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The wetting state of water on a rose petal

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The rose petal features surface structures that offer unique wetting properties. A water droplet placed on a rose petal forms a high contact angle but exhibits significant contact angle hysteresis, such that relatively large droplets remain stuck to the surface when it is tilted. Understanding this distinctive ‘parahydrophobic’ wetting behavior can provide insight into the design of highly nonwetting, yet highly adhesive, synthetic surfaces. Surface features of the rose petal are characterized via focused ion beam scanning electron microscopy, which reveals microscale papillae that are partially covered with nanoscale striae. The wetting state of water on a rose petal is directly visualized using confocal microscopy. This experimental evidence confirms the microscale wetting behavior on the papillae, but cannot resolve the wetting behavior on the nanoscale striae. To infer the wetting state on the striae, an energy-minimization-based model is developed and the results from the model are compared to the experimental evidence. In combination, the experimental findings and the model results reveal the wetting state of water on the hierarchical surface structure and explain the macroscopic wetting behavior of the rose petal.

1. Introduction

Unique and unexpected phenomena in nature often provide inspiration for the design of practical technologies. Plants, which moved from aqueous to land environments around 460

million years ago^[1], have been an abundant source for such inspiration. Plants feature diversified surface topologies and protective coatings.^[2] These topologies lead to unique interactions when they come in contact with water droplets, which are typically classified based on their affinity for water as signified by the macroscopic contact angle (CA) of the droplet.

Surface wettability can range from superhydrophilic (typified by $CA < 10^\circ$) to superhydrophobic ($CA > 150^\circ$). For a surface to be deemed superhydrophobic^[3] further requires that it exhibit very low contact angle hysteresis (CAH)^[4], to account for the observed ‘slippery’ behavior^[5] and self-cleaning characteristics^[6]. However, surfaces with a high contact angle ($CA > 150^\circ$) can also exhibit ‘sticky’ behavior characterized by high CAH; such surfaces are termed parahydrophobic.^[7] A rose petal is a prime example exhibiting such parahydrophobic behavior; this so-called petal effect^[8] has attracted significant research attention^[7] in an attempt to understand this somewhat puzzling wetting state.

Research over the last two decades has led to noteworthy progress in the synthesis of functional surfaces inspired by nature.^[9] Self-cleaning surfaces inspired by the lotus leaf^[10] have potential applications in enhancing the efficiency of solar cells, reducing surface drag, enhancing fluidic transport, and preventing water corrosion of batteries and fuel cells.^[5] Surfaces exhibiting the petal effect have been proposed for separation processes^[11] and collection of water via directional liquid transport.^[12–14] It has also been recently demonstrated that parahydrophobic surfaces are ideal for facilitating bubble nucleation and departure during boiling.^[15,16] Models of the wetting state are typically used to design surface topologies that provide the desired wetting characteristics.^[17] Unlike the lotus leaf, for which the wetting state has been confirmed and is well-accepted^[4], a recent review of the current understanding of parahydrophobic surfaces reveals a lack of experimental evidence to confirm the postulated wetting states on the rose petal.^[7]

As the surface morphology of natural surfaces is typically complex, and the features themselves delicate, it is difficult to obtain an accurate characterization of the microscopic wetting state. The existing explanation of the petal effect is based on a partially wetting ‘Cassie-impregnating’ state.^[7] The Cassie-impregnating wetting state is adapted to the dual-scale surface features of the rose petal^[18], namely microscale papillae (bumps) with nanoscale striae (folds)^[18] on top of each micro-papilla.^[19] Water droplets on the petal are thought to penetrate the gap between micro-papillae but not wet the nanoscale features. Although it was postulated that high apparent CA and high adhesion exhibited by surfaces could be explained by a mixed wetting state^[20], there has been no direct experimental evidence or visualization of these hypothesized wetting states on a rose petal. One recent study visualized the wetting state on a rose petal using top-down optical microscopy,^[21] and postulated the trapping of air at the surface; however, it is difficult to view the liquid-air and liquid-solid interfaces underneath the droplet using this technique. Progress has been made on visualizing the liquid-air and liquid-solid interfaces between and below condensing droplets^[22,23] and moving droplets^[24] on microstructured surfaces using scanning electron microscopy. The microscopic wetting behavior and movement of the contact lines of droplets on synthetic microstructures has also been visualized using confocal microscopy^[25,26]; however, this characterization approach has yet to be applied to a real biological surface. To date, proposed wetting states on a rose petal have been inferred only based on observations of high CA and high CAH.^[7,19,27] The strong adhesion and pinning of water droplets^[27] and air bubbles^[28] to the surface of other examples of parahydrophobic surfaces, such as peanut leaves^[29] and gecko feet^[30], is also attributed to their hierarchical structure.

