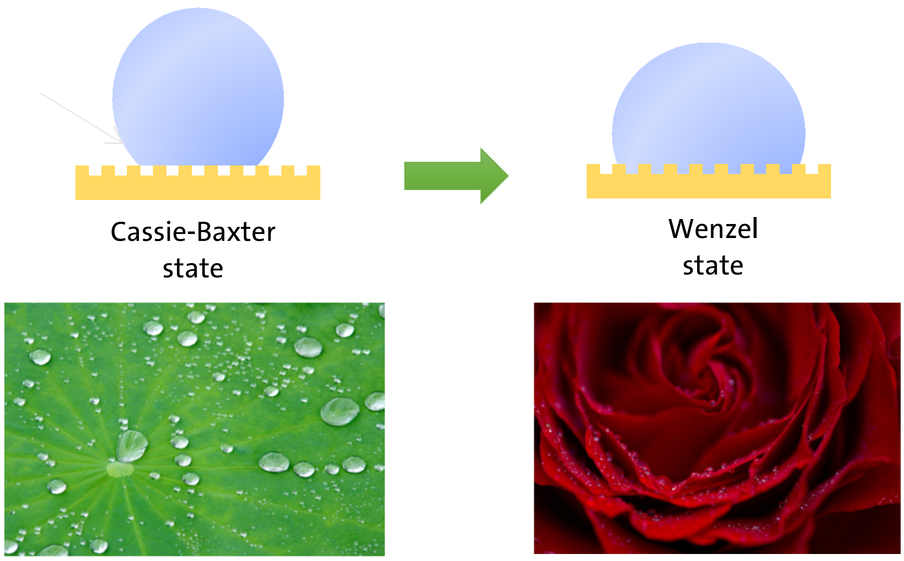
How contact angle measurements can help to understand the 'Rose Petal Effect'

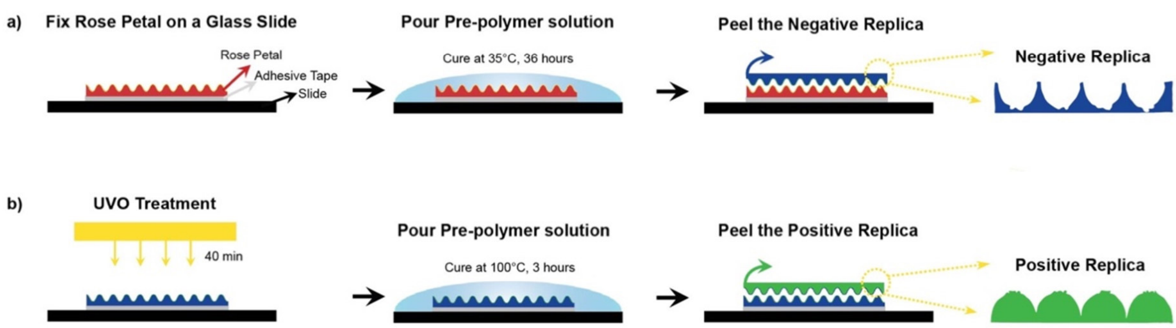
The wetting of rough surfaces from nature remains an interesting subject for investigation and a source of inspiration for synthetic materials. Roughness in combination with surface chemistry determines the wettability of a surface. Generally the contact angle (CA) is used to characterize the hydrophobicity and hydrophilicity of a solid surface. If the water CA is 0° < ϑ_0 < 90°, then the surface is usually called "hydrophilic", whereas a surface with water CA of 90° < ϑ_0 < 180° is usually called "hydrophobic". The most prominent example from nature for a highly hydrophobic surface is the lotus leaf with its unique surface properties leading to the so called "lotus effect". The lotus effect refers to surface roughness-induced ultra hydrophobicity resulting in a high water CA and a very low water CA hysteresis (ϑ_{CAH} < 10°) on its surface. The lotus effect is already well understood and has led to the development of different coatings, paints, roof tiles, fabrics and other surfaces that can stay dry and clean themselves. Several applications have been marketed, such as self-cleaning glasses installed in the sensors of traffic control units on German autobahns. While water easily rolls of from lotus like surface indicating a low adhesion, it was found that water drops stick strongly to rose petals. Rose petals also show a similarly high water CA but have a much higher water CA hysteresis which is contradictory to the "lotus effect" giving this surface characteristics the name "rose petal effect". What is the "rose petal effect"? And how can we make good use of contact angle measurements to understand it?

