Restoring Superhydrophobicity of Lotus Leaves with Vibration-Induced Dewetting

Jonathan B. Boreyko and Chuan-Hua Chen*

Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, USA

(Received 3 January 2009; published 21 October 2009)

A lotus leaf retains water repellency after repeated condensation in nature but becomes sticky to water drops after condensation on a fixed cold plate. Our experiments show that mechanical vibration can be used to overcome the energy barrier for transition from the sticky Wenzel state to the nonsticking Cassie state, and the threshold for the dewetting transition follows a scaling law comparing the kinetic energy imparted to the drop with the work of adhesion. The vibration-induced Wenzel to Cassie transition can be used to achieve antidew superhydrophobicity.

DOI: 10.1103/PhysRevLett.103.174502 PACS numbers: 47.55.dr

Antidew superhydrophobicity is a highly desired property for water-repellent materials [1]. When vapor condenses on a roughened surface, the liquid condensate naturally nucleates within the texture [2,3], resulting in the Wenzel state [4] where liquid penetrates into the texture. The Wenzel state is opposite to the Cassie state [5] where liquid suspends on top of the texture, the latter being the desired superhydrophobic state with a higher apparent contact angle and a much smaller contact angle hysteresis [1]. The condensate can also end up in a mixed Wenzel-Cassie state which typically has an undesirably large hysteresis similar to the Wenzel state [6,7]. To achieve antidew superhydrophobicity, a mechanism is required for transition from the Wenzel (or mixed) state to a complete Cassie state [1]. The challenge in achieving a Wenzel to Cassie transition lies in the energy barrier associated with the transition [8,9]. Reports of Wenzel to Cassie transition fall into two categories: coalescence of condensate drops in the process of condensation [7] and vaporization at the liquid-solid interface induced by an intense electric pulse [10]. The transition during condensation results from a small Wenzel drop being absorbed by a larger mixed Wenzel-Cassie drop; however, the merged drop still resides in the mixed state with a large hysteresis [7]. The transition by impulse heating leads to a complete Cassie drop [10]; however, the vaporization method is not suitable for many practical applications such as self-cleaning surfaces [11], antibiofoul materials [12], and dropwise condensers [13].

Water-repellent plants naturally exhibit antidew superhydrophobicity. A lotus leaf is known to be superhydrophobic owing to its two-tier surface roughness with nanoscale hairs on microscale bumps [14], which gives rise to rolling drops in the stable Cassie state. However, while the lotus leaf is superhydrophobic after repeated condensation processes in nature, it becomes sticky to condensate drops after condensation on a fixed cold plate in the laboratory [3]. We hypothesize that lotus leaves use mechanical energy constantly supplied by the natural environment (e.g., wind-induced vibration) to overcome the energy barrier for Wenzel to Cassie transition, a barrier related to the separation of the liquid-solid interface in the Wenzel state into liquid-air and air-solid interfaces in the Cassie state. This hypothesis is supported by the experiments reported here in which a sticky lotus leaf on a fixed cold plate becomes nonsticking on a vibrating plate. Although vibration has been used to overcome the energy barrier associated with contact angle hysteresis [15,16], the energy barrier for Wenzel to Cassie transition is fundamentally different and exists even if there is no contact angle hysteresis [8,9].

The experimental setup is shown in Fig. 1(a). Live lotus leaves, fresh from the stem to within 1 day, were used as the substrate. Egyptian and Chinese lotus leaves were used interchangeably without noticeable differences in the results. When a millimetric water drop was deposited on the lotus leaf, the drop consistently rolled off indicating a stable Cassie state. Two methods detailed below were used to introduce a Wenzel drop: one exploited the differential evaporation rate of ethanol and water, and the other used water condensate directly. No appreciable differences were observed between these methods, although the former offers more precise control of individual drops and the latter better approximates natural condensation processes. The Wenzel drop rested on a lotus leaf, which was fixed to a horizontal flat plate attached to a speaker cone (KLH Audio B-Pro6). The sticky Wenzel state was verified by

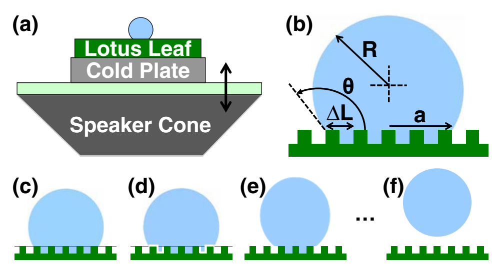

FIG. 1 (color online). (a) Experimental setup where the cold plate was used only for the condensation experiments; (b) parameters of the drop used in the model; (c)–(f) a hypothetical route for the gradual dewetting during a Wenzel to Cassie transition. Once dewetted, the water drop in (f) bounces on the lotus leaf, and lands in the Cassie state when its kinetic energy dissipates. Schematics not to scale.

