Multiple Wetting–Dewetting States of a Water Droplet on Dual-Scale Hierarchical Structured Surfaces

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ABSTRACT: Surfaces with microscale roughness can entail dual-scale hierarchical structures such as the recently reported nano/microstructured surfaces produced in the laboratory (Wang et al. Nature 2020, 582, 55−57). However, how the dual-scale hierarchical structured surface affects the apparent wetting/dewetting states of a water droplet, and the transitions between the states are still largely unexplored. Here, we report a systematic large-scale molecular dynamics (MD) simulation study on the wetting/dewetting states of water droplets on various dual-scale nano/near-submicrometer structured surfaces. To this end, we devise slab-water/slab-substrate model systems with a variety of dual-scale surface structures and with different degrees of intrinsic wettability (as measured based on the counterpart smooth surface). The dual-scale hierarchical structure can be described as “nanotexture-on-near-submicrometer-hill”. Depending on three prototypical nanotextures, our MD simulations reveal five possible wetting/dewetting states for a water droplet: (i) Cassie state; (ii) infiltrated upper-valley state; (iii) immersed nanotexture-on-hill state; (iv) infiltrated valley state; and (v) Wenzel state. The transitions between these wetting/dewetting states are strongly dependent on the intrinsic wettability ($E_n$), the initial location of the water droplet, the height of the nanotextures ($H_t$), and the spacing between nanotextures ($W_{n}$). Notably, $E_{in}=H_{t}$ and $E_{in}-W_{n}$ diagrams show that regions of rich wetting/dewetting states can be identified, including regions where between one to five states can coexist.

KEYWORDS: microscale roughness, dual-scale hierarchical structure, nano/near-microstructured surface, MD simulation, wetting state

INTRODUCTION

Knowledge of the wettability of surfaces has important implications in a wide range of scientific and technological fields, such as microfluidics, heat transfer, surface self-cleaning, surface coating, inkjet printing, drag reduction, and biomimetics. In addition to the dependence of chemical composition, the wettability of a surface is also dependent on the physical topography of the surface. For instance, very recently, we reported that the closed-loop topology of the nanowalls/nanochannels can result in unusual wetting behavior, i.e., multiple Wenzel states with apparent contact angles $>90^\circ$ on an orderly structured solid surface whose flat counterpart is superhydrophobic with a contact angle of $90^\circ$. Examples of dual- or multiscale hierarchical surface structures that have a significant effect on surface wettability are prevalent in nature, including lotus leaves, Viola tricolor, water strider legs, fishing spider Dolomedes triton, and shark skin. Previous experimental studies have shown that these natural surfaces exhibit superhydrophobic (or superoleophobic) properties, owing to the synergetic effects of the dual or multiscale hierarchical structures. Jiang and co-workers revealed a novel nanoscale structure on micrometer-scale papillae for the lotus surface. Branchlike nanostructures with a diameter of $\sim$120 nm were found on randomly distributed papillae with diameters ranging from 5 to 9 $\mu$m. Additionally, hierarchical structured surfaces are also commonly present in many biomimetic products and other artificial materials obtained via chemical or physical methods such as chemical vapor deposition (CVD), nano-self-masking fabrication, femtosecond laser surface processing (FLSP), and biotemplating nanofabrication. Notably, hybrid nanostructured/microstructured layers can be produced on the surfaces of metals, semiconductors, polymers, and glasses. Some of these specially made surfaces enable self-cleaning of dust contaminants.

Understanding the physics of wetting phenomena associated with water droplets is of fundamental importance in the design...
of nonsmooth surfaces with a desired wettability. Intense experimental effort has been devoted to studying the wetting process and the role of the hierarchical geometry. Chen et al. categorized droplet impingement on biomimetic lotus-like hierarchical superhydrophobic surfaces into three states, dewetting, microwetting, and nanowetting states, based on measuring contact-angles using high speed photography. McCarthy et al. pointed out that the microscale and nanoscale components of the lotus-like hierarchical superhydrophobic surfaces play distinct, but complementary, roles in repelling wetting from droplet impact. The nanoscale component provides a high antiwetting capillary pressure, while the microscale component impedes the development and propagation of pressures associated with liquid compression. However, to date, no direct experimental observation of wetting states on the dual-scale hierarchical surfaces at nanometer/submicrometer scales have been reported.

