Report on the experiment SI1745:
Wettability of superhydrophobic surfaces

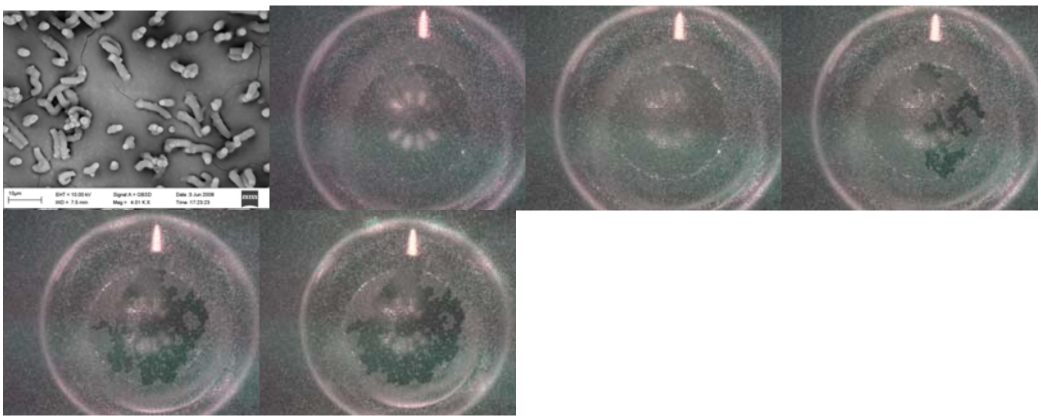
When a water drop is deposited onto a superhydrophobic surface, it can be accommodated in two ways, depending on the nature of the interface between the drop and the solid surface.
In the first case, called inhomogeneous or Cassie-Baxter regime, air or vapor is trapped at the interface between the surface asperities, while in the second case, called homogeneous or Wenzel regime, the solid surface is completely wetted. Both regimes can exhibits a large value of the contact angle, but only in the Cassie-Baxter regime the contact angle hysteresis is low enough to allow an easy sliding of the water drop. Unfortunately, in many artificial superhydrophobic surfaces a spontaneous transition from inhomogeneous to homogenous regime occurs. The study of this transition was the goal of the SI1745 experiment.

The experiment has been done in November 2008, at the ID03 beamline (EH1).

A custom experimental set-up, consisting in a digital microscope to observe the wet area of the sample from the bottom, a CCD camera to measure the contact angle and a computer controlled syringe pump to dispense a water drop on the sample, was mounted on the diffractometer table.
During the experiment microscope images of the contact area, images of the water drop shape and the GISAXS patterns were collected simultaneously during the wetting process.

The samples were polymer replica of commercial polycarbonate membranes, generally used as filters in biological or medical laboratory, which exhibit robust superhydrophobic properties, since the transition from Cassie-Baxter to Wenzel regime occurs in a time of several hundreds seconds as determined in previous experiments carried out at the Genova University.

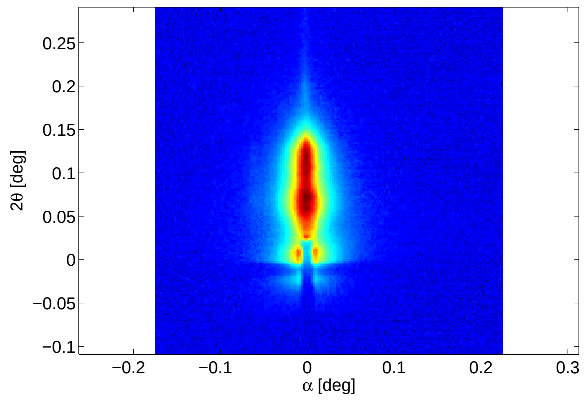
The typical experimental procedure was the following:
After the alignment of the X-ray beam, focused on the sample with a typical size of 20 x 20 um, a water drop, with a diameter of about 1.5 mm, was dispensed onto the sample, positioned directly in the focus of the digital microscope. With the lateral CCD camera, the evolution of the contact angle was measured, while GISAXS intensity maps were recorded.