temporarily tilting the leaf 90°. The speaker was vertically driven by a sinusoidal current, and the displacement was measured by a position sensing detector (Newport OBP-A-4L). The laboratory temperature was 21 °C and the relative humidity 51%, corresponding to a dew point of 10.5 °C. When used for condensation experiments, the cold plate was chilled to 5.0 °C by a circulating cold bath. Video images were captured by a Phantom v7.1 camera attached to an Infinity K2 microscope.

A Wenzel to Cassie transition was captured in Fig. 2(a). A water drop in the Wenzel state was introduced by exploiting the differential evaporation rate of water and ethanol [17]. When a 2.25 μL drop of 2:1 (vol) water:ethanol mixture evaporated on a lotus leaf, the volume shrank to 1.5 μL in 5 min at which point more than 90% of the drop volume was water (see supplemental Sec. S1 in [18]). At the 6th min, the lotus leaf was vibrated by the speaker, and a complete dewetting transition was observed at a frequency of 80 Hz and a peak-to-peak amplitude of 0.6 mm. During the 28 ms period of transition, the contact line gradually withdrew from the surface. Once dewetted, the drop would land in a stable Cassie state with the bouncing and rolling motion characteristic of a superhydrophobic drop. This transition was consistent with the fact that more than 90% of the drop is water at the time of vibration, and the Cassie state is the energetically favorable state for a water drop on the lotus leaf. A control case is shown in Fig. 2(b), where the initial 2.25 μL drop with 67% water was vibrated at 80 Hz and an amplitude up to 1.5 mm, but no transition was observed because the Wenzel state is energetically more favorable at a higher ethanol concentration. Note that if the vibration is too strong, a sticky residue will be left behind, even for pure water, resulting in an incomplete transition as in Fig. 2(c).

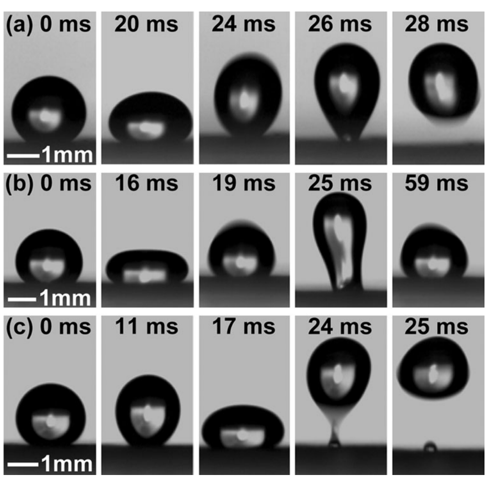

FIG. 2. (a) Vibration-induced Wenzel to Cassie transition of a drop of >90% water at a frequency of 80 Hz and a peak-to-peak amplitude of 0.6 mm; (b) No transition was observed for a drop of 67% water and 33% ethanol at 80 Hz and 1.5 mm. (c) Sticky residue was left behind under the same conditions as (a) except for a higher amplitude of 1.5 mm. Time stamps correspond to the time after initiation of vibration.

The vibration-induced Wenzel to Cassie transition is a plausible mechanism for the lotus leaf's sustained superhydrophobicity after repeated condensations. This hypothesis is supported by the observations in Fig. 3. When the lotus leaf on a horizontal cold plate was cooled below the dew point, water vapor condensed from the ambient air and accumulated on the leaf. In Fig. 3(a), the cold plate was fixed, and water condensate accumulated over the entire leaf. In Fig. 3(b), the cold plate was tilted 90° vertically and returned back to the horizontal position, and some sticky condensate remained on the leaf. In Fig. 3(c), the horizontal lotus leaf was vibrated at 80 Hz and 1 mm peak-to-peak amplitude for 1 s, and all of the condensate was removed except for a few very small drops. The drop removal was accomplished in two stages: vibration triggered Wenzel to Cassie transition of the initially sticky drops, and the mobile Cassie drops subsequently rolled off the leaf. Note that the first stage must precede the second one, as vibration alone is not sufficient to completely remove a Wenzel drop [Figs. 2(b) and 2(c)].

