, JPK) we measured the force on the superamphiphobic colloidal probe following our previous protocols ([21] and supporting information for a description of the force measurements). When the particle moved toward a water drop, it jumped into the drop as soon as it got into contact with the liquid surface [Fig. 2(a)]. We define this point as “zero” on the distance scale. Afterwards, the force increased almost linearly with the piezo height. Typically, several smaller jumps were observed in course of approach and retraction, which we attribute to the discontinuous movement of the contact line over the coating of the particle [22,23]. The slope of the linear part of the force curve is mainly due to the deformation of the liquid drop. Following an argument of Ducker et al. and Fielden et al. [24,25], the response of a bubble (drop in our case) can be modeled by an effective spring for small deformations compared to the drop size (diameter: roughly 4 mm). The stiffness of the drop can be calculated from the slope of the measured force in the constant compliance region and was typically 0.03 N/m, thus much lower than the spring constant of the cantilever.

Micrometer-sized particles with a finite contact angle ($\vartheta > 0$) assume a stable position in the air-liquid interface [27]. For a smooth spherical particle with a radius $R$ [Fig. 1(c)] the equilibrium position is given by [28–30]

$$\cos \beta = \cos (180^\circ - \vartheta) = \frac{R - \delta}{R}. \quad (1)$$

Here, $\beta$ is the angle describing the position of the macroscopic contact line and $\delta$ is the distance that the particle protrudes into the liquid phase [Fig. 1(c)]. The adhesion force

<table>
<thead>
<tr>
<th>Water SA layer</th>
<th>Peanut oil SA layer</th>
<th>Water fluorinated wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advancing</td>
<td>164°</td>
<td>157°</td>
</tr>
<tr>
<td>Receding</td>
<td>162°</td>
<td>149°</td>
</tr>
</tbody>
</table>
required to pull a smooth microsphere out of the liquid-air interface with surface tension $\gamma$ is [28,31]

$$F_{\text{adh}} = 2\pi\gamma R \cos^2 \frac{\theta}{2}. \quad (2)$$

In the derivation of Eq. (2), it was assumed that the contact angle $\theta$ is constant and the contact line is free to move over the particle surface and that the particle is small enough to neglect weight and buoyancy. Equation (2) implies that the adhesion force is independent of the load applied [32]. In contrast, a marked dependence on load $F_L$ was observed for superamphiphobic particles. The $F_{\text{adh}}$ versus $F_L$ curve showed two regimes: below $F_L = 50$ nN the adhesion force steeply increased starting at a minimal value of $\approx 20$ nN; above 50 nN the increase was more shallow.

It is instructive to compare this minimum adhesion to the force required to detach a single nanoparticle from the water-air interface. This force is given by Eq. (2) by replacing $R$ with the radius of the nanoparticle $r$ ($\approx 60$ nm) [Figs. 1(d),1(e)] and $\theta$ with the advancing contact angle on the fluorinated silicon wafer ($\theta = 115^\circ$, Table I). Then $F_{\text{adh}}^{\text{single}} = 8$ nN for water ($\gamma = 0.072$ N/m). Thus, an adhesion force as low as 20 nN indicates that just two to three nanoparticles formed capillary bridges at low load.

Moreover, from the measured minimal adhesion force, we can calculate the apparent, macroscopic contact angle for the superamphiphobic layer. Using Eq. (2) and $F_{\text{adh}} = 20$ nN, we get $\Theta = 175^\circ$. This contact angle quantitatively agrees with results obtained by laser scanning confocal microscopy [Fig. 3(a)] [33] but exceeds the angle measured with the sessile drop method by more than $10^\circ$ (Table I). This confirms the systematic errors of the sessile drop method using conventional cameras at very high contact angles [34]. To understand the origin of the linear increase of the adhesion force for applied loads above 50 nN, we explicitly consider the movement of the contact line over the well-separated nanoparticles. On approach of the microsphere the contact line has to overcome the line over the well-separated nanoparticles. On approach $F_{\text{adh}}$ versus $F_L$ curve showed two regimes: below $F_L = 50$ nN the adhesion force steeply increased starting at a minimal value of $\approx 20$ nN; above 50 nN the increase was more shallow.

