

# Turning a Superhydrophilic Surface Weakly Hydrophilic: Topological Wetting States

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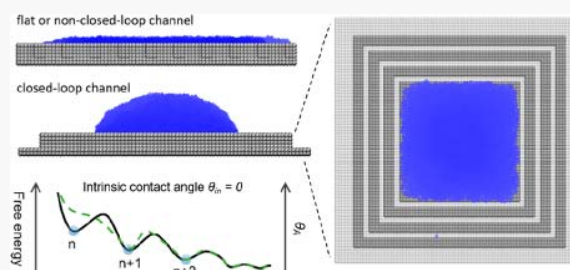
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**ABSTRACT:** For water droplets placed on a rough or structured surface, two distinct wetting states commonly observed are either the Wenzel state (droplets wet the surface without showing air pockets beneath the droplets) or the Cassie state (droplets reside on top of the structure with air pockets trapped beneath the droplets). Herein, we show molecular dynamics (MD) simulation evidence of a previously unreported wetting behavior, i.e., the rise of multiple Wenzel states on the structured surfaces whose flat-surface counterparts are superhydrophilic (i.e., complete wetting surfaces with the hallmark of zero contact angle for water droplets). Specifically, our MD simulations show that on the structured surfaces with topology of closed-loop nanowalls/nanochannels, the water droplet can exhibit multiple Wenzel wetting states with the apparent contact angles  $>0^\circ$ . We name these distinct multiple Wenzel states as “topological wetting states” because their existence can be attributed to the topology of the closed-loop nanowalls/nanochannels. Regardless of the shape of the closed loops, such topological wetting states can always arise due to the topological invariant (i.e., all closed loops entail the same topological genus value). This unusual wetting behavior is contrary to the conventional view (and to the prediction of the Wenzel equation), namely, a rough hydrophilic surface should have stronger hydrophilicity than its flat-surface counterpart.



## INTRODUCTION

A better understanding of the behavior of water droplets on rough or orderly structured surfaces has important implications in diverse fields, such as biological science,<sup>1–6</sup> microfluidics,<sup>7–9</sup> material manufacturing,<sup>10–15</sup> and products for everyday life. Surface structures can play an important part in controlling the wettability of surfaces.<sup>16–23</sup> Despite the considerable effort spent studying the effects of surface structures on surface wettability, exploration of new science regarding wetting/dewetting on rough or structured surfaces remains worthwhile.<sup>24–27</sup> If a water droplet is placed on a rough or orderly structured surface, the droplet commonly exhibits one of two states: the “Wenzel” state, wherein the droplet fully wets the structured surface without showing an air pocket beneath the droplet, or the “Cassie” state, wherein the droplet stays on top of the surface textures with an air pocket trapped by the surface textures beneath the droplet. The Wenzel state and the Cassie state of a water droplet and related intermediate states have been studied extensively.<sup>23,28–31</sup>

The wettability of a flat surface is commonly characterized by the contact angle of a liquid droplet on the surface. On a rough or orderly structured surface, however, the wettability of the surface can be characterized by the apparent contact angle (ACA;  $\theta_A$ ) of the liquid droplet. If a droplet is in the Cassie state, the ACA is usually determined by the Cassie–Baxter

equation,<sup>32</sup>  $\cos \theta_A = f_1 \cos \theta_{in} - f_2$ , where  $f_1$  and  $f_2$  are the area fraction of solid–liquid and solid–air interfaces, respectively, and  $f_1 + f_2 = 1$ .  $\theta_{in}$  is the intrinsic contact angle, defined as the contact angle on the corresponding flat surface. If a droplet is in the Wenzel state,<sup>33</sup> the ACA can be predicted from the Wenzel equation,  $\cos \theta_A = r \cos \theta_{in}$ , where  $r$  is a measure of the surface roughness or surface rugosity, defined as the ratio of the true area of the structured surface to the area of the projected surface.

Despite the success of equations for the Wenzel state and Cassie state for characterizing the wettability of structured surfaces, their universal validity is controversial.<sup>34–37</sup> For example, in 1945, Pease was the first to propose that the ACA is closely related to the line of the three-phase junction.<sup>34</sup> About 60 years later, Gao et al.<sup>35</sup> showed that the ACA can be determined solely by the interaction between the liquid droplet and surface at the three-phase contact line (TCL), and is not relevant to the interfacial area within the contact perimeter.

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This view sparked intense discussions on the validity and applicability of the Wenzel equation and the Cassie–Baxter equation,<sup>36,38–42</sup> and motivated development of newly proposed applicable conditions and compromised correction of those equations. Marmur et al.<sup>41</sup> argued that the Wenzel equation and the Cassie–Baxter equation are adequate if the droplet is sufficiently large compared with the typical length-scale of the surface roughness or chemical heterogeneity. Moreover, they proposed that the Wenzel equation and the Cassie–Baxter equation should be modified to account for local values of the roughness ratio and the area fractions of chemical heterogeneity. McHale<sup>42</sup> attempted to modify the Wenzel equation and the Cassie–Baxter equation by including the local value of roughness and Cassie–Baxter solid-fraction functions near the TCL based on the assumption that the droplet retains an average shape with axial symmetry. As a result, the modified Wenzel equation becomes  $\cos \theta_A(x) = r(x) \cos \theta_{in}$ , where the roughness or rugosity,  $r(x)$ , is the ratio of the true area of the structured surface to the area of its projection to the flat surface for a small representative region near the droplet perimeter at the location  $x$  (i.e.,  $r(x) = \Delta A_{True}(x)/\Delta A(x)$ , evaluated at  $x$ ). If the global roughness or rugosity,  $r$ , or the local roughness or rugosity at the perimeter,  $r(x)$ , is  $\geq 1$  in the original or modified Wenzel equation, then the rough or orderly structured surface (and at the perimeter) is expected to be more hydrophilic than the corresponding flat surface (i.e., the ACA of the rough surface should be less than  $\theta_{in}$ ).

We note that some special wetting states, such as the so-called “sunny-side-up” state, have been reported previously<sup>43–45</sup> for water droplets on pillared hydrophilic surfaces. Apparently, this “sunny-side-up” state is mainly due to water penetration on the rough surfaces. As such, the “sunny-side-up” state can exist only for  $\theta_{in} > 0^\circ$ , and the state would vanish by exhibiting a contact angle of  $0^\circ$  if  $\theta_{in} = 0^\circ$ . To our knowledge, a Wenzel state with a non-zero contact angle on a rough surface while its flat counterpart is superhydrophilic (on which the water droplet would be in the complete wetting state with  $\theta_{in} = 0^\circ$ ) has not been reported in the literature.

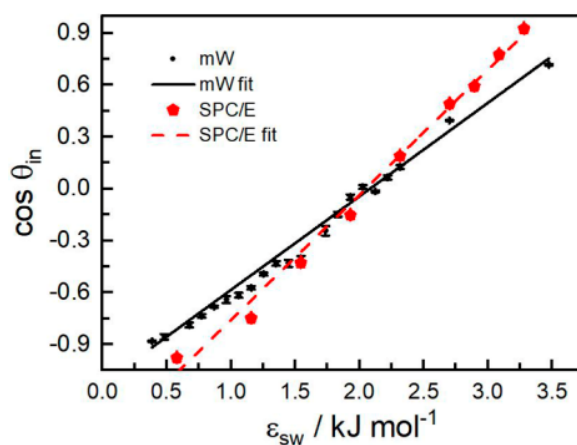
Herein, by considering a class of orderly structured surfaces with closed-loop nanowalls, our molecular dynamics (MD) simulations showed the remarkably distinct wetting behavior of droplets. Specifically, we observed that water could aggregate into a droplet with an ACA as large as  $60^\circ$  on an otherwise flat superhydrophilic surface with  $\theta_{in} = 0^\circ$ . This observation is contrary to the prediction of the (modified) Wenzel equation; that is, the droplet should completely wet the structured surface ( $\theta_A = 0^\circ$ ). Moreover, our MD simulations revealed previously unreported multiple Wenzel states of the droplet with different contact angles due to different locations of the TCL. This unexpected wetting behavior was attributed to the “closed-loop” nanowall topology on the surface. Therefore, we named these multiple Wenzel wetting states “topological wetting states”. Notably, the ACA of the droplet in the topological wetting states could not be predicted from the (modified) Wenzel equation. Instead, it was reliant on several external conditions: the intrinsic water-adsorption energy, droplet size, height of the closed-loop nanowalls, and width of the nanochannel (between the nanowalls) near the droplet perimeter. Unlike the “sunny-side-up” state, the multiple Wenzel states on the surface with closed-loop nanowalls/nanochannels would avert the penetration in the lateral direction, and thus can persist with  $\text{ACA} > 0^\circ$  even for  $\theta_{in} =$

$0^\circ$ . The physical mechanisms underlying the topological wetting behavior will be discussed below.