The mechanism for vibration-induced removal of condensate drops is further clarified by video imaging of the Wenzel to Cassie dewetting process shown in Fig. 4 (see also Sec. S2 in [18]). Sticky water condensate on a lotus leaf was obtained in the same manner as in Fig. 3(b). Upon initiation of vibration, the dewetting process started instantaneously for the two large condensate drops initially in the Wenzel state. Between 17 and 17.25 ms, when the leaf started to move downward while the drops were still moving upward by inertia, the complete dewetting of the left drop took place. The dewetting of the right drop occurred in a similar manner at 31.25 ms, which was the last frame before complete dewetting. After dewetting, both drops bounced on the leaf as a typical Cassie drop does [19], and the bouncing dynamics were similar to that of a non-coalescing drop on a liquid surface [20,21]. Note that the dewetting transition only took place for millimetric drops, and smaller condensate drops stayed in the sticky Wenzel state indefinitely unless absorbed by the larger ones.

The critical external forcing required to achieve a Wenzel to Cassie transition exhibits a distinct resonant character as in Fig. 5. At a given frequency, the threshold amplitude of vibration was experimentally identified by gradually increasing the amplitude until the dewetting transition took place. The threshold amplitude was plotted be-

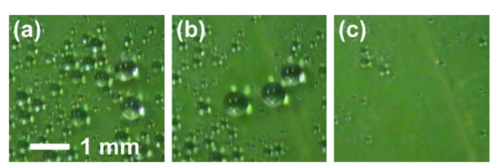

FIG. 3 (color online). (a) Condensate of water vapor on a lotus leaf horizontally attached to a fixed cold plate; (b) remaining sticky condensate after the leaf was vertically tilted and returned to the horizontal position; (c) the same lotus leaf after vibration on a speaker.

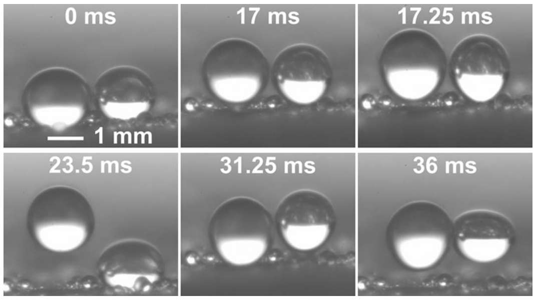

FIG. 4. Water condensate experiencing Wenzel to Cassie transition. Millimetric drops were dewetted, while smaller condensate drops stayed in the Wenzel state during vibration at an amplitude of 1 mm and 80 Hz. See supplemental video S1 in [18].

tween 15 and 150 Hz for a 1.5 μL Wenzel drop introduced in the same manner as Fig. 2(a). Two resonance modes were indicated by the local minima at 30 ± 2.5 Hz and 100 ± 2.5 Hz, respectively. These modes correspond to the first two resonance modes of a drop with a pinned contact line [22], and match the theoretical predictions of the first two resonance frequencies at 32 and 101 Hz (see Sec. S3 in [18] for details). The critical curve in Fig. 5 is qualitatively similar to that for the threshold of the opposite Cassie to Wenzel transition on a surface with microtextures [23].

The threshold condition for Wenzel to Cassie transition can be modeled by comparing the kinetic energy imparted by the vibrating speaker with the surface energy required to dewet the Wenzel drop. At resonance, the drop picks up the kinetic energy at the highest efficiency which is assumed to be approximately constant. The kinetic energy imparted to the drop E_K scales as

$$E_K \propto \tfrac{1}{2}\rho V(2\pi f A)^2, \tag{1}$$

where ρ and V are the density and volume of the drop, f is the external forcing frequency, A is half of the peak-to-peak amplitude of vibration, and $2\pi f A$ is the maximum speed of the speaker.

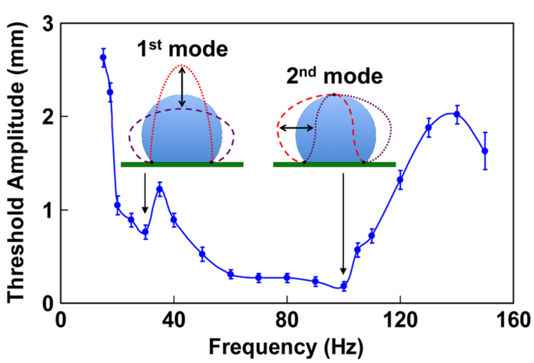

FIG. 5 (color online). Threshold peak-to-peak amplitude required for the dewetting transition of a 1.5 μL Wenzel drop. The local minima at 30 Hz and 100 Hz correspond to the first two resonance modes of the drop. Under vertical external forcing, the 1st and 2nd modes correspond to vertical and horizontal resonant motion of the drop, respectively.