Few computer simulations of wetting states on a dual nano/microscale hierarchical surface have been reported, due to the very high computing cost required to model large-scale systems with billions of atoms and molecules. To reduce the system size, previous molecular dynamics (MD) simulations typically involved dual subnano/nanoscale hierarchical surfaces. Because the two length scales are relatively close, the wetting behaviors on the subnano/nano two parts can interfere with one another and thus it can be harder to identify distinct wetting states on the dual-scale structured surface. Additionally, most previous MD simulations adopted a single-scale structured surface, e.g., a rough surface with a single length scale of nanopillared or nanotrapezoidal textures. These studies observed only two common wetting/dewetting states: the Wenzel state (in which water droplets are in full contact with the rough surface) and the Cassie-Baxter (or Cassie) state (in which water droplets are in contact only with the tops of the structured surface). For more realistic and common dual-scale (or multiscale) hierarchical surfaces, the presence of at least of two length scales (nano, micro, and larger etc.) renders the wetting/dewetting states of water droplet much more complex. Moreover, it is not fully understood how the dual-scale hierarchical surface interplays with the intrinsic
wettability, and the associated physical mechanics underlying the transition between wetting/dewetting states remains to be explored.

Here, we report a comprehensive large-scale MD simulation study of the wetting/dewetting behavior of a water droplet on a dual nano/near-submicrometer scale hierarchical structured surface. To accommodate these much finer length scales compared to previous MD simulations, a slab droplet/substrate system was devised and used. Five physical parameters associated with the slab droplet/substrate system were found to strongly affect the transition between various wetting states: (i) the topology of the nanotexture; (ii) the intrinsic adsorption energy \( E_{\text{in}} \) of a water molecule on the corresponding smooth surface, which is used to characterize the water–smooth surface interaction; (iii) the initial location of the droplet; (iv) the height of nanotextures \( H_1 \); and (v) the spacing between each unit of nanotextures \( W_1 \). From our MD simulations, we identified five distinct wetting states for a water droplet. One state occurred uniquely when the initial state was Cassie, and another occurred uniquely when the initial state was Wenzel. The dependence of the critical intrinsic adsorption energies on \( H_1 \) and \( W_1 \) was quantitatively analyzed. Importantly, the wetting diagrams plotted on the \( E_{\text{in}}-H_1 \) and \( E_{\text{in}}-W_1 \) planes were obtained, where between one to five states were found to coexist. Lastly, we discuss the implication of the obtained results to the wetting behavior on larger dual-scale structured surfaces. In view of the wide presence of rough surfaces with dual-scale or multiscale hierarchical structures in nature and industrial productions, it is of both fundamental and practical importance to explore the new wetting/dewetting states of a water droplet on a dual-scale hierarchical surface.

**METHODS**

All simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software. Due to the large size of the system, we chose the coarse-grained mW water model, which can correctly describe the thermodynamic properties and phase behavior of water both in bulk and in confinement. The surface atoms interacted with each water molecule via the 12-6 Lennard–Jones (12) potential with the size parameter \( \sigma_{\text{SW}} = 3.2 \) Å, and the energy parameter \( \epsilon_{\text{SW}} \) was varied in order to model surfaces from hydrophobic to hydrophilic. The cutoff distance for particle–particle interaction was 10 Å. The substrate surfaces considered were composed of atoms arranged in a cubic lattice with a lattice spacing of 4 Å. For simplicity, all the atoms of the substrate surfaces remained fixed throughout the MD simulations. The intrinsic contact angle (\( \theta_{\text{in}} \)) and intrinsic adsorption energy \( E_{\text{in}} \), whose definitions are given in the Supporting Information, were adopted to characterize the intrinsic wettability of the structured surfaces. Here, \( E_{\text{in}} = 4.748 \epsilon_{\text{SW}} \). Newton’s equations of motion were integrated by using the velocity Verlet algorithm with a time step of 5 fs. MD simulations are performed in the NVT ensemble with the temperature being controlled at 300 K using the Nose–Hoover thermostat. All MD simulations were undertaken for a time long enough \(( \geq 6.5 \) ns) for the water droplet to be fully relaxed.

As mentioned above, the fully atomistic MD simulation on a substrate with a dual nano/submicrometer scale structure would be extremely time-consuming. The large number of molecules needed to describe the wetting/dewetting behavior of a water droplet on such a surface would require significant computational power. To reduce the computational cost, we utilized a simplified slab water droplet/substrate system. A similar slab system with a flat surface, which was proven to be free of the system size effects on computing the contact angle, was used to compute the intrinsic contact angle of a water droplet. Specifically, Figure 1A and B shows the simplified smooth and hierarchical model systems, respectively, which consist of a thin slab of water, 20 Å wide \(( z \) and with a longer length \(( x \) and height \(( y \) as shown in Figure 1A, the contact angle was computed directly through fitting the \( x-y \) projection of the thin water slab droplet \(( 7200 \) water molecules). Typically, Figure 1B shows the water slab cuboid \(( 47 \) 616 water molecules) on a dual nano/near-submicrometer scale hierarchical structured model surface which exhibits nanotextures on near-submicrometer rectangle hills. Because the two length scales are not so close, it is expected that the interference between the wetting behaviors on the major (hill) and minor (nanotexture) structures can be avoided. Each unit of the nanotextures had a constant width of 12 Å, and these units were separated by a distance \(( W_1 \) of 20 Å on each near-submicrometer hills. So the width of the rectangle nanocavity is 8 Å. The height of nanotextures \(( H_1 \) was set to 16 Å, while the height