At a constant average density of nanoparticles per unit length $\kappa$, the total capillary force is

$$F_L = 4\pi\gamma \kappa R \sin \beta \sin^2 \frac{\theta}{2}. \quad (4)$$

Here, $2\pi R \sin \beta$ is the circumference of the rim [Fig. 1(d)]. Equation (4) implies that the rim will slide to a position given by $\beta$ if a load $F_L$ is applied. On retraction, the adhesion force is

$$F_{\text{adh}} = 4\pi^2 \gamma \kappa r R \sin \beta \cos^2 \frac{\theta}{2}. \quad (5)$$

Dividing Eq. (5) by Eq. (4) allows us to relate the adhesion force to the load,

$$F_{\text{adh}} = \frac{F_L}{\tan^2 (\Theta/2)}. \quad (6)$$

Equation (6) shows that $F_{\text{adh}}$ is proportional to the load multiplied with a geometric factor that contains the material’s contact angle. With a slope of 0.34 (Fig. 2(b), solid line) we obtained $\theta = 105^\circ$, which is between the advancing and receding contact angles measured on flat surfaces (Table I).

Finally, we explored whether the coated microspheres keep their resistance to wetting of liquids with low surface tension. Here we choose peanut oil, $\gamma = 0.035$ N/m. For the first approach the force versus distance curves resembled those for water (Fig. 4, 1st). In contrast to water, the microsphere jumped into the drop of peanut oil at contact, resulting in an attractive force of 20 nN. After further piezo movement of 2.0 $\mu$m, zero force was reached again. Using Eq. (1) and $\Theta$ instead of $\theta$, the penetration depth to zero force leads to an advancing apparent contact angle of $\Theta = 154^\circ$ with $R = 19.4$ $\mu$m. This time the contact angle determined by confocal microscopy exceeded those calculated from the minimum adhesion force, revealing different interactions of the liquid with the flat and highly curved surfaces.
impalement pressure is \( P = 2.2 \) kPa. Because \( P_c > P \), peanut oil is expected to impale the superamphiphobic layer. For water, \( P = 9.5 \) kPa and \( P_c = 7.2 \) kPa; thus, the depinning pressure prevents water from impaling the superamphiphobic layer. Thus, impalement of a superamphiphobic layer by a liquid is prevented for radii of curvature larger than a critical radius \( R_c \),

\[
R > R_c = \frac{d^2}{r \sin^2(\theta/2)}.
\]

In reality the nanospheres forming the superamphiphobic layer are more randomly arranged rather than in a regular array. Impalement is most likely at places where they coincidentally have a large spacing. Therefore, the distance \( d \) corresponds more to the maximal distances between nanospheres rather than the mean distance. In general, the condition for maintaining the air cushion is more complicated because the detailed shape of all nanospheres needs to be considered, i.e.,

\[
P > \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right).
\]

Here, \( R_1 \) and \( R_2 \) are the two principal radii of curvature of the oil-air interface. Equation (9) is valid for a concave surface. Notably, if the liquid-repellent layer has a convex surface, such as in coated capillaries, liquid repellency should be enhanced. Thus, a convex surface should increase the effective impalement pressure by \( \gamma (1/R_1 + 1/R_2) \). The air cushion is stabilized.

These results demonstrate the potential of colloidal probe spectroscopy to gain insight into the wetting behavior of superamphiphobically coated microspheres. It allows one to measure large contact angles, which are difficult to determine with the sessile drop method. We have demonstrated that the wetting of superamphiphobically coated microspheres is qualitatively different from the continuous movement of a contact line on a smooth, very lyophobic sphere. This is due to the difference between the microscopic and macroscopic contact angle caused by entrapment of air. Experiments with peanut oil showed that a convex structure is easily impaled, even if the same layer in a planar geometry repels the oil. Impalement is caused by the capillary pressure associated with the liquid cavity of radius \( R \) formed around the particle, demonstrating that superamphiphobicity is a function of curvature. This limit is directly relevant for fabricating superamphiphobic fabrics and grids, which have been suggested for water-oil separation, gas exchange, or for designing floating objects.

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