In this work we directly observe the microscale wetting state on a rose petal, including the profile of liquid-air interfaces below the droplet, in three-dimensional detail. We first perform scanning electron microscopy (SEM) and focused ion beam scanning electron microscopy

(FIB-SEM) on a fresh rose petal to understand the exact topology and feature dimensions of the petal surface, which includes both microscale papillae and nanoscale striae. We then perform high-resolution, three-dimensional confocal microscope scanning to precisely visualize the location of the liquid-air interface. The autofluorescence^[31] characteristic of the rose petal is used to tag the surface, whereas a low concentration of dye added to the water helps visualization of the liquid-air interfaces. Cross-sectional images obtained from the confocal scan show clear evidence of a liquid-air interface where the droplet contacts the surface, confirming that the liquid only partially wets the gaps between the microscale papillae. This observation is in direct contrast to the prevailing hypothesis of a Cassie-impregnating wetting state for the rose petal. An energy-minimization-based model, along with the experimentally measured surface parameters, are used to confirm the complete wetting state considering both the microscale and nanoscale surface features.

2. Results and Discussion

The macroscopic wetting behaviour of a fresh rose (Red Freedom, South American; **Figure 1** (a)) is characterized. The average apparent static contact angle and contact angle hysteresis are found to be $151^\circ \pm 3^\circ$ (Figure 1 (b)) and $105^\circ \pm 4^\circ$ respectively. An SEM image is acquired to view the surface features on the rose petals (details of the sample preparation procedures are included in the Experimental Section). The SEM image reveals that the petal surface (adaxial epidermis) comprises a tight-packed array of microscale bumps (micro-papillae; Figure 1 (c) and (d)) with nanoscale striae (wrinkled folds) on the top of each micro-papilla (Figure 1 (e)).^[18] Confocal microscopy scanning (details in the Experimental Section) is performed to visualize the microscopic wetting state of water. The image reconstructions reveal the wetting state of water on the rose petal, including the presence of trapped air under the water-air interfaces that form between the micro-papillae. **Figure 2** shows composite images of the dyed water emission, rose surface autofluorescence emission, and interface reflection signals. A top-down

view of a single z -slice is shown on the left; on the right, x - and y -slices are shown through the center of several micro-papillae. A representative sketch of the emission signals surrounding a single micro-papilla is presented based on the wetting behaviors observed across the entire surface. The locations of the micro-papillae are easily visible from the autofluorescence emission signal (red in Figure 2). However, there is no emission signal from the top portion of each papilla. The reflection signal (dark blue) traces along the top of each papilla as expected, but there are also flat regions in this signal that connect between the papillae, indicating the presence of a horizontal liquid-air interface at a depth of $9.0 \pm 1.3 \mu\text{m}$ below the top of each papilla (the depth was obtained by taking an average of the measurements at 20 different locations from the confocal scanning images). The light blue region indicating emission from the dyed water is always adjacent to the upper side of the dark blue reflection signal region. A very weak autofluorescence emission signal is also observed from the crevices between each papilla. To more fully characterize the geometry of these features not visible from confocal scanning, we performed a FIB-SEM on the pretreated rose petal.