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**Figure 2.** Snapshots of the equilibrated water droplet on the model surface with parallel nanowalls, after MD time \( \geq 6.5 \) ns. (A–D) Starting from the initial configuration shown in Figure 1B with the water slab (red cuboid) in the Cassie state; (E–H) starting from the initial configuration shown in panel (D) with the water slab in the Wenzel state. The intrinsic adsorption energy \( E_{\text{in}} \) and the intrinsic contact angle \( \theta_{\text{in}} \) for the smooth surface are shown beneath each snapshot. The final equilibrium state of the water droplet is described in the bottom of each panel.
(H₂) and the width (W₂) of the near-submicrometer hills were 64 and 116 Å, respectively. The gap distance between adjacent near-submicrometer hills, i.e., the width (W₃) of the rectangle-like valley, was 60 Å. The thickness of the slab and the length of the whole model system were 20 and 528 Å, respectively. Periodic boundary conditions were applied such that the water slab was repeated to infinity in the z-direction. These structural parameters were used for all simulations unless otherwise mentioned.

Three representative topographies of the nanotexture patterns were considered, mimicking different dual hierarchical structures in the real world. The first nanotexture pattern (Figure 1C) had what can be described as parallel nanowalls along the z-direction as seen in some structured surfaces in the laboratory or on surfaces of living species such as shark skin, butterfly wings, and cactus. The second pattern (Figure 1D) was dispersed nanopillars, separated by a constant distance (20 Å) from each other. This topography exhibits fully connected and percolating nanochannels, as seen on many artificially fabricated surfaces and on the surface of living species such as lotus leaves. The third pattern (Figure 1E) was a network of nanopillars like a checkerboard with disconnected nanocavities, as seen on surfaces with nanopores or tightly fabricated nanostructures.

## RESULTS AND DISCUSSION

In the MD simulations with the mW water model, initially, a water cuboid consisting of 47 616 water molecules was placed on the top of the nanotextures, i.e., the water droplet was initially in the Cassie state. Then the system was relaxed for a simulation time of 6.5–30 ns until the wetting state of the water droplet reached equilibrium. This series of MD simulations showed that the final state of the water droplet was dependent on the intrinsic water-surface interaction

$$E_{\text{in}} = 4.748 \varepsilon_{SW},$$

where the strength of the LJ interaction parameter εₜₜ varied from 0.19 to 4.82 kJ/mol. Note again that here intrinsic adsorption energy $$E_{\text{in}}$$ was used to characterize the water–smooth surface interaction.

**Parallel Nanowalls**

For the water droplet on the surface with parallel nanowalls, snapshots of the equilibrated water droplets on surfaces with different $$E_{\text{in}}$$ are shown in Figure 2. Four different partial wetting/dewetting states were observed as $$E_{\text{in}}$$ increased from 0.92 to 22.91 kJ mol⁻¹: Cassie state (Figure 2A), where the water droplet stays on the top of the nanotextures; infiltrated upper-valley (IFUV) state (Figure 2B), where only the upper section of the valley between the near-submicrometer hills is infiltrated with water; immersed nanotexture-on-hill (IMNTH) state (Figure 2C), where nanotextures on the near-submicrometer hills are fully immersed in the water droplet but the nanotextures in the valley are not; and Wenzel states (Figure 2D), where all the nanotextures and valleys are completely immersed in the water droplet. The transition from one state to another, among the four partial dewetting/wetting states, could be controlled by changing the parameter $$E_{\text{in}}$$.

Accordingly, three critical intrinsic adsorption energies ($$E_{\text{in}}^{\text{CW}}$$) for the state-to-state transition were estimated: (1) below $$E_{\text{in}}^{\text{CW1}} = 9.16 \pm 0.46 \text{ kJ mol}^{-1},$$ the water droplet adopted the Cassie state; (2) above this up to $$E_{\text{in}}^{\text{CW2}} = 10.08 \pm 0.46 \text{ kJ mol}^{-1},$$ the water droplet adopted the IFUV state; (3) above this up to...
$E_{\text{in}}^{\text{CW3}} = 20.16 \pm 0.46 \text{ kJ mol}^{-1}$, the water droplet adopted the IMNTH state; and (4) above $E_{\text{in}}^{\text{CW3}}$ the water droplet adopted the Wenzel state.