## METHODS

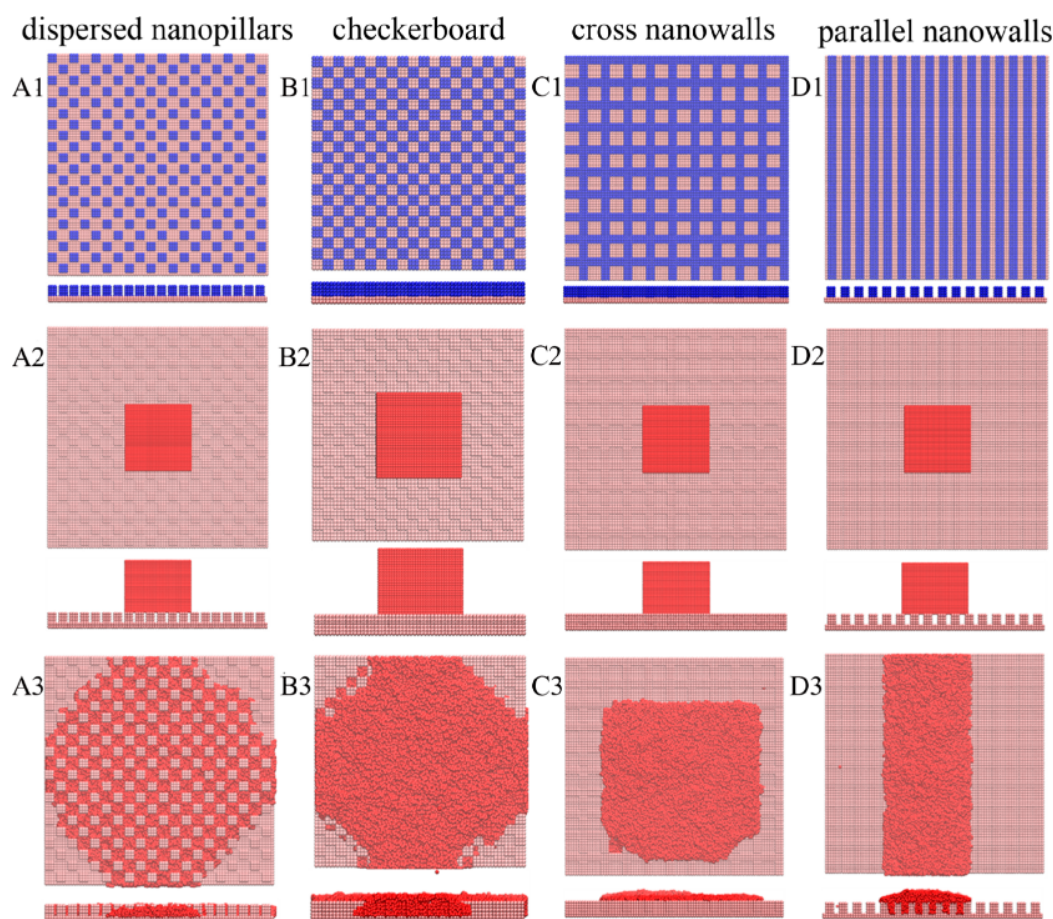
Most series of MD simulations were undertaken using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software.<sup>46</sup> In these series of MD simulations, water is described by the coarse-grained monatomic water (mW) model,<sup>47</sup> which has been proven previously to be able to yield the thermodynamic properties and phase behavior of water in bulk and in confinement reasonably well.<sup>48–53</sup> In addition, a previous MD simulation has also shown that the mW model can successfully describe the wetting behavior of various surfaces with different degrees of hydrophilicity.<sup>53</sup> The surface atoms interact with water molecules via the 12-6 Lennard-Jones (LJ) potential (truncated at a cutoff distance of 10 Å unless otherwise specified) with LJ parameter  $\sigma_{SW} = 3.2$  Å, whereas LJ parameter  $\epsilon_{SW}$  can be varied. The surfaces considered consisted of atoms arranged in a simple cubic lattice with a lattice constant of 4 Å. The model structured surfaces with different topologies were constructed with two layers of surface atoms as the bottom substrate, above which were the nanopillars/nanowalls composed of layers of atoms in the normal ( $y$ ) direction and with different channel/cavity patterns in the lateral  $xz$  plane. The lateral length of the model surfaces ranged from 21.2 nm  $\times$  21.2 nm to 46.4 nm  $\times$  43.4 nm ( $x \times z$ ). For simplicity, all the atoms of the surfaces remained fixed throughout the MD simulations. Periodic boundary conditions were applied in three dimensions, and the equations of motion were integrated using the velocity Verlet algorithm with a time step of 5 fs. MD simulations were undertaken using the NVT ensemble, in which the temperature was controlled at 300 K using a Nosé–Hoover thermostat. Data collected in the final 12.5 ns were used to compute the contact angle.

One particular series of MD simulations were undertaken using the extended single point charge (SPC/E) water model and the Gromacs-2019 package<sup>54</sup> as a benchmark test to compare with the wetting behavior based on the simpler mW model. Interactions between water molecules and surface atoms are described by the LJ potential with a cutoff distance of 10 Å. The long-range interaction is handled by the shift method. As shown in Figure 1, both mW and SPC/E water



**Figure 1.** Intrinsic contact angles from MD simulations based on the mW and SPC/E water models.

models give rise to a similar trend as well as a linear relationship between  $\cos \theta_{in}$  and  $\epsilon_{SW}$ . In general,  $\theta_{in}$  decreases with increasing  $\epsilon_{SW}$  and becomes  $0^\circ$  at a specific critical value of  $\epsilon_{SW}$ . This critical value of  $\epsilon_{SW}$  is 3.932 kJ mol<sup>-1</sup> for the mW model, slightly larger than that (3.377 kJ mol<sup>-1</sup>) for the SPC/E model. This benchmark test confirms that the simple mW model can be used to describe the topological wetting behavior on structured surfaces.