A $65 \mu\text{m} \times 40 \mu\text{m}$ rectangular section is cut out of the center of the fixed rose sample, using FIB-SEM milling performed at 20 kV and using a very low current (9.6 nA) so as to prevent damage to the features by overheating. After FIB milling, the exposed micro-papilla cross sections are imaged at different tilt angles (**Figure 3**). It is observed that the average peak-to-peak pitch between the three visible papillae is $\sim 18 \mu\text{m}$, and each papilla is $\sim 42 \mu\text{m}$ tall. The papillae are densely packed and conform to each other at a depth of $\sim 14 \mu\text{m}$ from their tops (this depth was measured from the FIB-SEM images by taking an average over 5 different locations). The depth of the crevices ($\sim 14 \mu\text{m}$) between papillae is generally greater than the penetration depth of the liquid into the crevices (liquid-air interfaces observed at a depth of $\sim 9 \mu\text{m}$). This confirms the presence of trapped air between the micro-papillae and the water droplet underside, indicating that the droplet is in a *composite* wetting state. This observation contradicts the existing postulate in the literature of a Cassie-impregnating state on a rose petal,

which assumes that the water completely wets these microscale features (but does not wet the smaller scale striae).^[7,19,32]

Schematic side- and top-view drawings of the petal features and microscale wetting state, gleaned from the combined confocal, SEM, and FIB-SEM observations, is presented in **Figure 4** (a). We observed from the SEM images (Figure 1) that each micro-papilla has nanoscale striae; these striae do not cover the entire surface of the papilla. While the wetting state on the microstructures is revealed from the confocal scanning, it is not clear whether water wets the nanoscale striae texture.

We postulate two possible wetting states for the striae as illustrated in Figure 4 (b), one in which these features are wetted by the water (Wenzel^[33] state) and another in which the water is suspended on top of the striae (Cassie-Baxter^[34] state). Because we have established that the micro-papillae are in a composite wetting state (liquid partially penetrating the gaps), we name these two possible wetting states based on the combined microscale and nanoscale wetting states as composite-Wenzel (C-W) and composite-Cassie-Baxter (C-CB) states.

We develop an energy-minimization-based model of the droplet sitting on the rose petal, considering both possible wetting states, to predict the apparent contact angle associated with each state. These predicted contact angles are compared with the experiments to determine which wetting state yields an accurate prediction of the measured macroscopic wetting behavior. To determine the total energy, the system is defined as the surface with the droplet sitting on it, where the area of the surface is equal to the area covered by the liquid at the droplet footprint. The total energy of the system (G) when a droplet sits on a surface is given as^[35]

$$G = A_{LV}\gamma_{LV} - A_{SL}\gamma_{LV} \cos \theta_e \quad (1)$$

where A_{LV} is the total liquid-air interfacial area, A_{SL} is the total solid-liquid interfacial area, γ_{LV} is the liquid-air interfacial tension, and θ_e is the equilibrium contact angle or Young's contact angle.^[25] A detailed derivation of Equation 1 is given in the supporting information. We

estimate A_{LV} and A_{SL} based on the geometric shape and dimensions obtained from the experimental visualizations. A repeating triangular packing arrangement with an average pitch (p) between micro-papillae of $\sim 18 \mu\text{m}$ was observed in the top-down SEM image (Figure 1). The area of the droplet footprint, using a spherical cap approximation, is given by^[35]

$$A_{base} = \pi R^2 \sin^2 \theta \quad (2)$$

where R is the radius of the droplet and θ is the apparent contact angle of the droplet.

The interfacial areas are first calculated for the C-W wetting state. The total solid-liquid area for the C-W wetting state is

$$A_{SL} = A_{SL,r} \times N_r \quad (3)$$

where $A_{SL,r}$ is the wetted solid-liquid area of each repeating micro-papilla and $N_r \left(= \frac{4}{\sqrt{3}} \frac{A_{base}}{p^2} \right)$

is the number of repeating units under the entire droplet footprint. The wetted area is calculated as

$$A_{SL,r} = 0.5 \times [S_{qf} + r_n \times S_{fg}] \quad (4)$$

where r_n is the nanoscale roughness defined as the ratio of the surface area with roughness to the footprint area and S_{qf} and S_{fg} are the areas comprising the regions marked from q-f and f-g in Figure 4(b). These areas are calculated by fitting a curve to the micro-papilla feature edge, as depicted with a red dashed line in the SEM image in the left of Figure 4(b), and rotating around the axis. The location of point q, *i.e.*, the height of the liquid-air interface from the base (h_w), is obtained from the confocal images in Figure 2. The position of the liquid-air interface is measured at 20 different locations and the average is found to be $9.0 \pm 1.3 \mu\text{m}$. The roughness r_n of the striae on top of each micro-papilla is obtained from an atomic force microscopy (AFM)^[36] scan. The AFM scan is taken over a $3 \mu\text{m} \times 5 \mu\text{m}$ area at three different locations and the average r_n is obtained as 1.7 ± 0.7 . The liquid-air interfacial area A_{LV} is calculated as