In addition, another initial configuration for the water droplet being in the Wenzel state was also considered, as shown in Figure 2D. In this series of MD simulations, four wetting/dewetting states were recognized as $E_{\text{in}}$ reduced from 22.91 to 0.92 kJ mol$^{-1}$: the Wenzel state (Figure 2E); the infiltrated valley (IFV) state (Figure 2F), where only the valley between the near-submicrometer hills was infiltrated by water and no nanotextures were filled by water; the IFUV state (Figure 2G); and the Cassie state (Figure 2H). This new sequence of wetting states is almost like a backward sequence of the previous one, in which the gradual decrease of $E_{\text{in}}$ resulted in sequential transition from the Wenzel to the Cassie state. For these state transitions, the corresponding three critical intrinsic adsorption energies ($E_{\text{in}}^{\text{WC}}$) were as follows: (1) above $E_{\text{in}}^{\text{WC1}} = 8.25 \pm 0.92 \text{ kJ mol}^{-1}$, the water droplet adopted the Wenzel state; (2) below this down to $E_{\text{in}}^{\text{WC2}} = 5.96 \pm 0.46 \text{ kJ mol}^{-1}$, the water droplet adopted the IFV state; (3) below this down to $E_{\text{in}}^{\text{WC3}} = 3.67 \pm 0.46 \text{ kJ mol}^{-1}$, the water droplet adopted the IFUV state; and (4) below $E_{\text{in}}^{\text{WC3}}$ the water droplet adopted the Cassie state. Here, the IFV state was a new wetting state not seen in the sequence where the Cassie state was the initial configuration and with decreasing surface water interaction.

Contrary to the Figure 4. Simulations of a water droplet on the model surface with checkerboard-like nanopillars, (A, B) with $H_1 = 16 \text{ Å}$ and (C, D) with $H_1 = 12 \text{ Å}$. (Ai–Di) Initial configuration of the water droplet and (ii–v of A–D) remaining snapshots of the corresponding equilibrium wetting/dewetting states at different values of $E_{\text{in}}$. In panels (A) and (C), the Cassie state was the initial configuration; in panels (B) and (D), the Wenzel state was the initial configuration. The intrinsic adsorption energy $E_{\text{in}}$, intrinsic contact angle $\theta_{\text{in}}$, and name of the final equilibrium wetting/dewetting state are shown beneath each snapshot.

For the water droplet on the surface with dispersed nanopillars, snapshots of the equilibrated water droplets on surfaces with different $E_{\text{in}}$ are shown in Figure 3. The initial configuration for the water cuboid was on the nanopillars (Figure 3A). Once the water droplet reached equilibrium, three distinct wetting/dewetting states were observed in a forward sequence: Cassie (Figure 3Aii), IMNTH (Figure 3Aiii), and Wenzel (Figure 3Av) states. On the other hand, if the initial configuration for the water droplet was a Wenzel state (Figure 3Bi), after equilibration, three distinct wetting/dewetting states were observed in a backward sequence: Wenzel (Figure 3Bii), IFUV (Figure 3Biii), and Cassie (Figure 3Biv) states. Contrary to the
The critical intrinsic adsorption energies for the three topographies. Black open, red solid, and violet open symbols (circles, parallel nanowalls; stars, dispersed nanopillars; squares, checkerboard-like nanopillars) represent the critical adsorption energies of the first, second, and third transitions, respectively. (A, C) from the Cassie to Wenzel state, \( E_{\text{in}}^{\text{CW1}} \); (B, D) from the Wenzel to Cassie state, \( E_{\text{in}}^{\text{WC1}} \); vs either \( H_1 \) at fixed \( W_1 = 20 \) Å or \( W_1 \) at fixed \( H_1 = 12 \) Å. The solid curves represent exponential-function fittings to the critical intrinsic adsorption energy vs the height of the nanotextures \( H_1 \) (A, B) or vs the intrananotexture distance \( W_1 \) (C, D). Black line, \( E_{\text{in}}^{\text{CW1}} \) or \( E_{\text{in}}^{\text{WC1}} \); red line, \( E_{\text{in}}^{\text{CW2}} \) or \( E_{\text{in}}^{\text{WC2}} \); violet line, \( E_{\text{in}}^{\text{CW3}} \) or \( E_{\text{in}}^{\text{WC3}} \). Left panel pictures display the zoom-in views of the selected areas marked by the green dashed rectangles.

Comparison of the Effects of the Three Topographies

The critical intrinsic adsorption energies obtained for the three prototype surface topographies are compared in Figure 5A and B. The results demonstrate that the critical intrinsic adsorption energy \( E_{\text{in}}^{\text{CW1}} \) shows little dependence on the topology of the nanotexture. \( E_{\text{in}}^{\text{CW2}} \) for the parallel nanowalls nanotexture is almost the same as that for the checkerboard-like nanotexture but is slightly larger (\( \sim 1.97 \) kJ mol\(^{-1}\)) than that for the dispersed nanopillars nanotexture (Figure 5A). \( E_{\text{in}}^{\text{CW3}} \) is 5.27 and 7.78–7.92 kJ mol\(^{-1}\) smaller for the dispersed nanopillars and checkerboard-like at \( H_1 = 12–16 \) Å, respectively, indicating that the parallel nanopillars can prevent the infiltration of the water droplet into the valley.

