APPLICATION NOTE 9

Dynamic contact angles on superhydrophobic surfaces

This application note illustrates how the Attension Theta Optical Tensiometer can be used for measuring advancing and receding contact angles on superhydrophobic surfaces.

Introduction


For creating a superhydrophobic surface, two factors are required. First, the surface must have suitable roughness at micro- and nanoscales. Second, the surface must have a hydrophobic surface chemistry. [6] A famous model surface for superhydrophobicity from nature, the lotus leaf, has 10-micron papillae in combination with a nanostructure created by hydrophobic wax crystals. This combination results in a surface with water contact angles of about 160°, and enables droplets to roll off at a tilt angle smaller than 5°. [7] The facile movement of the droplets indicates that the contact angle hysteresis, i.e., the difference between the advancing and receding contact angle is small.

Only if the contact angle hysteresis is negligible, the wetting properties of a surface can be characterized by a static contact angle, which is measured by placing a droplet to the surface and optically determining the contact angle. Generally for rough surfaces, dynamic, i.e., advancing and receding contact angles need to be measured, since a static contact angle can take any value between the advancing and receding ones. In principle, the dynamic contact angles can be defined either by changing the droplet volume or by tilting the droplet or by using a Wilhelmy plate method with the force tensiometry. This application note describes the dynamic contact angle measurement by changing the droplet volume on superhydrophobic surfaces, as illustrated in Figure 1.

Figure 1. The principle of dynamic contact angle measurement.
Case study: Superhydrophobic tracks for low-friction, guided transport of water droplets

Microfluidics is a growing field of science which studies the behavior of fluids in microscale. The application areas for microfluidics range from analytical and diagnostic microchips to microfluidic fuel cells. Water-based liquids can be manipulated in these devices by integrating superhydrophobic areas or superhydrophobic tracks on them. Mertaniemi et al. have demonstrated such tracks for enabling fast and simple transport of water droplets in microfluidic devices. [8]

The superhydrophobic tracks were prepared in metal plates by milling or laser cutting and in silicon by ion etching. The metal surfaces were coated using a combination of silver microstructure and a fluorinated thiol surfactant, and the silicon wafers were coated with a fluoropolymer in CF₃ plasma. Figure 2 shows a water droplet in a superhydrophobic track.

Wetting properties of a superhydrophobic copper surface were characterized using the Attension Theta optical tensiometer. The measured data on five different spots on the surface is shown in Figure 3.

![Figure 2. A Water droplet in a superhydrophobic track.](image)

![Figure 3. Dynamic contact angles on a superhydrophobic copper surface.](image)
First, a 1-µl droplet was applied on the surface, and the needle was lowered behind the drop so that the tip was about at the midway of the droplet height. The volume of the droplet was slowly increased to 2 µl, at a drop rate of 0.05 µl/s. In order to minimize hysteretic effects, the addition of water was stopped for 30 s before starting the contact angle measurement.

To measure the advancing contact angle, the volume of the droplet was increased from 2 µl to 10 µl at 0.05 µl/s, recording images at 0.6 frames per second. Next, the droplet volume was increased to 15 µl and decreased back to 11 µl. After this, the droplet volume was decreased slowly to 10 µl. In order to minimize hysteretic effects, the removal of water was stopped for 30 s before starting the receding contact angle measurement.

The receding contact angle was measured by decreasing the volume at a rate of 0.05 µl/s, starting at a drop volume of 10 µl. Images were recorded at 0.6 frames per second until the drop lost contact with the surface.

The water contact angles of different materials used for preparing superhydrophobic tracks are shown in Table 1. The similarity of contact angle values of the zinc and copper surfaces was expected, since both surfaces were coated using the same method. However, the larger variance of receding contact angles observed for the zinc surface suggests that the coating had some defects. The very small contact angle hysteresis of the silicon surface makes it the optimal choice for applications where extremely high mobility of water droplets on a surface is desired.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>ADVANCING CONTACT ANGLE</th>
<th>RECEDING CONTACT ANGLE</th>
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<tbody>
<tr>
<td>Copper</td>
<td>166°±2°</td>
<td>164°±2°</td>
</tr>
<tr>
<td>Zinc</td>
<td>168°±2°</td>
<td>166°±4°</td>
</tr>
<tr>
<td>Silicon</td>
<td>170°±2°</td>
<td>170°±2°</td>
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</tbody>
</table>

Table 1. Dynamic contact angles of a 6 µl water droplet on superhydrophobic surfaces.

Conclusions

Superhydrophobic surfaces, i.e., surfaces with a contact angle larger than 150° and a small contact angle hysteresis, are desired for their special wetting properties. Water droplets applied to a superhydrophobic surface easily slide off, if the surface is tilted slightly. For obtaining a superhydrophobic surface, a suitable roughness in combination of a hydrophobic surface chemistry is required. Wetting properties of superhydrophobic surfaces can be characterized by measuring dynamic contact angles using an optical tensiometer.

References