

A new effect observed on superhydrophilic surfaces using the capillary bridge probe method

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Utilizing the unique properties of the recently introduced capillary bridge probe method, water contact angles were determined on lightly corroded glass surfaces. A new observation was obtained in these complete wetting situations: the receding contact line starts to advance again during the increase of the bridge length.

Keywords: Wetting; Contact angle; Capillary bridge; Superhydrophilic surface; Glass corrosion

Introduction

Measurement of low contact angles is challenging. The developed indirect Capillary Bridge Probe method combines the accuracy of the Wilhelmy method and the general usability of the sessile drop method without their limitations. The method is based on the use of a liquid bridge as a probe: the capillary bridge of the test liquid is stretched between the rim of the base of a cylinder and the investigated surface under equilibrium conditions. The advancing contact angle on the sample can be measured during the stepwise decrease of the bridge length. The receding contact angle is determined during the retraction of the cylinder. The contact angle is calculated from Delaunay's analytical solution, while the necessary parameters are obtained from the measured capillary force and from the automated analysis of the captured image of the liquid bridge. The bridge is formed from a pendant drop. This unique feature ensures that the advancing contact line finds dry (not prewetted) surface.

The readvancing phase

A new effect was observed during the measurements on freshly acid-cleaned glass surfaces, *i.e.* in complete wetting situations. The receding contact line starts to advance again during the increase of the bridge length, see Figure 1.

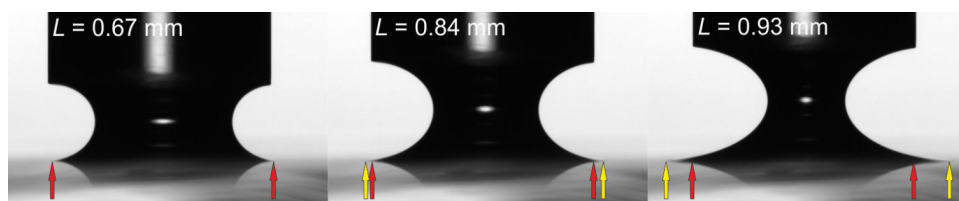


Figure 1. Images of a water capillary bridge taken during the retraction of the cylinder. The receding contact line starts to advance again after a given bridge length (L). The capillary bridge was formed on a glass slide treated freshly in sulphuric acid. Note that images show equilibrium states, not snapshots of a dynamic process.

The measured capillary force does not exhibit hysteresis. The contact radius started to increase in the retraction phase, around the bridge length corresponding to bridge formation (Figure 2a). It can be observed in Figure 2b that the advancing and receding contact angles are equal within their standard deviation: $4.7^\circ \pm 0.3^\circ$ and $4.5^\circ \pm 0.3^\circ$, respectively. The measured contact angle in the readvancing phase, *i.e.* the readvancing contact angle is much lower, its value is $1.0^\circ \pm 0.1^\circ$. When the receding contact line starts to advance again, it finds prewetted surface, therefore the resulted contact angle is much smaller.

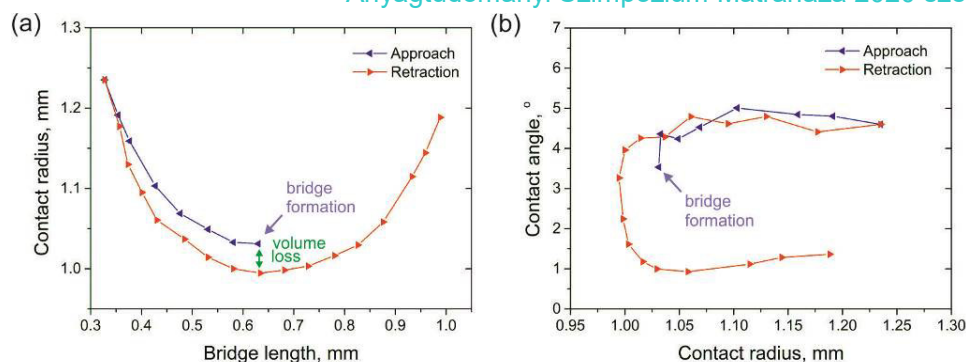


Figure 2. (a) Contact radius as a function of the bridge length measured on a glass surface treated in concentrated sulfuric acid. (b) Contact angle on the glass surface versus the contact radius. Advancing and receding contact angles are equal, while the readvancing contact angle is lower, because the readvancing contact line finds prewetted surface.

Corroded glass surfaces

Hereafter, lightly corroded glass slides were investigated: how does the water contact angle change as a function of the exposure time to air. Microscope glass slides were cleaned and soaked in 3:1 Piranha-solution. The measurement was started directly after the cleaning process on a glass slide, while other samples were soaked for four days at room temperature. The samples were measured periodically in different positions, and they were left in the humid atmosphere (94%) of the sample chamber between the measurements.

The advancing and receding contact angles were determined to be equal ($3.6^\circ \pm 0.1^\circ$ and $3.6^\circ \pm 0.4^\circ$, respectively) by the first measurement. Their values increase (surface hydroxyl group density decreases) but remain equal for ca. 150 min, and finally significant hysteresis can be observed, while the readvancing phase disappears (increasing amount of surface inhomogeneity). On the contrary, the advancing, receding, and readvancing contact angles remain almost unchanged on the soaked sample. A slight increase of ca. 1° can be observed for both after 260 min.

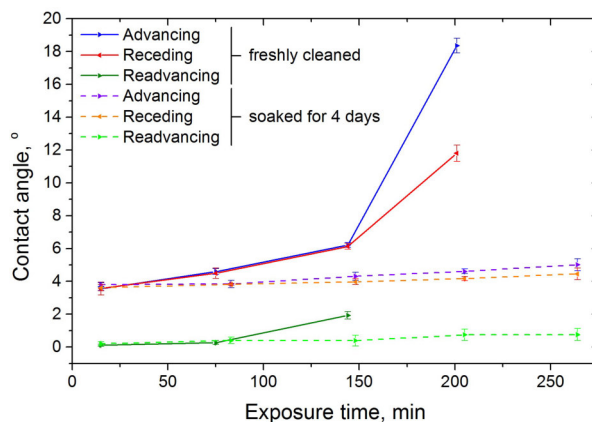


Figure 3. Advancing, receding, and readvancing contact angles on glass slides as a function of exposure time to humid air (94%). The measurements were performed directly after the cleaning process (continuous lines), and after soaking the sample in ultrapure water for four days (dashed lines). The superhydrophilic character and the readvancing phase of the directly measured surface disappear, while the alteration zone formed by corrosion preserves the super-hydrophilicity.

References

- [1] N. Nagy: Contact Angle Determination on Hydrophilic and Superhydrophilic Surfaces by Using $r-\theta$ -Type Capillary Bridges, *Langmuir* **35**, 2019, 5202-5212