On the other hand, \( E_{\text{in}}^{\text{CW1}} \) for the nanotexture of parallel nanopillars was about 0.69 (0.46) kJ mol\(^{-1}\) larger than that for the dispersed nanopillars nanotexture and 2.06 (2.06) kJ mol\(^{-1}\) smaller than that for the checkerboard-like nanotexture at \( H_1 = 12–16 \) Å.
12 (16) Å (Figure 5B). \( E_{W1}^{WC2} \) for the parallel nanowalls nanotexture was nearly the same as that for the checkerboard-like nanotexture at both \( H_1 = 12 \) and 16 Å, which was 0.80 (1.37) kJ mol\(^{-1}\) smaller than that for the dispersed nanopillars at \( H_1 = 12 \) (16) Å. The difference in \( E_{W1}^{WC3} \) for the three topographies varied within 1.37 kJ mol\(^{-1}\), in the order of parallel nanowalls < checkerboard-like nanopillars < dispersed nanopillars. However, each of the six intrinsic adsorption energies obtained from the three types of topographies exhibited a similar trend as the height of nanotextures varied.

In view of the similar trend and generally small differences (except for \( E_{W1}^{CW3} \)) among the intrinsic adsorption energies from the three topographies, as well as the same five wetting/dewetting states, the next section focuses on the parallel nanowalls nanotexture as the representative model to further illustrate the effects of structural parameters, \( H_1, W_1, W_2, \) and \( W_y \) on the wetting/dewetting transition.

**Critical Intrinsic Adsorption Energies and Diagrams of Wetting States**

For \( H_1 \) changing from 4 to 20 Å at fixed \( W_1 = 20 \) Å, Figure 5(A) shows the corresponding critical adsorption energies \( (E_{W1}^{CW1}, E_{W1}^{CW2}, \) and \( E_{W1}^{CW3} \)) for the sequential transitions from the Cassie to the Wenzel states. Interestingly, all the three critical adsorption energies increase as \( H_1 \) increases.

By fitting exponential-function curves to the critical adsorption energies vs \( H_1 \) (see solid line in Figure 5A), the following relations are obtained:

\[
E_{W1}^{CW1} = 13.91 - 14.95\exp(-0.07H_1) \\
E_{W1}^{CW2} = 10.87 - 9.47\exp(-0.16H_1) \\
E_{W1}^{CW3} = 20.83 - 8.45\exp(-0.17H_1)
\]

Here, the units for all the critical adsorption energies \( E_{W1}^{CW} \) (or \( E_{W1}^{CW} \)) are kJ mol\(^{-1}\) and for \( H_1 \) are Å.

The relations (Figure 5B) between the critical adsorption energies and \( H_1 \) for the reverse sequence of transitions from the Wenzel to the Cassie states \( (E_{W1}^{CW1}, E_{W1}^{CW2}, \) and \( E_{W1}^{CW3} \)) are as follows:

\[
E_{W1}^{WC1} = 8.28 - 11.13\exp(-0.39H_1) \\
E_{W1}^{WC2} = 4.27 + 0.14\exp(0.16H_1) \\
E_{W1}^{WC3} = 3.72 - 4.47\exp(-0.28H_1)
\]

Note that \( E_{W1}^{WC1}, E_{W1}^{WC2}, \) and \( E_{W1}^{WC3} \) generally increase as \( H_1 \) increases, and these trends are the same as those for \( E_{W1}^{CW1}, E_{W1}^{CW2}, \) and \( E_{W1}^{CW3} \).

The dependence of the critical adsorption energy on the intranotexture distance \( W_1 \) was also investigated at fixed \( H_1 = 12 \) Å. Figure 5C shows the exponential-function fitting to the critical adsorption energies \( (E_{W1}^{CW1}, E_{W1}^{CW2}, \) and \( E_{W1}^{CW3} \)) vs \( W_1 \) for the sequence of transitions from the Cassie to the Wenzel state. Clearly, \( E_{W1}^{CW2} \) (above which the water droplet prefers the IMNTH states) decreased as \( W_1 \) increased. This indicates that increasing \( W_1 \) leads to a lower critical intrinsic adsorption energy for transitions from IFUV to IMNTH states. Similarly, \( E_{W1}^{CW1} \) (above which the water slab prefers the IFUV state) exhibited a decreasing trend as \( W_1 \) increased, since the width of the upper region of the valley, determined by the distance between the two nanowalls adjacent to the valley and on the near-submicrometer hills, generally increased as \( W_1 \) increased.