$$A_{LV} = A_{ext} + (A_{LV,r}) \times N_r \quad (5)$$

where A_{ext} is the liquid-air interfacial area of the spherical cap droplet outside the droplet footprint given as^[35]

$$A_{ext} = 2\pi R^2(1 - \cos \theta) \quad (6)$$

and $(A_{LV,r}) \times N_r$ is the liquid-air interfacial area of each repeating unit under the droplet as presented in **Figure 5** (a). This area is determined from

$$A_{LV,r} = \left(\frac{\sqrt{3}}{4} p^2 - 0.5 \times \pi R_w^2 \right) \quad (7)$$

where R_w is the radius of each micro-papilla at the location from where the nanoscale roughness features begin, as depicted in Figure 4(b). Substituting equation 2, 3, 4, 5, 6 and 7 into equation 1, we obtain an expression for the free energy in the C-W wetting state as

$$G = 2\pi R^2 \gamma_{LV} (1 - \cos \theta) \left[1 + \frac{(1 + \cos \theta)}{2} \times (K_1 - K_2 \cos \theta_e) \right] \quad (8)$$

where, $K_1 = \frac{4}{\sqrt{3}} p^{-2} \times \left(\frac{\sqrt{3}}{4} p^2 - 0.5 \times \pi R_w^2 \right)$ and $K_2 = \frac{4}{\sqrt{3}} p^{-2} \times 0.5 \times (S_{qf} + r_n \times S_{fg})$.

Minimizing the free energy in equation 8 with a constraint that the droplet volume

$\left(V = \frac{2}{3} \pi R^3 - \pi R^3 \cos \theta + \frac{1}{3} \pi R^3 \cos^3 \theta \right)$ remain constant, we get

$$\cos \theta = -(K_1 - K_2 \cos \theta_e) \quad (9)$$

Following an analogous approach, the relation between θ and θ_e is obtained for the C-CB wetting state. The expression is identical to equation 8, except that K_1 and K_2 for the C-CB wetting state are

$$K_1 = \frac{4}{\sqrt{3}} p^{-2} \times \left[\left\{ \frac{\sqrt{3}}{4} p^2 - 0.5 \times \pi R_w^2 \right\} + \left\{ 0.5 \times S_{fg} \times (1 - f_n) \right\} \right] \text{ and}$$

$$K_2 = \frac{2}{\sqrt{3}} p^{-2} \times [S_{qf} + (r_n - f_n) \times S_{fg}]$$

where the additional term f_n represents the fractional liquid-solid interface area (i.e., area of the liquid in contact with the nanoscale striae features) relative to the total solid footprint area.^[27] This fractional area is estimated to be ~50% from measurement of the features from the top-down SEM image of Figure 1(e) converted to black and white^[37]. The error in the extracted value of f_n is estimated to be on the order of $\pm 10\%$.

The equilibrium contact angle is extracted from confocal scans of the outer edge of the droplet contact area, using the same confocal scanning approach as described in the Experimental Section. The contact angle is measured at different locations along the perimeter of the droplet footprint, yielding an average value $96^\circ \pm 3^\circ$. An example confocal image used in the measurement of the contact angle at one location is presented in **Figure 6**.

The apparent contact angles predicted by the energy minimization model (equation 9) for the two possible wetting states are compared to the experimental values in **Figure 7**. The measured apparent contact angle ($151^\circ \pm 3^\circ$) matches the model prediction for the C-CB wetting state (153°) and differs significantly from the value predicted for the C-W wetting state (127°). Even with the uncertainties included, the theoretical model predictions do not overlap for the two possible wetting states; the C-CB state predictions match the range of experimentally measured values. From the results presented in Figure 7, it is clear that the wetting state on the rose petal is the composite-Cassie-Baxter (C-CB) state, in which the liquid only partially penetrates and wets the gaps between micro-papillae and is suspended atop the nanoscale striae features separated by air gaps.