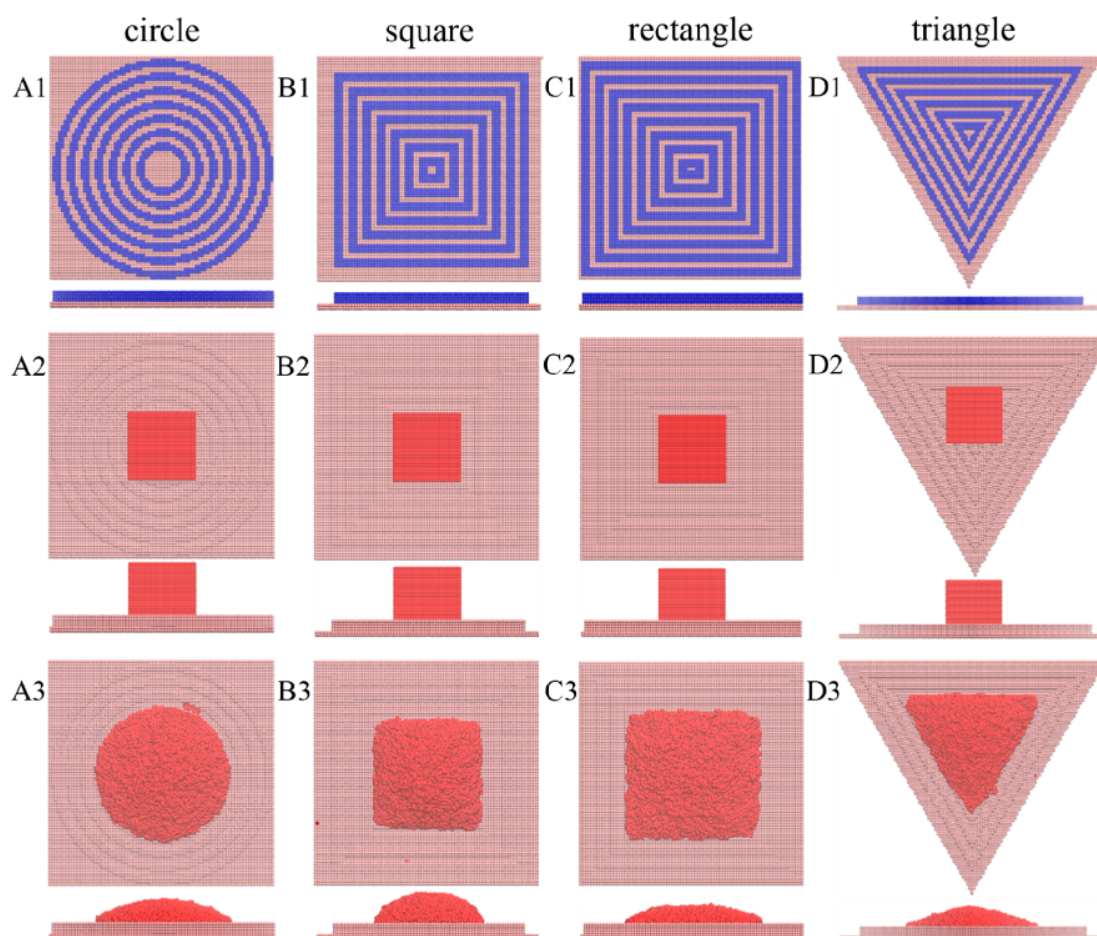
**Figure 2.** Wetting behavior of a water droplet on model surfaces with different topologies consisting of connected or unconnected nanochannels. Selected top and side views of surface models: model I with dispersed nanopillars and fully connected nanochannels, denoted as “dispersed nanopillars”; model II with checkerboard nanopillars and nanocavities, denoted as “checkerboard”; model III with a fully connected nanowall-network and ordered cavity pattern, denoted as “cross nanowalls”; model IV with parallel nanowalls and parallel nanochannels, denoted as “parallel nanowalls”. (A1–D1) The bare surface structures (without water on top). (A2–D2) The initial configurations with a water cube (containing 25 600 water molecules) placed on top and center of the surfaces. (A3–D3) The final “snapshots” of the system after MD simulations of >12 ns. Water molecules and surface wall/cavity atoms are in red and blue/light pink, respectively.

## RESULTS AND DISCUSSION

**Wetting Behavior Dependent upon Surface Topology.** For easy observation of surface topology-dependent wetting, we focused on the superhydrophilic flat surfaces on which the droplet tends to be in the complete wetting state (i.e.,  $\theta_{in} = 0^\circ$ ). To characterize the strength of water molecule–surface interaction in the superhydrophilic regime, we introduced the parameter of intrinsic adsorption energy ( $E_{in}$ ), which is defined as the adsorption energy of a water molecule on a flat surface. Specifically,  $E_{in}$  is calculated as the minimum LJ potential energy between a single water molecule and the corresponding flat atomic surface, and it has a linear dependence on  $\epsilon_{SW}$ , i.e.,  $E_{in} = 4.748\epsilon_{SW}$  in our simulations. Through a series of test MD simulations, we found that  $\theta_{in}$  decreased with increasing  $E_{in}$ , and eventually  $\theta_{in}$  became  $0^\circ$  for  $E_{in} \geq 18.669$  kJ mol $^{-1}$ . Therefore, we first chose a model surface with  $E_{in} = 18.783$  kJ mol $^{-1}$  ( $\epsilon_{SW} = 3.956$  kJ mol $^{-1}$ ) to study the wetting behavior of a water droplet on corresponding structured surfaces with various morphologies whose flat-surface counterparts were all in the regime of  $\theta_{in} = 0^\circ$ . [Movie S1](#) shows a MD simulation of a water droplet spreading rapidly on a superhydrophilic flat surface and arriving at a contact

angle of  $0^\circ$ . According to the (modified) Wenzel equation, the ACA of the water droplet on the corresponding rough surface should be  $0^\circ$  (i.e., the rough surface should be superhydrophilic as well). To our knowledge, there are no literature reports on the possible Wenzel state of a droplet with a non-zero ACA on a rough surface whose counterpart superhydrophilic flat surface possesses an intrinsic contact angle of  $\theta_{in} = 0^\circ$ . Unexpectedly, we found that the structured surfaces with closed-loop nanowalls could indeed exhibit a non-zero ACA, contrary to the conventional view.

First, to illustrate the conventional view of the effect of the surface topologies on the wetting behavior, several simple structured surface models with nanopillars distributed in various patterns were employed ([Figure 2](#) and [Figure S1](#)). The nanopillars had a height of 16 Å. Surface model I, the “dispersed nanopillars” ([Figure 2A1](#)), consisted of discrete nanopillars distributed in a square-lattice pattern with appreciable separation (12 Å) from one another. Thus, the bottom substrate could be considered to be a fully connected network (i.e., the structured surface could be viewed as having percolated nanochannels). Surface model II, the “checkerboard” ([Figure 2B1](#)), consisted of nanopillars located in a “checkerboard” pattern in which the smallest distance between



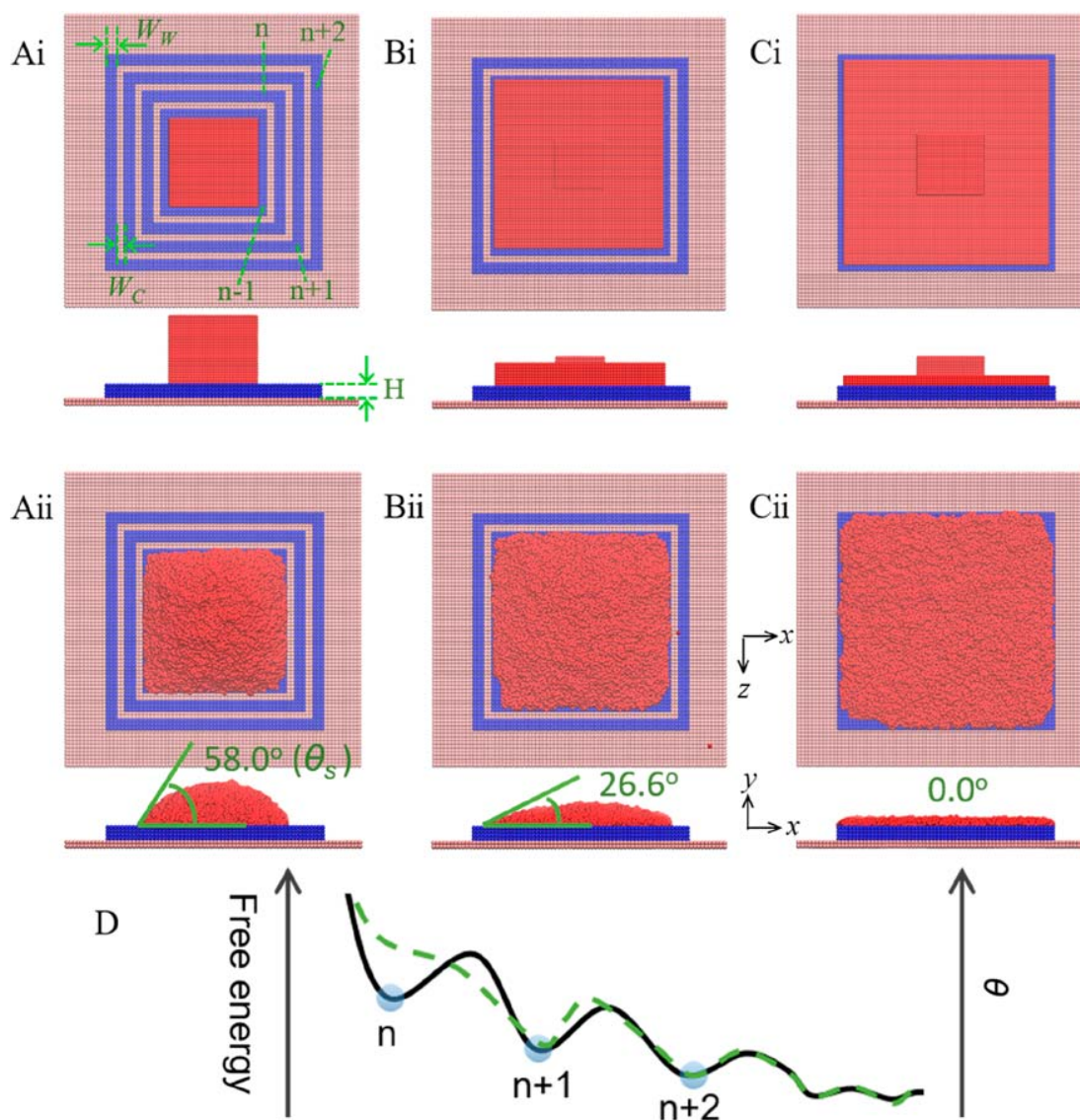
**Figure 3.** Wetting behavior on model surfaces with circle, square, rectangle, and triangle shaped closed-loop nanowalls/nanochannels. (A1–D1) The bare surface structures. (A2–D2) The initial configurations with a water cube (containing 25 600 water molecules) placed on top and center of the surfaces. (A3–D3) The final snapshots of the water after MD simulations of 100+ ns. Water molecules and substrate atoms are in red and blue/light pink, respectively, with the nanowall atoms in blue in (A1–D1).