In contrast, \( E_{W1}^{CW3} \) exhibited little dependence on \( W_1 \) and the width of the upper region of the valley between near-submicrometer hills. The obtained relations are given as follows:

\[
E_{W1}^{CW1} = 2.16 + 21.59\exp(-0.07W_1) \\
E_{W1}^{CW2} = 4.87 + 10.62\exp(-0.04W_1) \\
E_{W1}^{CW3} = 19.71 + 0.001\exp(-0.05W_1)
\]

The coefficients of the exponential term in eqs 7 and 8 are 21.59 and 10.62, respectively, reflecting the dependence of \( E_{W1}^{CW1} \) and \( E_{W1}^{CW2} \) on \( W_1 \). In contrast, the much smaller coefficient of 0.001 in eq 9 reflects the near-independence of \( E_{W1}^{CW3} \) on \( W_1 \).

As a comparison, Figure 5D shows the exponential-function fitting to the critical adsorption energies \( (E_{W1}^{CW1}, E_{W1}^{CW2}, \) and \( E_{W1}^{CW3} \)) vs \( W_y \) for the sequence of transitions from the Wenzel to the Cassie state. \( E_{W1}^{CW1} \) and \( E_{W1}^{CW2} \) decreased with the increase of \( W_y \) while \( E_{W1}^{CW3} \) also exhibited little dependence on \( W_y \). The obtained relations are given below:

\[
E_{W1}^{CW1} = 1.46 + 15.14\exp(-0.04W_y) \\
E_{W1}^{CW2} = 4.54 + 25.26\exp(-0.16W_y) \\
E_{W1}^{CW3} = 2.57 + 2.21\exp(-0.03W_y)
\]

Note that \( E_{W1}^{CW1} \) and \( E_{W1}^{CW3} \) correspond to two reverse sequences of transitions (transition from the Cassie to the IFUV state vs transition from the IFUV to the Cassie state). The curve of \( E_{W1}^{CW3} \) shows clear hysteresis compared with that of \( E_{W1}^{CW1} \) (Figure 5A vs B, C vs D), similar to the transition between two common wetting/dewetting states, the Wenzel and Cassie states, on single-scale structured surfaces.

The simulation results demonstrate that all the critical adsorption energies for both the sequential transition from the Cassie state to the Wenzel state and the sequential transition from the Wenzel state to Cassie state increase as \( H_1 \) increases while they decrease as \( W_1 \) increases. This is because the critical adsorption energy reflects or is related to the free energy barrier from one wetting state to another and the energy barrier is mainly contributed by the change of the surface tension energy of the droplet which increases with increasing \( H_1 \) while it decreases with increasing \( W_1 \). Additionally, it is worth noting that the water droplet can stay in a non-Wenzel wetting state, e.g., the IMNTH state, even when the intrinsic contact angle is 0° (at \( E_{min} = 18.67 \) kJ mol\(^{-1}\); see Figure 5A and 5C). This phenomenon can be attributed to the topography of the parallel nanowalls nanotexture which has the same effect in the direction normal to the nanowalls as the closed-loop nanowalls. As reported previously by us, the topology of closed-loop nanowalls/nanochannels on a surface can introduce an unbalanced force applied to all water molecules along the triple-phase contact line (TCL) which hinders the outward diffusion of the TCL, thereby leading to the phenomenon of the topological wetting state (i.e., the water droplet is in a Wenzel state with a contact angle > 0° even when the intrinsic contact angle of the water droplet is 0°). Likewise, the parallel nanowalls here also introduce an unbalanced force on all water molecules along the TCL in parallel to the nanowalls, thereby blocking the outward diffusion and infiltration of water into the deeper valley and resulting in the IMNTH state with a nonzero contact angle (rather than the Wenzel state) even when \( \theta_{min} = 0° \).
interesting wetting behavior indicates that the parallel nanowalls topography can lead to apparently higher hydrophobicity for rough surfaces.

Overall, the wetting of a water droplet on the dual nano/near-submicrometer scale hierarchical surface can be classified into multiple states, depending on how the water droplet infiltrates into the cavities between the nanotextures and the valley between the near-submicrometer hills. Starting from the Cassie state, the top of the nanotextures and the near-top section of the valley are in direct contact with the water droplet. With gradually increasing $E_{in}$, the next rising state is the IFUV state due to the wider distance between the hills (e.g., Figure 2B), followed by the IMNTH state (e.g., Figure 2C). The nanotextures within the valley can be immersed in water once contacted with the water droplet. With gradually increasing $E_{in}$, the next rising state is the IFV state (e.g., Figure 2F) which renders the dewetting capillary pressure sufficiently lower, leading to the IFV state (Figure S1), consistent with previous experimental deduction.22 Note that the valley appears to result in an extra dewetting capillary pressure to reduce the tendency of wetting the nanotextures within the valley. Meanwhile, the smaller nanotexture enables less contact if the water droplet is in the IFV state or the IFUV state, leading to a much smaller interaction between the water droplet and the dual-scale structured rough surface compared to that between the water droplet and the corresponding flat surface. The two factors together cause the dual nano/near-submicrometer scale hierarchical surface to favor a higher dewetting tendency.