The work required to dewet an impaled drop is given by the incremental work of adhesion. The work of adhesion between the liquid and solid phase, $w_{SL} = \gamma(1 + \cos\theta_Y)$, is the energy required to separate a flat liquid-solid interface into a liquid-vapor and a solid-vapor interface, where γ is the surface tension of the liquid and θ_Y is the Young's contact angle of the flat surface [24]. The incremental work of adhesion is motivated by the gradual receding of the contact line during the threshold dewetting process [schematically shown in Figs. 1(c)–1(f)]. This gradual dewetting process is evident even with the amplitude well above the threshold (e.g., the right drop in Fig. 4).

The modeling of the two-tier roughness is still an open question and we elect to adopt the following approach. The two-tier roughness can be hypothetically formed in two steps: nanoscale roughness is first deposited on a flat surface, and on this nanotexture a water drop would exhibit an apparent contact angle (θ_n); the nanotexture with the equivalent contact angle θ_n is subsequently bent into a surface with microscale roughness [25]. As such, the lotus leaf can be modeled as a surface with only microtexture (as in Fig. 1) as long as θ_n is taken as the local contact angle. Based on this model, the energy required to overcome the work of adhesion from Fig. 1(c) to 1(d) scales as

$$E_S \propto \gamma(1 + \cos\theta_n)(2\pi a \Delta L r_m), \tag{2}$$

where a is the contact radius, ΔL is the distance between two adjacent microscale pillars of the lotus leaf [Fig. 1(b)], and r_m is the roughness ratio [1] associated with the microscale roughness only. For a lotus leaf, $\Delta L \approx 20\ \mu$m and $r_m \approx 2$ based on the micrograph in [14]. Physically, E_S is the work of adhesion associated with the first step of dewetting where the initial contact radius recedes by ΔL, the intermicropillar separation stipulating the minimum shrinkage of contact radius. Because of the gradual dewetting process, the required surface energy E_S scales as a, not a^2. For a Wenzel drop on the lotus leaf, the apparent and equivalent contact angles are related by $\cos\theta = r_m \cos\theta_n$ [4].

Comparing the imparted kinetic energy [Eq. (1)] and the work of adhesion [Eq. (2)],

$$\frac{E_K}{E_S} \propto \frac{\rho\Phi(\theta, r_m)}{\gamma\Delta L} f^2 A^2 R^2, \tag{3}$$

where the nondimensional function Φ is given by

$$\Phi(\theta, r_m) = \frac{\pi^2(1 - \cos\theta)^2(2 + \cos\theta)}{3\sin\theta(r_m + \cos\theta)}. \tag{4}$$

With r_m estimated to be 2 and θ measured as 140° for Wenzel drops reported here, $\Phi = 16$. At threshold for dewetting, $E_K \approx E_S$. According to Eq. (3), for a drop of fixed density and surface tension on an approximately homogeneous lotus leaf (i.e., with uniform r_m and ΔL),

$$f_{res} A_{cr} R \approx \text{const}, \tag{5}$$

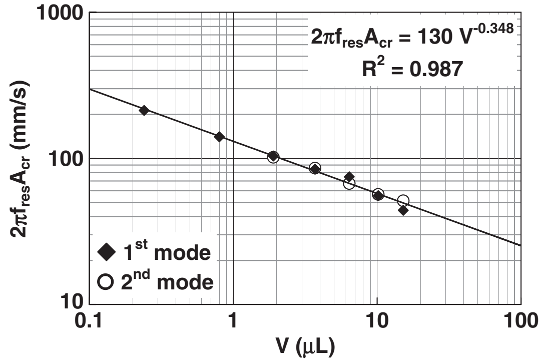

FIG. 6. The threshold velocity of vibration as a function of initial drop volume. Each data point was recorded when a marginal Wenzel to Cassie transition was observed while the speaker was driven at the 1st or 2nd resonance frequency. The coefficient of determination (R^2) of the linear fit is 0.987.

where f_{res} is the resonance frequency, A_{cr} is the threshold amplitude, and R is the initial radius of the drop.

The scaling law given by Eq. (5) is supported by the experimental data in Fig. 6. On a horizontal lotus leaf after condensation and tilting [as in Fig. 3(b)], water drops between 0.24 and 15.2 μL were deposited onto the sticky condensate remaining on the leaf, and vibration was used to induce marginal transition from the sticky Wenzel state to the rolling Cassie state. For a drop of given initial volume, the speaker was driven at the calculated 1st and 2nd resonance frequencies [18], and the threshold amplitude for Wenzel to Cassie transition was measured for each case. At both resonance modes, the maximum speed of the speaker ($2\pi f_{\mathrm{res}} A_{\mathrm{cr}}$) was proportional to $V^{-0.348\pm0.016}$. Since $R \propto V^{1/3}$, Eq. (5) holds within experimental uncertainty. Note that $E_K/E_S \simeq 2$ [Eq. (3)] for all marginal transitions in Fig. 6 and both resonance modes in Fig. 5. This close-to-unity ratio is further evidence that the transition is triggered by the imparted kinetic energy overcoming the incremental work of adhesion.