two nearest nanopillars was 5.656 Å. As such, water molecules could pass through the gap between the two nearest nanopillars, and nanochannels on this surface could be viewed as a percolated network. Likewise, the “*ab*-checkerboard” surface (Figure S1A1), which consisted of rectangle nanopillars also exhibited percolated nanochannels so that water molecules could pass through the gap between the nearest nanopillars. In stark contrast, surface model III, “cross nanowalls” (Figure 2C1), consisted of a fully connected nanowall network (with various ordered cavity patterns). Other nanowall-connected patterns like “blocked checkerboard” and “blocked *ab*-checkerboard” surfaces were also built (Figure S1B1,C1). Unlike the surface models represented by the “dispersed nanopillars” and the “checkerboard”, in these patterns the ordered cavities did not form connected nanochannels. Surface model IV, the “parallel nanowalls” surface (Figure 2D1) was a special case in that it consisted of parallel nanowalls and parallel nanochannels.

Initially, a water droplet (cube) was placed on top of these model surfaces (Figure 2A2–D2 and Figure S1). These surfaces were superhydrophilic in the flat form due to the relatively high water adsorption energy of  $E_{in}$  (18.783 kJ mol<sup>-1</sup>). MD simulations showed that water molecules diffused faster on surfaces with connected nanochannels than on surfaces with unconnected nanochannels. Nevertheless, on

surface models other than the “parallel nanowalls”, including the nanochannel-connected surface models with a relatively separated nanopillar pattern (Figure 2A), or checkerboard or similar patterns (Figure 2B and Figure S1A), or the nanochannel-unconnected surface models with ordered cavities (Figure 2C and Figure S1B,C), the water droplet could eventually reach the equilibrium state with the ACA being 0°. In other words, these structured surfaces were all superhydrophilic as well (on which water would be in the complete-wetting state), in accordance with the Wenzel equation. For the “parallel nanowalls” surface model, however, water spread along the parallel nanochannels whereas the parallel nanowalls stopped the water spreading along the direction perpendicular to the nanochannels. The final ACA in the nanochannel direction was 0°, whereas the ACA in the perpendicular direction was >0°. Ultimately, we expected the ACA to become 0° if the model supercell was long enough in the nanochannel direction to allow the water to fill the nanochannels.

In view of the intriguing blocked spreading of water along the direction normal to the parallel nanochannels on the surface model with “parallel nanowalls”, we investigated the wetting behavior of a water droplet on a special class of model surfaces with closed-loop nanowalls/nanochannels. To this end, several model surfaces with various closed-loop nano-

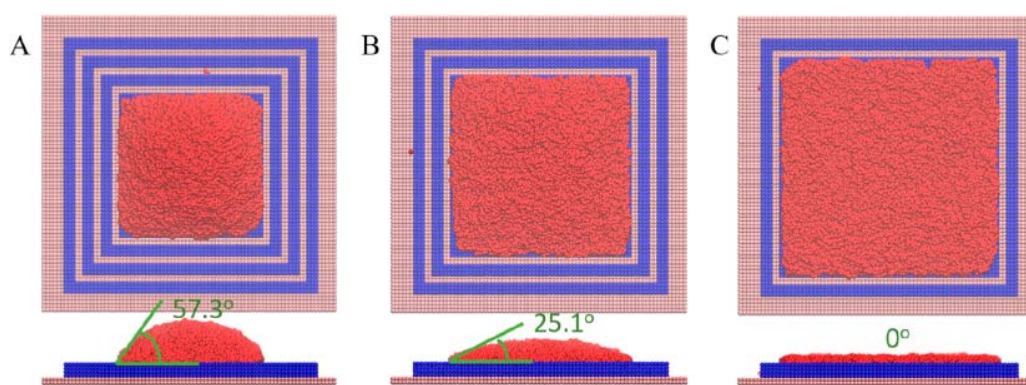


**Figure 4.** (A–C) Dependence of the final ACA on the initial edge location of the droplet. (Ai–Ci) and (Aii–Cii) show the initial and final snapshots of MD simulations, respectively, where the model surfaces with the square-loop nanowalls/nanochannels in A–C are identical and the water droplets are all composed of 25 600 water molecules. The duration of the MD simulation is >23 ns. Water molecules and substrate atoms are in red and blue/light pink, respectively, with the nanowall atoms in blue. (D) A schematic plot of the free-energy surface for the water droplet in different topological wetting states (black solid line) and destabilized loop- $n$  Wenzel state (green dashed line).

walls/nanochannels (circle, square, rectangle and triangle) were constructed (Figure 3A1–D1). Initially, a water droplet (cube) was placed on top of these model surfaces (Figure 3A2–D2). After 100+ ns MD simulations for each system, the water droplet was universally in a Wenzel state with a non-zero contact angle (Figure 3A3–D3 and Movies S2–S5). In other words, none of these surfaces were apparently superhydrophilic, even though their flat counterparts were superhydrophilic (on which water would be in the complete-wetting state), a behavior that was markedly inconsistent with the Wenzel equation. Closer inspection of Movies S2–S5 reveals that the TCL of the water droplet appeared to be “pinned” by one closed-loop nanowall on the model surfaces. As such, the overall shape of the TCL and ACA of the water droplet were dependent upon the geometry of the closed loops. Indeed, the droplet on the surface with circle-loop nanowalls/nanochannels exhibited a circular TCL whereas that on the surface

with square-loop nanowalls/nanochannels exhibited a square-like TCL (Figure 3A3,B3).