Conversely, starting with the Wenzel state, as $E_{in}$ is gradually reduced, the water droplet is withdrawn first from the smaller scale nanotexture to reduce the tension while the valley is still filled by water, which is the IFV state (e.g., Figure 2F). IFV seems to be an intermediate state where the water–surface interaction is not strong enough to overcome the dewetting capillary pressure due to the nanocavity within the nanotextures. As $E_{in}$ is further reduced, the water droplet is withdrawn from both the valley and nanotextture cavities (Figure 2G) to reduce tension. The dewetting capillary pressure appears to increase as the height of nanotextures increases but decrease as the intrananotexture distance increases (see CW2 curves in Figure SA and C). Thus, it is expected that, on the dual-scale nano/near-submicrometer surface, if the width of the valley is wide enough to render the dewetting capillary pressure lower than that due to the cavity between nanotextures, the IFV state (Figure 2F) tends to form if the Cassie state is the initial configuration. This deduction is further confirmed by a test simulation with a larger valley width ($W_1 = 204 \text{ Å}$) which renders the dewetting capillary pressure sufficiently lower, leading to the IFV state (Figure S1), consistent with previous experimental deduction.22 Note that the valley appears to result in an extra dewetting capillary pressure to reduce the tendency of wetting the nanotextures within the valley. Meanwhile, the smaller nanotexture enables less contact if the water droplet is in the IFV state or the IFUV state, leading to a much smaller interaction between the water droplet and the dual-scale structured rough surface compared to that between the water droplet and the corresponding flat surface. The two factors together cause the dual nano/near-submicrometer scale hierarchical surface to favor a higher dewetting tendency. Besides the effects of $H_1$ and $W_1$, the
effects of the width of the hill ($W_1$) and the valley ($W_2$) on the critical intrinsic adsorption energies have also been analyzed (see the Supporting Information for details).

To summarize, with the Cassie and the Wenzel states being viewed as the two extreme initial conditions for a water droplet, the final wetting/dewetting states at any $E_{in}$ can exhibit two limiting cases: either a strongly dewetting state or a strongly wetting state. Between these two limiting states, other intermediate states as shown above can be attained. For example, at a certain $E_{in}$ if a Cassie initial configuration results in an IFUV state whereas a Wenzel initial configuration results in a Wenzel state, then IFUV, IMNTH, IFV, and Wenzel states can coexist at this given $E_{in}$ due to different starting locations of the water droplet. On the other hand, if both the Cassie initial configuration and the Wenzel initial configuration can result in an IFUV state, then only the IFUV state would exist, regardless of any starting location of the water droplet. One special case is that if a Cassie initial configuration results in an IFUV state whereas a Wenzel initial configuration results in an IFV state, the IMNTH state would be excluded because the water−surface interaction cannot overcome the dewetting capillary pressure due to the nanotexture. Thus, in this case, only IFUV and IFV states can coexist. From these analyses, the order of wetting strength among the five above-identified wetting states is determined as shown in Figure 6A, according to which intermediate states can be easily obtained after demarcating the two extreme wetting/dewetting conditions. Furthermore, the wetting/dewetting states of the water droplet can be changed by changing the $E_{in}$ and the length of $H_1$ and $W_1$ of the nanotexture. A wetting/dewetting diagram on the $E_{in}$−$H_1$ plane, according to eqs 1−6 for $W_1 = 20$ Å, can be obtained (Figure 6B). For $H_1$ in the range of 4−20 Å, three monostate regions are identified: the Cassie state at low $E_{in}$, the IFUV state in a small region at relatively high $E_{in}$ and the Wenzel state at much higher $E_{in}$, and three bistate-coexistence regions, one tristate coexistence region, one tetrasate coexistence region, and one pentastate coexistence region. Likewise, the wetting/dewetting diagram can be also plotted on the $E_{in}$−$W_1$ plane (Figure 6C) according to eqs 7−12 for $H_1 = 12$ Å. In this diagram, there are three monostate regions, three bistate coexistence regions, one tristate coexistence region, and one tetrasate coexistence region. Within each multistate coexistence region, the final wetting state of the water droplet is dependent on its initial configuration. To verify this conclusion, a new series of MD simulations was performed using the five different prototype wetting states identified in Figure 2 as initial configurations and with the same values of $E_{in}$ and $H_1$ ($E_{in} = 8.70$ kJ mol$^{-1}$ and $H_1 = 20$ Å), which, together, reflect a point (P) in the pentastate coexistence region (II) in Figure 6B. The obtained equilibrium state of the water droplet was identified as one of the five corresponding wetting/dewetting states, and, in all, a total of five proposed states were identified (Movies S9−S13), confirming the above conclusion. Additionally, for a surface with different structural parameters, although the values of the critical adsorption energies and the boundaries of wetting-state regions in the wetting/dewetting diagram could be different, the coexistence of multiple wetting states can still arise.