3. Conclusions

Detailed scanning shows that the rose petal surface geometry has microscale bumps (papillae) with nanoscale wrinkled folds (striae) on top of the center portion of each micro-papilla. A direct characterization of the microscale wetting state of water on the rose petal is performed

using confocal microscopy to simultaneously visualize the surface, water phase, and reflecting interfaces. The water is seen to only partially wet the gaps between micro-papillae in a composite wetting state; it does not fully wet these surface features in contrast to previous postulation in the literature. An energy-minimization-based model is used to estimate the wetting state of water on the nanoscale striae features; based on a comparison of the model predictions against experiments, the water is determined to have a Cassie-Baxter wetting state on these features. The macroscale wetting characteristics of the rose are attributed to a composite-Cassie-Baxter wetting state formed on its multi-scale surface structure.

Experimental Section

Wetting Characterization: A fresh rose petal was rinsed with water and then dried thoroughly with pure nitrogen gas. The petals were removed and affixed flat against a glass slide using double-sided tape. The slide holding the petal was placed on a goniometer (Ramé-hart, 290-F1) stage and a 5 μl water droplet was gently deposited on the petal. The apparent static contact angle was measured at 6 different locations on the petal. The contact angle hysteresis was characterized by measuring the advancing and receding contact angles using a standard sessile drop method: a small volume of water (0.25 μl) was pumped into and then out of a 10 μl sessile drop present on the petal to measure the advancing and receding angles, respectively, at which contact line motion was observed. To characterize the adhesion of water to the petal, larger water droplets of 20 μl to 25 μl were placed on the petal, and the goniometer stage was tilted in 1° increments until the droplet started to slide. The droplet started sliding when the tilt angle was 72° for the 20 μl droplet, 60° for the 22 μl droplet, and 54° for the 25 μl droplet. Based on the gravitational force acting on the droplets parallel to the substrate, the adhesive force per unit droplet footprint area was estimated to be $\sim 31 \pm 1 \mu\text{N}/\text{mm}^2$ (averaged over the 20 μl , 22 μl , and 25 μl droplet volumes).

Scanning Electron Microscopy: A fresh rose petal was fixed in 2% paraformaldehyde and 2% glutaraldehyde in a 0.1 M sodium cacodylate buffer initially. They were then post-fixed in buffered 1% osmium tetroxide, dehydrated in a graded ethanol series, and critical point dried (Tousimis Autosamdri-931). The dried specimens were then sputter-coated with platinum (Cressington 208HR). These pretreatments preserve the surface geometry of the petals, which would otherwise lose their shape if dried out when drawing a high vacuum during the SEM scan (FEI Nova NanoSEM 200).

Confocal Microscopy: A fresh rose petal affixed to a glass slide was placed on the stage of an upright confocal microscope (Zeiss LSM 880). A 40× water dipping objective was used for scanning at x - y resolution of 0.18 μm . A ~ 15 μl droplet of water containing Alexa Fluor 647 dye, was placed gently on top of the rose petal using a micro-pipette. The dye concentration was maintained at 5 μM , low enough to ensure that it would not change the surface tension of water; a direct surface tension measurement using the pendant drop method (Ramé-hart, 290-F1) showed that the dyed water had a surface tension of 71.5 ± 0.3 mN/m at room temperature, relative to a measurement of 72.0 mN/m for pure water. A sequential confocal scan was performed using 3 different laser sources. The rose petal was observed to provide a significant autofluorescence^[31] emission signal when excited with a 561 nm laser; a peak emission was identified at 602 nm by performing a wavelength scan over the entire visible range. A 488 nm laser was then used in a reflection mode to capture the surface-liquid-air interfaces and a 633 nm excitation laser helped visualize the dyed water via its peak emission at 665 nm. To visualize a vertical section of the rose petal, the interfaces, and the dyed water, a z -stack acquisition set at 0.625 μm intervals with total depth of 30 μm was scanned. A video that progresses through each frame of the captured stack is provided in the Supporting Information (Movie S2).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Characterization of rose petal: (a) fresh rose as acquired; (b) side-view goniometer image during static contact angle measurement; and (c) SEM image of the rose petal, with insets showing magnified views of (d) an individual microscale bump (papilla) with (e) nanoscale striae on top.