The unexpected wetting behavior shown in Movies S2–S5 suggests new physical chemistry of the wetting on this special class of structured surfaces. To further illustrate this wetting behavior, a nanogap of 8 Å was carved out by removing several atoms at either the side or the vertex of one triangle-loop (Figure S2Ai,Bi) near the TCL. MD simulations clearly showed that water could spread further on both surfaces because the broken loop allowed the water at the TCL to invade into the neighboring outer-loop channel (Figure S2Aiii,Biii and Movies S6 and S7). In view of the strong topology-dependent wetting behavior on the surfaces with closed-loop nanowalls/nanochannels, we named these special Wenzel states of water droplets as “topological wetting states”. Note that this topological wetting behavior can be also observed in an independent series of MD simulation with a



**Figure 5.** Snapshots of a water droplet at the end of MD simulations (>45 ns) with the initial configuration of the water droplet shown in Figure 4Aii while the surface entails a different value of the adsorption energy  $E_{in}$  of a water molecule: (A)  $E_{in} = 19.239 \text{ kJ mol}^{-1}$ , (B)  $E_{in} = 19.700 \text{ kJ mol}^{-1}$ , and (C)  $E_{in} = 20.155 \text{ kJ mol}^{-1}$ . Water molecules and substrate atoms are in red and blue/light pink, respectively, with the nanowall atoms shown in blue.

more realistic three-atomic-site SPC/E water model (see Methods and Supporting Information). Indeed, as shown in Movie S8, water can also maintain in a droplet state with  $ACA > 0^\circ$  on a square-loop surface while its corresponding planar counterpart exhibits completely wetting (Movie S9). Moreover, another independent series of benchmark simulations were performed, by considering the effect of hydrogen-bonding interaction based on Stillinger–Weber potential between the mW water<sup>46–52</sup> and the mW solid substrate<sup>53</sup> (see Supporting Information). The wetting phenomena observed (Movies S10 and S11) are consistent with those obtained without considering the hydrogen-bonding interaction between water and substrate (Movies S1 and S3). Additionally, we have performed independent test simulations to make sure that the topological wetting is free of the artifacts due to short cutoff distance, as previously reported.<sup>55</sup> In these test simulations, we increased the cutoff distance value to 25.6 Å, where the two independent sets of simulations with the mW model and with the SPC/E water model, respectively, show a water nanodroplet with  $ACA > 0^\circ$  on a square-loop surface but in the complete-wetting state on the corresponding planar surface (Movies S12 vs S13 and S14 vs S15).

**Topological Wetting States.** Here, the topology of square loop nanowall was chosen as a representative model surface to illustrate the topological wetting states of a water droplet. Initially, a water droplet (cube) was placed on top of the surface (Figure 4Ai). The flat counterpart of this surface was superhydrophilic due to relatively high adsorption energy of water ( $E_{in} = 18.783 \text{ kJ mol}^{-1}$ ). During a 33 ns MD simulation, the droplet reached a Wenzel state within 2–3 ns, where the TCL of the droplet was pinned by a square loop nanowall (numbered as  $n$ th loop nanowall) so that the droplet exhibited a finite ACA (Figure 4Aii). For ease of description, we defined this Wenzel state as the “loop- $n$  Wenzel state.” The ACAs of the square-like droplet were anisotropic, with the smallest one being along the diagonal ( $xz$ ) direction and the largest along the side ( $x$  or  $z$ ) direction. The ACA measured near the center of a square side, termed “side ACA” ( $\theta_s$ ), as shown in Figure 4Aii, was  $58.0^\circ$ .

For other related situations, the height of the initial droplet with the same number of water molecules was adjusted to be lower so that the droplet could become flatter. When the outermost edge of the initial droplet was initially beyond the boundary of  $n$ th loop nanowall but within the  $(n+1)$ th loop

nanowall (Figure 4Bi), the TCL of the final droplet was pinned by the  $(n+1)$ th loop nanowall. Thus, the droplet adopted the loop- $(n+1)$  Wenzel state, and exhibited a smaller side ACA ( $26.6^\circ$ ) (Figure 4Bii). In contrast, if the edge of the initial droplet was located beyond the  $(n+1)$ th loop nanowall (Figure 4Ci), the final droplet adopted the loop- $(n+2)$  Wenzel state, exhibiting an ACA of  $0^\circ$  (Figure 4Cii). In this case, the structured surface behaved like a superhydrophilic surface. Thus, the final state of the droplet on the surface with multiple closed-loop nanowalls apparently hinged on its initial location, especially the relative location of the edge of the droplet versus the nearest closed-loop nanowalls. The potential energy of the three (meta-)stable Wenzel states shown in Figure 4Aii–Cii followed the order Aii > Bii > Cii, indicating that the final complete wetting state with the lowest ACA was the most stable state, which is in accordance with the Wenzel equation.

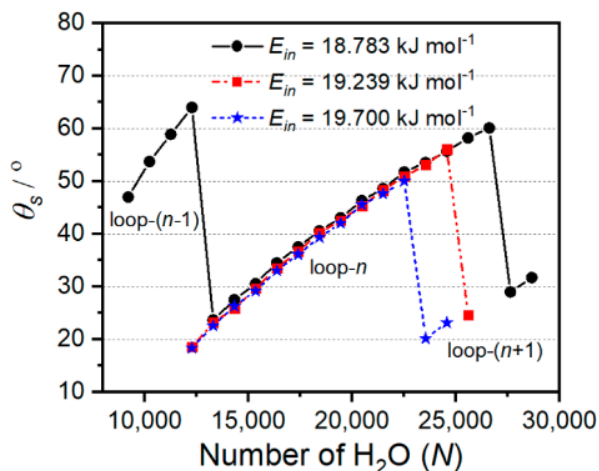
The results detailed above suggest that multiple topological wetting states, characterized by the loop- $n$ ,  $n+1$ ,  $n+2$  Wenzel states, etc., may exist, depending on the relative location of the TCL of the droplet with respect to the nearest closed-loop nanowall/nanochannel. Existence of such multiple topological wetting states can be understood via a schematic plot (black solid line in Figure 4D) for a given water droplet. With the increase in the range of the TCL, the free energy of the Wenzel state decreases, and so does the ACA. Topological wetting states with an  $ACA > 0^\circ$  are metastable states, and they correspond to local minima on the free-energy surface. Conversely, the behavior of the droplet is also related to the kinetics, which can lead to multiple topological wetting states.

Next, we investigated the effect of water adsorption energy  $E_{in}$  (as a measure of the superhydrophilicity of the corresponding flat surface) on the topological wetting state of a water droplet. In a new series of MD simulations, the initial location of the droplet was kept the same as that shown in Figure 4Ai). With  $E_{in}$  increasing to  $19.239 \text{ kJ mol}^{-1}$  ( $\epsilon_{sw} = 4.052 \text{ kJ mol}^{-1}$ ), the droplet maintained the loop- $n$  Wenzel state with a side ACA of  $57.3^\circ$  (Figure 5A) after MD simulations for >45 ns. With  $E_{in}$  increasing to  $19.700 \text{ kJ mol}^{-1}$  ( $\epsilon_{sw} = 4.149 \text{ kJ mol}^{-1}$ ), the droplet adopted the loop- $(n+1)$  Wenzel state with a smaller side ACA of  $25.1^\circ$  (Figure 5B). The results of MD simulations suggested that the free-energy barrier from the loop- $n$  Wenzel state to loop- $(n+1)$  Wenzel state decreased with increasing  $E_{in}$ , and that the barrier could

even reach zero at  $E_{in} \approx 19.700 \text{ kJ mol}^{-1}$  such that the loop- $n$  Wenzel state was no longer a local minimum, as shown schematically by the green-dashed line in Figure 4D. Hence, with  $E_{in}$  increasing further to  $20.155 \text{ kJ mol}^{-1}$  ( $\epsilon_{SW} = 4.245 \text{ kJ mol}^{-1}$ ), the droplet adopted the loop- $(n+2)$  Wenzel state with an ACA  $\approx 0^\circ$  (Figure 5C).

Overall, the tendency to exhibit multiple topological wetting states for the water droplet became weaker as the surface-water interaction increased. We wanted to know the critical value of  $E_{in}$  above which the droplet could only reach the most stable Wenzel state (i.e., complete wetting state). Hence, we constructed a model surface with the  $n$ th loop nanowall/nanochannel as the outermost nanowall/nanochannel while a relatively small water droplet (12 288 molecules) was placed initially on the surface. The new MD simulations showed that for  $E_{in} > 21.988 \text{ kJ mol}^{-1}$  ( $\epsilon_{SW} > 4.631 \text{ kJ mol}^{-1}$ ), water could always diffuse spontaneously along the structured surface until the droplet reached the complete-wetting state with an ACA of  $0^\circ$  (Movies S16 and S17). In other words, this model surface always behaved like a superhydrophilic surface, which was in accordance with the Wenzel equation. This result also suggested that multiple topological wetting states occurred for  $E_{in} < 21.988 \text{ kJ mol}^{-1}$ .