Finally, we note that although dimensions of the systems used in MD simulation are much smaller than those in realistic applications, many wetting/dewetting phenomena exhibit length-scale independence. For example, the computed contact angle of nanodroplets and measured contact angle of macroscopic droplets are nearly the same on the same type of flat surface, regardless of the huge size difference. Here, our atomic simulation study focuses on the dual-scale nano/near-micrometer roughness. The latter is already notably larger, compared to the dual-scale subnano/nanoscale roughness reported in previous simulation study, where the minor (nanotexture) and major (hill) structures were considered. With the much large model system considered here, we are able to observe the generic behavior of nanodroplets on the dual-scale structured surface (for example, whether water enters the gap between nanopillars) while avoiding the apparent interference between the wetting behaviors on dual-scale surfaces with minor and major structures not largely separated in the length scale. This generic behavior shows little dependence on the actual size of the droplet. Therefore, we expect that the obtained results can mimic those wetting/dewetting behaviors of larger water droplets on the realistic surfaces with dual-scale roughness. Furthermore, to investigate the effect of size on the wetting states on dual-structured surfaces, we built a larger model system with larger structural parameters, which results in consistent conclusions. The system size has a total length of 1056 Å, as shown in Figure S2A. A droplet with 90 954 water molecules is placed on the surface, and the whole system contains 98 424 atoms. When the droplet is initially in the Cassie state, the equilibrium states are Cassie, IFUV, IMNTH, and Wenzel states with increasing intrinsic water−surface interaction (Figure S2Bl−Bv), as characterized by intrinsic adsorption energy $E_{in}$. If the droplet is initially in the Wenzel state, the equilibrium states are Wenzel, IFV, IFUV, and Cassie states with decreasing $E_{in}$ (Figure S2Ci−Cv). These are all consistent with the results obtained from the 528 Å length model used in the simulations illustrated above, although the critical adsorption energy which is determined by the structure dimensions such as $W_1$ and $H_1$ (as shown Figure 5) could be different due to different structural parameters. Moreover, the wetting details do not depend on the whole system size when the scale is larger than a certain scale (∼several nanometers). Therefore, the various wetting/dewetting states observed in our simulations are expected to be also seen in larger-sized realistic systems.

CONCLUSION

A large-scale MD study on the wetting/dewetting behavior of a water droplet on dual nano/near-submicrometer scale hierarchical surfaces is presented. Our model systems are based on a thin slab of nanotexture-on-near-submicrometer-hill with different strengths of surface−water interaction. Three typical topologies of nanotextures are considered. Overall, the final wetting/dewetting state of the water droplet is dependent on the droplet initial location on the surface. If starting with the Cassie state, four wetting/dewetting states are observed in our MD simulations, in the (forward) sequence of the Cassie, the infiltrated upper-valley, the immersed nanotexture-on-hill, and the Wenzel states, as the water−surface interaction increases. On the other hand, if starting with the Wenzel state, the four states in the (backward) sequence of the Wenzel, the infiltrated valley, the infiltrated upper-valley, and the Cassie states are observed as the water−surface interaction decreases. The forward/backward sequences represent sequential transitions from the Cassie to the Wenzel state and vice versa, and are not symmetric. In both sequences, the immersed nanotexture-on-hill state and the infiltrated valley state are unique intermediate states. In both forward/backward
sequential wetting/dewetting transitions, the corresponding three critical intrinsic adsorption energies to characterize transitions are determined. These critical intrinsic adsorption energies appear to be correlated with the height of the nanotextures ($H_1$) and the intrananotexture distance ($W_1$). On the basis of the final wetting/dewetting states originated from the two limiting initial conditions, two wetting/dewetting diagrams are plotted on the $E_w$-$H_1$ plane and on the $E_w$-$W_1$ plane, respectively. These new insights into the multiple wetting/dewetting states on dual-scale hierarchical structured surfaces will not only deepen our understanding of generic wetting/dewetting phenomena on rough surfaces but also have important implications for the fabrication of self-cleaning and anti-icing surfaces with high water/ice repellence and durability, as well as to the manipulation of the wetting properties of rough surfaces through controlling the synergetic interplay of the dual nano- and submicrometer structures by design.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00183.

Behavior of a water nanodroplet starting from the initial configuration in the Wenzel state on a nanotexture-on-near-submicrometer-hill surface at Point P, with the nano-droplet staying in the Wenzel state (MP4)

Behavior of a water nanodroplet starting from the initial configuration in the IMNTH state on a nanotexture-on-near-submicrometer-hill surface at Point P, with the nano-droplet staying in the IMNTH state (MP4)

Behavior of a water nanodroplet starting from the initial configuration in the IFV state on a nanotexture-on-near-submicrometer-hill surface at Point P, with the nano-droplet staying in the IFV state (MP4)

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Notes

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