In conclusion, mechanical vibration was used to induce Wenzel to Cassie transition on lotus leaves. The experimental results and scaling laws show that kinetic energy was converted to surface energy to overcome the work of adhesion of the Wenzel drop. It is plausible that water-repellent leaves constantly exploit vibration to restore superhydrophobicity after natural condensations. Although the vibration of a lotus leaf on a stem is at much lower frequency and higher amplitude compared to that on a speaker, the vibration velocities of both cases are comparable (order of 0.1 m/s). In addition to water-repellant plants, our work is also applicable to engineering systems requiring antidew superhydrophobicity. For instance, vibration can be used to promote rapid removal of condensate trapped in the Wenzel state and enhance the effectiveness of superhydrophobic dropwise condensation (see a proof-of-concept in [13]). Inspired by lotus leaves, naturally existing vibrations can be harvested to achieve sustained antidew superhydrophobicity.

We wish to acknowledge startup funds from the Pratt School of Engineering at Duke University, and discussions with D. Bliss, P. Marszalek, and P. Phelan.

*chuanhua.chen@duke.edu

[1] D. Quere, Annu. Rev. Mater. Res. **38**, 71 (2008).
[2] R. Narhe and D. Beysens, Phys. Rev. Lett. **93**, 076103 (2004).
[3] Y. Cheng and D. Rodak, Appl. Phys. Lett. **86**, 144101 (2005).
[4] R. Wenzel, Ind. Eng. Chem. **28**, 988 (1936).
[5] A. Cassie and S. Baxter, Trans. Faraday Soc. **40**, 546 (1944).
[6] K. Wier and T. McCarthy, Langmuir **22**, 2433 (2006).
[7] C. Dorrer and J. Ruhe, Langmuir **23**, 3820 (2007).
[8] C. Ishino, K. Okumura, and D. Quere, Europhys. Lett. **68**, 419 (2004).
[9] N. Patankar, Langmuir **20**, 7097 (2004).
[10] T. Krupenkin *et al.*, Langmuir **23**, 9128 (2007).
[11] R. Blossey, Nature Mater. **2**, 301 (2003).
[12] Y. Koc *et al.*, Lab Chip **8**, 582 (2008).
[13] C. Chen *et al.*, Appl. Phys. Lett. **90**, 173108 (2007).
[14] C. Neinhuis and W. Barthlott, Ann. Bot. **79**, 667 (1997).
[15] C. Andrieu, C. Sykes, and F. Brochard, Langmuir **10**, 2077 (1994).
[16] E. Decker and S. Garoff, Langmuir **12**, 2100 (1996).
[17] Although the wax coating on lotus leaves slowly dissolves in pure ethanol, a millimetric drop of 2:1 ethanol:water mixture has negligible effects on the lotus leaf if the majority of the ethanol evaporates in a few minutes. The apparent contact angle of a pure water drop on a lotus leaf does not change appreciably after exposure to such drops.
[18] See EPAPS Document No. E-PRLTAO-103-045945 for supplemental information: Sec. S1. Evaporation of water/ethanol mixture; Sec. S2. Dewetting transition of water condensate; and Sec. S3. Resonance frequencies of a pinned drop. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[19] D. Quere, Rep. Prog. Phys. **68**, 2495 (2005).
[20] Y. Couder *et al.*, Phys. Rev. Lett. **94**, 177801 (2005).
[21] T. Gilet and J. Bush, Phys. Rev. Lett. **102**, 014501 (2009).
[22] X. Noblin, A. Buguin, and F. Brochard-Wyart, Eur. Phys. J. E **14**, 395 (2004).
[23] E. Bormashenko *et al.*, Langmuir **23**, 12217 (2007).
[24] A. Adamson and A. Gast, *Physical Chemistry of Surfaces* (Wiley, New York, 1997), 6th ed.
[25] This modeling approach is also motivated by our preliminary observation that it is possible to wet the microscale roughness without wetting the nanoscale roughness (to be discussed elsewhere). In addition, microscopic imaging indicated that the microscale roughness is uniformly wetted (i.e., no mixed Wenzel-Cassie state as far as the microscale roughness is concerned).