Figure 2. Composite confocal microscopy image reconstructions showing the interface between water and a rose petal at different cross-sectional views. The image on the left shows a plane section parallel to the rose petal surface that slices through the surface micro-papillae. Orthogonal sections (indicated by xz and yz) provide a side-view of slices through several micro-papillae; a representative sketch of the composite signal for a single micro-papilla is also presented.

Figure 3. Focused ion beam scanning electron microscopic image of the rose petal adaxial epidermis: (a) sample viewed at a tilt angle of 25°; and (b, c) magnified images of individual sectioned bumps viewed at a 53° tilt.

Figure 4. Schematic drawing of the features on the rose petal surface and the interfaces formed with a sessile water droplet on top: (a) top and side views of the features and dimensions obtained from the confocal scans and SEMs; (b) side view of the micro-papilla features (geometric nomenclature indicated) with inset showing two possible wetting states in the nanoscale striae features on top of each microscale papilla. A FIB-SEM image shows zoomed-in view of the top part of a single micro-papilla.

Figure 5. Liquid-air and solid-liquid interface in a single repeating unit. A top-down schematic showing the key dimensions and interface areas of the repeating unit is depicted for (a) the composite-Wenzel (C-W) wetting state, and (b) the composite-Cassie-Baxter (C-CB) wetting state; the insets show representative 3D views of the micro-papilla and liquid geometries.

Figure 6. Measurement of the equilibrium contact angle using confocal microscopy. The representative confocal scanning xz image shows a section view of the outer contact line where the droplet footprint meets the rose surface. The inset above shows an enlarged view of the droplet interface at the contact line and the measured contact angle.

Figure 7. Comparison of the experimentally measured apparent contact angle with the theoretically predictions for the two different wetting states, composite-Wenzel (C-W) and composite-Cassie-Baxter (C-CB). The range of the predicted apparent contact angle represents the estimated uncertainty in the equilibrium CA (θ_e), liquid-air interface position (h_w), nanoscale roughness (r_n), and the fraction of the nanoscale roughness in contact with the liquid (f_n), for both wetting states.

Table of contents entry:

Direct three-dimensional confocal imaging is performed to reveal the wetting state of water on a rose petal. An energy-minimization-based model, in combination with the experimental observations, indicates a unique wetting state with the presence of trapped air beneath the droplet between the micro-papillae.

Keyword: wetting, interfaces, petal effect, parahydrophobic, confocal imaging

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The wetting state of water on a rose petal

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Supporting Information

The wetting state of water on a rose petal

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S1. Total energy of the system

To determine the equilibrium conditions of a drop sitting on a heterogeneous surface, a minimization of the Gibbs energy for the system^[1,2] is performed.

To perform the Gibbs energy minimization, we define the system bounds as the surface area covered by the liquid at the droplet footprint. The effect of gravity is neglected while considering the equilibrium shape of the droplet. The Gibbs energy of the system before placing the droplet (Figure S1 (a)) on the top of the surface is $A_{SV}\gamma_{SV}$, where A_{SV} is the total solid-air area and γ_{SV} the solid-air interfacial tension. In the presence of the droplet, the solid-air area (A_{SV}) will be completely replaced by the liquid (A_{SL}) for the system. The Gibbs energy of the system in Figure S1(b) is therefore

$$\begin{aligned} G &= A_{SL}\gamma_{SL} - A_{SV}\gamma_{SV} + A_{LV}\gamma_{LV} \\ &= A_{SL}(\gamma_{SL} - \gamma_{SV}) + A_{LV}\gamma_{LV} \quad \text{as, } A_{SV} = A_{SL} \end{aligned} \quad (S1)$$

where γ is the interfacial tension, A is the interfacial area, and the subscripts S , L , and V represent the solid, liquid, and air, respectively. Substituting Young's equation^[3] ($\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_e$) into equation S1 yields

$$G = A_{LV}\gamma_{LV} - A_{SL}\gamma_{LV} \cos \theta_e \quad (\text{S2})$$

where, θ_e is the equilibrium contact angle or Young's contact angle.

Figure S1. System configuration (a) before placing the droplet, and (b) in the presence of the droplet.

S2. Movie S2: A movie showing the z-stack acquisition of the composite state of water on a rose petal using confocal microscopy.

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