**Critical Droplet Size.** In this series of MD simulations, the droplet size was changed by adjusting the height of the initial droplet (cube) whereas the location of the perimeter (or the TCL) was kept fixed. The time scale of this series of MD simulations was typically  $\geq 20 \text{ ns}$ . The side ACA of the droplet at the end of MD simulations versus the number ( $N$ ) of water molecules is shown in Figure 6. For  $E_{in} = 18.783 \text{ kJ mol}^{-1}$ ,



**Figure 6.** Size-dependent ACA of a water droplet near the center of a square side ( $\theta_s$ ). Model surfaces with a water-molecule adsorption energy  $E_{in} = 18.783, 19.239,$  and  $19.700 \text{ kJ mol}^{-1}$ , respectively, are shown as black circles (solid line), red squares (dashed-dotted line), and blue stars (dashed line).

when  $N$  increased from 9216 to 12 288, the droplet was in the loop- $(n-1)$  Wenzel state, whereas the side ACA increased. The dependence of the side ACA  $\theta_s$  on droplet size can be given by the following equation:

$$\cos \theta_s = 1.406 - N/12662.9 \quad (1)$$

When  $N$  increased from 12 288 to 13 312, the side ACA decreased sharply from  $64.0^\circ$  to  $23.7^\circ$  due to the transition of the metastable state of loop- $(n-1)$  to the loop- $n$  Wenzel

state. For  $N$  in the range of 13 312–26 624, the droplet maintained the loop- $n$  Wenzel state while the side ACA increased monotonously with  $N$  up to  $60.1^\circ$ . The relationship between the side ACA and droplet size was given by

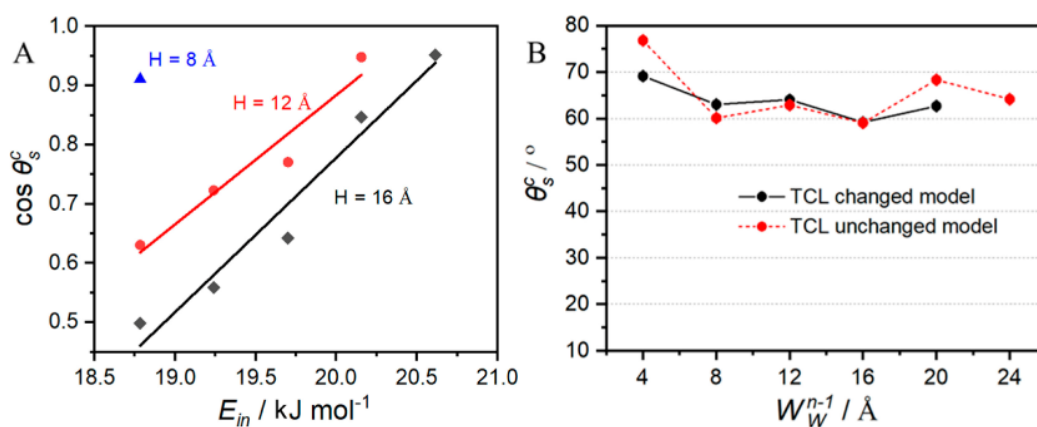
$$\cos \theta_s = 1.348 - N/31252.6 \quad (2)$$

When  $N$  increased further to 27 648, the droplet started to diffuse into the channel beyond the  $n$ th loop nanowall/nanochannel, and adopted the loop- $(n+1)$  Wenzel state with the side ACA decreasing sharply from  $60.1^\circ$  to  $29.0^\circ$ . These results also suggested that, for a certain loop Wenzel state, there existed a critical droplet size ( $N^c$ ) below which this Wenzel state could exist, whereas beyond critical size this Wenzel state became destabilized and the droplet reached another loop Wenzel state with a larger TCL or even reaches the most stable state with the ACA being  $0^\circ$ . The corresponding ACA of the droplet in this critical size was defined as the “critical ACA” ( $\theta^c$ ). Here, for the loop- $(n-1)$  Wenzel state, the side critical ACA was  $64.0^\circ$  whereas, for the loop- $n$  Wenzel state, the side critical ACA was  $60.1^\circ$ .

For  $E_{in} = 19.700$  and  $19.239 \text{ kJ mol}^{-1}$ , the obtained critical ACAs were slightly less than those for  $E_{in} = 18.783 \text{ kJ mol}^{-1}$  due to the slightly stronger adsorption of water molecules on the surfaces (Figure 6). However, interfacial water molecules represent only a very small portion of whole droplet, so the difference in the ACAs obtained from the higher  $E_{in}$  was negligible when the droplet was in the same loop Wenzel state. However, the critical ACAs in the same Wenzel state decreased as  $E_{in}$  increased, indicating that stronger surface-water interaction leads to a weaker pinning capability of the nanowalls toward the droplet.

Additionally, a series of MD trajectories show the dynamics of transition from the loop- $n$  to the loop- $(n+1)$  Wenzel states. Given a surface with closed-loop nanowalls/nanochannels, when the number of water molecules ( $N$ ) in a droplet (kept in the loop- $n$  state) exceeds  $N^c$  of the loop- $n$  state with  $\theta > \theta^c$ , the TCL can no longer be stably pinned by the edge of the  $n$ th nanowall. If a water cluster with a few molecules succeeds to reach the nanochannel of  $(n+1)$ th loop and is large enough to contact the top water nanodroplet that distributes in the area within the  $n$ th loop wall at a certain point (as a starting point), as illustrated in Figure S3A, the top water nanodroplet would support more water molecules for diffusion or penetration in the  $(n+1)$ th channel. For those water molecules arriving in the nanochannel, they would connect with the top nanodroplet if  $N$  is sufficiently large so as to extend the nanodroplet TCL (see Movies S2, S4, and S8). When the entire nanochannel is occupied by water, the nanodroplet would further relax to finally reach the loop- $(n+1)$  state. Note that the starting point is not exclusive if water molecules are abundant. In another word, the top nanodroplet can start penetrating at several points at the same time, and in this way, the nanodroplet can reach loop- $(n+1)$  state more quickly.

**Effect of Nanowall/Nanochannel Parameters on Topological Wetting States.** To ascertain the quantitative relationship between topological wetting states and water-surface interaction, we focused on the loop- $n$  Wenzel state and considered  $E_{in}$  in the range  $18.783$ – $20.615 \text{ kJ mol}^{-1}$ . The adopted model surface is depicted in Figure S3B. Figure 7A shows the cosine of the side critical ACA ( $\cos \theta_s^c$ ) versus  $E_{in}$  at different nanowall heights ( $H = 16, 12,$  and  $8 \text{ \AA}$ ). At  $H = 16 \text{ \AA}$ ,



**Figure 7.** (A) The critical side ACA for a droplet on square-loop channel surfaces in the loop- $n$  Wenzel state versus the intrinsic adsorption energy at different nanowall heights,  $H = 16, 12,$  and  $8 \text{ \AA}$ , respectively. (B)  $\theta_s^c$  versus the width of nanowall ( $W_W^{n-1}$ ) near the TCL at the loop- $(n-1)$  Wenzel state.

the fitted straight line in Figure 7A was given by the following equation:

$$\cos \theta_s^c = 0.261E_{in} - 4.438 \quad (3)$$

For lower  $H$ , the critical ACA was smaller, suggesting that the free-energy barrier from the loop- $n$  Wenzel state to loop- $(n+1)$  Wenzel state decreased with  $H$ . Specifically, at  $H = 12 \text{ \AA}$ , the relationship between  $\theta_s^c$  and  $E_{in}$  was given by

$$\cos \theta_s^c = 0.218E_{in} - 3.483 \quad (4)$$

The slope of the straight line increased with  $H$ , so the pinning capability of the closed-loop nanowall with a higher  $H$  was more sensitive to the change in  $E_{in}$ .  $E_{in}$  in eqs 3 and 4 should be in the units  $\text{kJ mol}^{-1}$ .