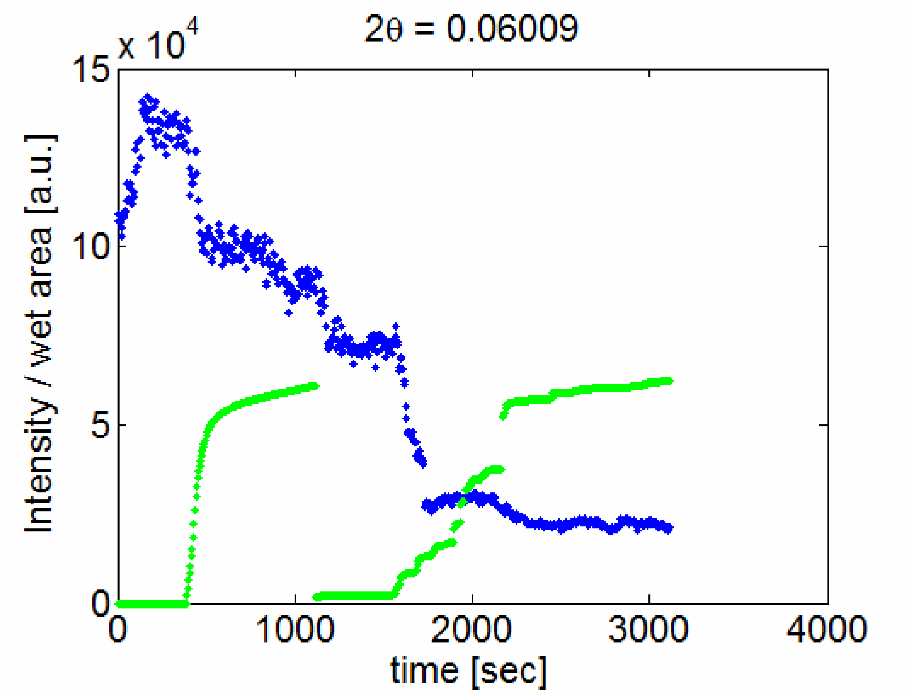
In Fig.1 we report a SEM image of a sample (photo a) and a typical time evolution of the wet area (dark regions) as seen by the digital microscope.

After the water drop has been deposited onto the sample (photo b), the image becomes more and more blurred (photo c). This effect is due to water which starts to wet the sample asperities, without touching the surface. We call this regime “first wave” . After a time, water touches the surface and the wet area enlarges more and more, invading all the contact area (“second wave” , photos d-f).

A GISAXS intensity map is reported in Fig. 2 . This map confirms the absence of any lateral correlation in the nanometer scale, as already suggested by the SEM image.



During the wetting process, the GISAXS map does not change in shape, but only in intensity, indicating that there is the absence of nanometric superhydrophobicity.
Collecting all the data, we can correlate the GISAXS values to the extension of the wet area, as reported in Fig.3



Blue dots represent the GISAXS intensity measured at $\alpha = 0°$ and $2\theta = 0.06°$, while green dots represent the evolution of the wet area (from 0 to 1000 sec the first wave, from 1000 to 3000 sec the second wave). It is evident that the GISAXS intensity decreasing is time-correlated with the increasing of the wet area. This result clearly shows that X-ray can be used to study the superhydrophobic effect, opening new possibilities in the field since the method can be applied also in samples which are not optically transparent .

Roughly speaking, the GISAXS intensity decreases as a function of the wet area because the difference in density between water and PDMS is very small and then X-ray photons impinging on wet regions are not more reflected towards the detector but are transmitted into the sample bulk.

In conclusion we have been able to correlate the images collected with three different camera in order to follow the wetting process in superhydroophobic surfaces. Even though the GISAXS pattern has not shown new structure in the nanometric region this techniques open new possibilities for the study of opaque samples. Moreover the intensity in the specular plane has specific and unforeseen behaviors depending on the value of Qperp. A detailed analysis of this dependence is in progress.