The wetting of surfaces can be a complex problem due to the micro-, nano- and hierarchical structures on the surfaces. Both, lotus leafs and rose petals, have rough surfaces consisting of micro and nanostructures. Surfaces can be characterized by several wetting states, such as the Cassie & Baxter state (lotus) where entrapped air leads to an incomplete coverage of the surface or the Wenzel state (rose) where the surface is completely covered (**Scheme 1**).



Scheme 1: *Comparison between Cassie-Baxter and Wenzel state*

Understanding the wetting of rough surfaces is very important in order to design functional surfaces for various applications. While the lotus effect is well understood, there are still many open questions regarding the rose petal surface and a lack of direct evidence on the precise wetting state. To shed light on these issues Ghosh et al. set out to generate replicas of rose petal surfaces to study their wetting behavior and unveil the mechanism behind the "rose petal effect".



Scheme 2: *The double molding replication technique used for fabrication of rose petal a) Negative Replica and b) Positive Replica*

The fabrication of positive and negative replicas of real rose petals was carried out by a soft lithographically method on cross-linked PDMS (**Scheme 2**). The thus generated surfaces (real rose pedal, negative replica and positive replica) were characterized by contact angle measurement in terms of the apparent contact angle (ϑ^*), advancing (ϑ_a) and receding contact (ϑ_r) angles. As shown in **Table 1**, the ϑ^* and contact angle hysteresis ϑ_{CAH} of the replicas are nearly identical to the real rose petal. They all have a high CA (ϑ^* ~ 140°) and high contact angle hysteresis (ϑ_{CAH} ~ 70°, much higher than that of lotus leaf surface which are typically >10°). On the one hand, a high CA is a sign for low liquid–solid adhesion. On the other hand, high CA hysteresis is a sign for high liquid–solid adhesion. To find out the real situation, an adhesion strength test was done that showed surface adhesive force for the three surfaces (real rose petal (184 μN), negative replica (200 μN) and positive replica (175 μN)) are much higher than that of lotus leaf surfaces, corresponding to above ϑ_{CAH} data. These results furthermore show that the adhesion strength primarily depends on the hierarchical geometry of the substrate rather than chemical composition of the material itself.

Table 1: *Characterization of Surface Wettability (n ≥ 3)*

	Apparent Contact Angles (ϑ^*)	Contact Angle Hysteresis $\vartheta_{CAH} = (\vartheta_a - \vartheta_r)$
Rose Petal	140.1 ± 5°	76 ± 5°
Negative Replica	136.8 ± 3°	70 ± 3°
Positive Replica	138.5 ± 2.6°	75 ± 1.3°

The morphologies of all three types of surfaces were investigated by *in-situ* imaging methods, like confocal laser scanning microscopy (CLSM) and underwater *in-situ* atomic force microscopy (AFM). Slightly reduced roughness of the secondary folds could be seen in both replicas during AFM tests under water. From their measurements the authors concluded that “rose petal effect” is caused by a Cassie impregnating wetting state. That means water fails to penetrate into the nano-grooves of surface resulting in air pockets trapped around the secondary nano-folds structure.

Overall, this research could show that the “rose petal effect” derives from a Cassie impregnating wetting state leading to high water contact angles, a big water contact angle hysteresis and a strong water adhesion. Not only can this research help to understand the interesting science behind the “rose petal effect” phenomenon, but also provides ideas to generate new functional materials with special properties by varying the surface roughness for various applications.

An OCA 15 Pro Contact Angle Goniometer (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Replicating and resolving wetting and adhesion characteristics of a Rose petal; Udita Uday Ghosh, Sachin Nair, Anuja Das, Rabibrata Mukherjee, Sunando DasGupta; *Colloids and Surfaces A* **2019**, 561, 9-17; DOI: 10.1016/j.colsurfa.2018.10.028