Next, the effect of the channel width ( $W_C$ ) (Figure 4Ai) on topological wetting state was examined at  $H = 16 \text{ \AA}$ . Again, we focused on the loop- $n$  Wenzel state at which the nearest channel to TCL had a width of  $W_C^n$  (see Figure S4 for the model surfaces with various  $W_C^n$ ).  $\theta_s^c$  values at  $W_C^n = 12 \text{ \AA}$  and different  $E_{in}$  are given in Table 1. At a smaller channel width of

**Table 1.**  $\theta_s^c$  in the Loop- $n$  Wenzel State at Different Water-Molecule Adsorption Energies,  $E_{in}$ , and Different  $W_C^n$

$\epsilon_{sw}/\text{kJ mol}^{-1}$	$E_{in}/\text{kJ mol}^{-1}$	$\theta_s^c$		
		$W_C^n = 8 \text{ \AA}$	$W_C^n = 12 \text{ \AA}$	$W_C^n \rightarrow \infty$
4.052	19.239	$<18.6^\circ$	$56.1^\circ$	$>56.1^\circ$
4.149	19.700	$<18.6^\circ$	$50.1^\circ$	$49.9^\circ$
4.245	20.155	$<18.6^\circ$	$32.2^\circ$	$36.1^\circ$
4.342	20.615	$<17.8^\circ$	$17.8^\circ$	$35.4^\circ$

$W_C^n = 8 \text{ \AA}$ , the loop- $n$  Wenzel state transformed into the loop- $(n+1)$  Wenzel state even when the droplet had a relatively small number of water molecules (12 288), indicating  $\theta_s^c < 18.6^\circ$  for  $E_{in}$  being in the range of 18.783–20.155  $\text{kJ mol}^{-1}$  ( $\theta_s^c \approx 18.6^\circ$  in the loop- $n$  state). Hence,  $\theta_s^c$  at  $W_C^n = 8 \text{ \AA}$  was smaller than that at  $W_C^n = 12 \text{ \AA}$ . Conversely, if the channel width was large enough (in the limit of  $W_C^n \rightarrow \infty$ ), the droplet could no longer reach the  $(n+1)$ th loop Wenzel state. Compared with  $\theta_s^c$  at  $W_C^n = 12 \text{ \AA}$ , the obtained  $\theta_s^c$  values at  $W_C^n \rightarrow \infty$  (Table 1) displayed an apparent increase at  $E_{in} = 20.155$  and  $20.615 \text{ kJ mol}^{-1}$  although a negligible difference at

$E_{in} = 19.700 \text{ kJ mol}^{-1}$ . In summary, the critical ACA clearly increased with  $W_C^n$  unless  $W_C^n$  became too large.

The effect of the nanowall width  $W_W$  (Figure 4Ai) near the TCL on  $\theta_s^c$  was also investigated. In this series of MD simulations, the side ACA in loop- $(n-1)$  Wenzel state on the surface with various  $W_W^{n-1}$  was computed at  $E_{in} = 18.783 \text{ kJ mol}^{-1}$  ( $\epsilon_{sw} = 3.956 \text{ kJ mol}^{-1}$ ). Here,  $W_W^{n-1}$  was changed in two ways, that is, adding atoms layer-by-layer on the  $(n-1)$ th nanowall: (i) inward (toward to the center of water droplet) so that the TCL did not move (Figure S5); (ii) outward so that the TCL moved outward (Figure S6). In both cases,  $\theta_s^c$  of the droplet in the loop- $(n-1)$  Wenzel state versus  $W_W^{n-1}$  (from 4 to 20  $\text{\AA}$ ) is shown in Figure 7B. In the case of an unchanged TCL,  $\theta_s^c$  ranged between  $59.1^\circ$  and  $68.3^\circ$  at  $W_W^{n-1} \geq 8 \text{ \AA}$ . The larger  $\theta_s^c$  ( $76.8^\circ$ ) at  $W_W^{n-1} = 4 \text{ \AA}$  was attributed to the much smaller nanowall width with only one layer of atoms so that the local adsorption energy of water on the side surface of the nanowall was apparently smaller than that of the regular bulk surface. In the case of a changed TCL,  $\theta_s^c$  varied in nearly the same range ( $59.2^\circ$ – $69.1^\circ$ ). Hence, the width of nanowall had a negligible effect upon the critical ACA of the droplet.

**Theoretical Mechanisms and Discussions.** To explore the physical mechanism underlying this unusual phenomena, we first presented a theoretical framework to describe the pinning or movement of TCL of a droplet in the Wenzel state on a rough surface (see Section E of the Supporting Information for more details). From the view of thermodynamics, the energy of replacement per unit area of the solid surface ( $\gamma_{sv}$ ) with the solid-liquid surface ( $\gamma_{sl} + \gamma_{lv}$ ) is less than 0 for rough surface whose flat counterpart is superhydrophilic (on which water would be in the complete-wetting state, i.e.,  $\theta_{in} = 0^\circ$ ). Here,  $\gamma_{sv}$ ,  $\gamma_{sl}$ , and  $\gamma_{lv}$  are solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, respectively. Thus, the instantaneous contact angle  $\theta$  in the Wenzel state should always be  $0^\circ$  for corresponding rough surface. This is the primary reason why water droplet on surfaces with nanopillars or similar patterns as shown in Figure 2 does not exhibit a contact angle  $\theta > 0^\circ$ .

In principle, surface with closed-loop nanowalls/nanochannels should also have a contact angle of  $0^\circ$ . However, for water droplet on this type of rough surfaces, the net attractive force applied on any water molecule located at the TCL is in the inward direction toward the nanowalls as shown in Figure S8. Thus, the unbalanced force applied on all water



molecules along the TCL by the surface would block the outward motion of the TCL which has to first move down into the nanochannel if the water droplet was to expand to a larger area (with smaller  $\theta$ , or even  $\theta = 0^\circ$ ). In other words, this outward motion would encounter an energy barrier that would block the water droplet from moving beyond the edge of the nanowall and thus can maintain the droplet in a metastable Wenzel state with  $\theta > 0^\circ$ .

Next, we consider a water droplet is in a Wenzel state with the TCL pinned by a closed-loop nanowall. For simplicity, we use a circular nanowall with radius  $R_W$  for analysis. In this case, the total number of water molecules in the droplet is

$$N = \frac{\rho N_A \pi R_W^3}{3M} f(\theta) + N_B \quad (5)$$

$$f(\theta) = \frac{(1 - \cos \theta)(2 + \cos \theta)}{\sin \theta(1 + \cos \theta)} \quad (6)$$

where  $\rho$  and  $M$  are the density and molecular molar mass of water, respectively.  $N_A$  is the Avogadro constant.  $N_B$  is the number of water molecules in the bottom nanochannel, which is a constant when the TCL is pinned.  $f(\theta)$  has monotonously increasing relationship with  $\theta$  (approximately linear relation with  $\cos \theta$  for  $20^\circ \leq \theta \leq 80^\circ$ , and with  $\theta$  for  $0^\circ < \theta < 20^\circ$ ; see Figure S9). Thus,  $\theta$  monotonously increases with  $N$  when the droplet TCL is pinned by the closed-loop nanowall, consistent with our simulation results shown in Figure 6. For  $20^\circ \leq \theta \leq 80^\circ$ ,  $\cos \theta$  can be approximately considered as linearly dependent on  $N$ . This explains why we obtained a linear relation in eqs 1 and 2. Moreover,  $\theta$  can be accordingly calculated once the droplet size and the surface structure are identified. (See Section F in the Supporting Information for the deductions above and related plots.)

Furthermore, assuming the water droplet is in the loop- $n$  state, when the volume of the droplet (or  $N$ ) increases, the droplet's contact angle increases, and the driving force per unit length  $\gamma_{lv}|\cos \theta - \cos \theta_Y|$  applied by the surface tension can be strong enough to overcome the energy barrier. Here, we use Young's equation,  $\cos \theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$ , and  $\cos \theta_Y$  could be larger than 1 in the case of the complete-wetting state. As such, the loop- $n$  state is no longer stable, and the droplet adopts the loop- $(n+1)$  state. From this aspect, the energy barrier of the wetting transition from the loop- $n$  to the loop- $(n+1)$  states for a droplet on a surface with closed-loop nanowalls/nanochannels can be written in terms of two parts:  $\Omega = \Omega_r - \Omega_d$ , where  $\Omega_r$  and  $\Omega_d$  are the energy barrier due to the unbalanced force from the closed-loop nanowall/nanochannel near the TCL and the energy increase due to driving force applied by the surface tension, respectively. Because  $\Omega_d$  is determined by  $f_d = \gamma_{lv}(\cos \theta_Y - \cos \theta)$ ,  $\Omega_d$  decreases and thus  $\Omega$  increases linearly with increasing  $\cos \theta$ . When  $\theta$  increases to  $\theta^c$ ,  $\Omega = 0$ , and thus  $\Omega_r = \Omega_d(\theta = \theta^c)$ . In this case,  $\Omega_r$  decreases linearly with increasing  $\cos \theta^c$  and the critical contact angle  $\theta^c$  can be considered as a measure of the energy barrier  $\Omega_r$  due to the closed-loop nanowall/nanochannel.

According to the deduction shown above, higher nanowall height would result in higher  $\Omega$  and therefore larger  $\theta^c$ , because higher nanowall can accumulate stronger unbalanced interaction. Likewise, smaller width of the nanochannel at the TCL can offset larger part of the inward unbalanced interaction, thereby decreasing  $\theta^c$ . On the other hand, when  $E_{in}$  increases, the driving force  $f_d$  becomes stronger due to the increased

$\cos \theta_Y$ , leading to decreased  $\theta^c$ . All these analyses explain our simulation results well, suggesting that the energy barrier of the local wetting transition from the loop- $n$  to the loop- $(n+1)$  states decreases with  $N$  because larger  $N$  gives smaller  $\cos \theta$  which leads to larger  $\Omega_d$ .

To numerically evaluate the energy barrier for the transition from the loop- $n$  to the loop- $(n+1)$  states, we have adopted metadynamics simulations (with the plumed code) for three relatively small droplets (involving number of water molecules  $N = 6,144, 7,168$  and  $9,126$ , corresponding to apparent side contact angle  $\theta_s = 21.5^\circ, 29.7^\circ$  and  $47.0^\circ$ , respectively) on the square-loop surface in the loop- $n$  state and with  $E_{in} = 18.783 \text{ kJ mol}^{-1}$  ( $\epsilon_{sw} = 3.956 \text{ kJ mol}^{-1}$ ) to ensure  $\theta_{in} = 0^\circ$ . (See Section G of the Supporting Information for details.) For  $N = 6144, 7168$ , and  $9126$ , the estimated energy barriers ( $\Omega$ ) are approximately  $91.8 k_B T, 67.8 k_B T$ , and  $33.5 k_B T$ , respectively. Figure S10D shows that  $\Omega$  decreases almost linearly with increasing  $N$ , consistent with the above deduction. According to the transition-state theory, the lifetime ( $t_c$ ) of loop- $n$  state can be written as  $t_c = t_0 \exp(\Omega/k_B T)$ , where  $t_0, k_B$ , and  $T$  are the attempt frequency, Boltzmann constant, and temperature, respectively. Adopting  $t_0 = 10^{-13} \text{ s}$ ,<sup>27</sup> the estimated lifetimes for the three different sized droplets (Table S1) are rather long and can even reach the magnitude order of  $10^{26} \text{ s}$ . This suggests that the topological wetting states can be observed in the laboratory.

In summary, the key physics that leads to the distinct wetting phenomena is that the surface roughness in closed-loop topology can give rise to the unbalanced force and associated pinning effect along the fully closed TCL of the droplet. As a result, the height of the closed-loop nanowall, the width of the closed-loop nanochannel, the strength of surface-water interaction, and the size of the droplet are all important factors for controlling the topological wetting state. Besides the highly symmetric closed-loop nanowalls/nanochannels, realistic surfaces with irregular convex-hull shapes of closed-loop nanowalls/nanochannels are also expected to exhibit the topological wetting behavior, although the water droplet would adapt an irregular shape from the top view. This is due to the topological invariant as both the highly symmetric and irregular closed loops entail the same genus value (as the genus value of a donut). A simple isolated flat island or high platform would also lead to similar Wenzel state for a droplet less than the critical size ( $N \leq N^c$ ). Moreover, the topological wetting behavior associated with the surface with the closed-loop nanowalls/nanochannels may even arise on hydrophilic or even weakly hydrophilic surfaces. If so, the topological wetting behavior is expected to be quite generic, regardless of strong/weak polarization effect of the surfaces.

## CONCLUSIONS

We investigated the wettability of structured surfaces with various topologies, whose corresponding flat surfaces were superhydrophilic (on which a water droplet would exhibit an intrinsic contact angle  $\theta_{in} = 0^\circ$ ). MD simulations showed that the structured surfaces with non-closed-loop channels and nanopillars continued to be superhydrophilic with the apparent contact angle (ACA) being zero, in accordance with the prediction of the Wenzel equation. However, on a special class of structured surfaces with closed-loop nanowalls/nanochannels, the water droplet exhibited unusual multiple Wenzel states (on which a water droplet exhibits  $\text{ACA} > 0^\circ$ ), which was not consistent with the prediction of the (modified) Wenzel

equation. We named these distinct multiple Wenzel states “topological wetting states” because their existence was attributed to the topology of the closed-loop nanowalls/nanochannels. Such topological wetting states are generic, regardless of the shape of the closed loops, due to the topological invariant (i.e., all closed loops entail the same topological genus value). The associated ACAs of water droplets in different topological wetting states were dependent upon other external conditions: initial location of the droplet perimeter, intrinsic adsorption energy of the surface toward the water molecule, and droplet size. There existed critical droplet sizes or critical ACAs beyond which metastable Wenzel states could be destabilized. In general, the critical ACA increased with increasing nanowall height and nanochannel width at the TCL, but exhibited negligible dependence upon the nanowall width. Mechanisms of the topological wetting and the transition between two neighboring metastable Wenzel states are discussed. The estimated time scales of the topological wetting states suggest that these metastable states are very likely to be observed in the laboratory. In closing, we conclude that this unusual topological-wetting phenomenon not only calls for reconciliation with the (modified) Wenzel equation but also stimulates development of new conceptions in surface chemistry in general and wetting thermodynamics in particular.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c07224>.

Benchmark MD simulation methods, supporting Figures S1–S10 and Table S1, and theoretical framework and deductions (PDF)

Movie S1. Behavior of a droplet on a flat surface (MP4)

Movie S2. Behavior of a droplet on a circle-loop structured surface (MP4)

Movie S3. Behavior of a droplet on a square-loop structured surface (MP4)

Movie S4. Behavior of a droplet on a rectangle-loop structured surface (MP4)

Movie S5. Behavior of a droplet on a triangle-loop structured surface (MP4)

Movie S6. Behavior of a droplet on a triangle-loop structured surface at a break at the side of the nanowall (MP4)

Movie S7. Behavior of a droplet on a triangle-loop structured surface at a break at the vertex of the nanowall (MP4)

Movie S8. Behavior of a droplet on a square-loop structured surface based on the SPC/E water model (MP4)

Movie S9. Behavior of a droplet on a flat surface based on the SPC/E water model (MP4)

Movie S10. Behavior of a droplet on a flat surface described by the mW model with water-surface H-bonding interaction (MP4)

Movie S11. Behavior of a droplet on a square-loop structured surface described by the mW model with water-surface H-bonding interaction (MP4)

Movie S12. Behavior of a droplet on a square-loop structured surface with the mW water model (MP4)

Movie S13. Behavior of a droplet on a flat surface with the mW water model (MP4)

Movie S14. Behavior of a droplet on a square-loop structured surface with the SPC/E water model (MP4)

Movie S15. Behavior of a droplet on a flat surface with the SPC/E water model (MP4)

Movie S16. Diffusion of a droplet on a square-loop structured surface, where the water droplet experiences brief relaxation and then diffuses along the surface of the nanowall (MP4)

Movie S17. Diffusion of a droplet on a square-loop structured surface, where the water droplet diffuses along the surface of the nanowall without showing a relaxation process (MP4)

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### Notes

The authors declare no competing financial interest.

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