# Atomistic Dewetting Mechanics at Wenzel and Monostable Cassie-Baxter States

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Water adhesion underlies wettabilities, and thus hydrophobicities, and defines surface properties like self-cleaning, icephobicity and many others. The nanomechanics of water adhesion, especially in the dynamic dewetting processes, has not been fully investigated. Here in this article, atomistic modeling and molecular dynamics simulations were utilized to probe the adhesion mechanics of water droplets on nanopillars and flat surfaces, covering dewetting at the Wenzel and the newly discovered monostable Cassie-Baxter states. The simulations were able to identify intermediate dewetting states on rough surfaces, resolve transition between wetting states under force. The results revealed characteristic features of dynamic water adhering stress underpining dewetting at nanoscale, which provided deepening knowledge on surface dewetting mechanics. This work complements nanoscale dewetting experiments for new fundamental insights in studies including nanoroughness design, enhanced oil recovery, anti-icing and others.

### Introduction

Water wetting is one of the most common phenomena in daily life. With the so-called Lotus effect became a known scientific term<sup>1</sup>, water wetting began to attract a large number of research interests, especially those focused on surface superhydrophobicity, self-cleaning and anti-icing<sup>2–6</sup>. It is proven that water wetting is a complex process greatly influenced by nanoscale roughness<sup>7–9</sup>. New discoveries on intriguing wetting dynamics, for instance directional and oscillating friction mediated water transport<sup>10–12</sup>, indicates new insights are always needed for a better understanding of the simple yet life-dependent matter, water.

Water wetting on a smooth surface is generally quantified by its contact angle (CA)<sup>13</sup>. Larger water contact angles indicate higher surface hydrophobicity. The balance of forces on the threephase contact line of a water droplet follows the classical Young's equation<sup>14</sup>. For wetting on rough surfaces, there are two wellaccepted water wetting states, namely the Wenzel (WZ) and the Cassie-Baxter (CB) states<sup>15,16</sup>. At the WZ state, a water droplet can invade into surface hierarchical structures, which leads to large contact area. In contrast, water droplets maintain their integrity at the CB states, and remain on top of rough surface topographies leaving the nanoscale grooves being dry. From a single water molecule point of view, the two wetting states are resulted from the energy difference between surface energy of the substrate and the molecular interactions among water molecules<sup>7,17</sup>. When water molecules energetically favor more in self association into the three-dimensional hydrogen-bonding network in water than in adsorbing onto certain solid surfaces, the CB state is then more favorable. It is known that the CB state is key to superhydrophobicity on natural materials surfaces, for instance the non-wetting property of lotus leaves<sup>2</sup>, flower petals<sup>18</sup>, beetle's back and water strider's leg<sup>19,20</sup>. The CB state might also lead to high water mobility, and many surprising properties that are desired for new surface technologies<sup>21–23</sup>. Thus, realizing stable CB states on surfaces with designed nanoscale topographies has been the same common focus of many successful bio-inspired researches<sup>24–27</sup>.

Maintaining the CB state of water drops on a rough surface is however highly challenging. Transition from the CB to the Wenzel states were observed, with the detailed underlying energy landscape even being quantified on specific systems<sup>28–31</sup>. It was speculated that the CB state was always metastable<sup>32</sup>, and transitions from WZ to CB were not possible<sup>33</sup>, unless with external energy input<sup>34–37</sup>. Although spontaneous transitions from the the Wenzel to the CB states were observed by theoretical approaches<sup>30,31</sup>, it is only until very recently that the first monostable CB state was created in experiments<sup>38</sup>, which revolutionized the understanding of wetting in general. It was found that the required nanoroughness for monostable CB state on nanopillars was:

$$(1-f)/(r-f) < -\cos\theta_r,\tag{1}$$

where f, r and  $\theta_r$  are surface fraction, roughness factor and water receding contact angle, respectively. Otherwise the wetting is the normally observed bistable state with the CB state being

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metastable, if:

$$(1-f)/(r-f) > -\cos\theta_E,$$
(2)

or the WZ state being metastable, if:

$$-\cos\theta_r < (1-f)/(r-f) < -\cos\theta_E, \tag{3}$$

where  $\theta_E$  is the water equilibrium contact angle<sup>38</sup>.

One fundamental question concerning water wetting awaits for fully investigation is the nanomechanics of water adhesion. Generally, analytical and empirical approaches were commonly employed for explaining experimental water adhesion results, which were rooted in the same classic continuum theories in the field <sup>15,16,39</sup>. For instance, Laplace pressure and energy gradient were used to explain water droplet migration on conical wires and silk fibers<sup>10,40</sup>. A complex framework of gravitational potential, local pinning and adhesion energy were employed to quantify the dynamics of sliding water droplets<sup>41</sup>, and to elucidate the superhydrophobicity of the self-cleaning lotus effect<sup>28</sup>. These studies commonly took a static analysis approach, and had difficulty in revolving details of the nanoscale mechanics in the dynamics process of dewetting. Utilizing continuum mechanics based approaches, for example finite-element analysis with cohesive zone model, it is still not possible to capture the mechanical characteristics of nanoscale water adhesion. Furthermore, wetting phenomena on nanoscale could notably deviate from classical predictions<sup>42</sup>, which is critical to multiple nanodevices aimed for tailored hydrophobicities<sup>43-45</sup>. Studies on this respect are still limited.

This study focused on the nanomechanics in the process of dewetting a nanoscale water droplet from flat and nano-textured surfaces, and importantly at varied wetting states including the newly discovered monostable CB state. Pulling forces were used in atomistic modeling and simulations for probing water droplet adhesion that was not covered in other studies focusing on spontaneous wetting transitions or water film dewetting  $^{29,30,46}$ . The simulations provided theoretical and quantitative references of nanoscale mechanics for experiments in manupulating water droplets for different purposes,  $^{47-49}$  and for future multiscale studies on dewetting studies involving nanoscale water adhesion in nanoroughness design, water transport in nanochannels in enhanced oil recovery, water thin film for ice adhesin in anti-icing, biosensing and many others  $^{43,50-53}$ .

## Methods

This study concentrated on accessing water adhesion mechanics in nanoscale dewetting using atomistic modeling and Molecular Dynamics (MD) simulations. The atomistic models of substrates included flat and rough solid surfaces for water adhesion at varied wetting states, which were comparable to former studies on spontaneous wetting transitions and water film dewetting <sup>29–31,42,46</sup>. The main effort of the work, however, was devoted to probe the nanoscale water adhesion mechanical quantities, and dewetting mechanism on surface nanotopographies.

#### Atomistic models

One key factor defining water wetting is the surface energy. On rough nanotopographies, higher surface energy leads to the WZ state, while lower ones favor the CB state<sup>13,15,39</sup>. Silicon was chosen for creating substrates, flat surface and nanopillars, representing high surface energy in this study, with atomic parameters adopted from the OPLS force field<sup>54</sup>. Specifically, all the silicon atoms were electrically neutral, and interacted with water molecules only by van der Waals forces. The surface energy of the silicon substrates was determined by the energy well depth,  $\varepsilon$ , of the silicon atoms. The detailed atomistic parameters are given in Table. 1. Similar to former studies<sup>29-31</sup>, a new atom type with a much lower  $\varepsilon$ , termed C9, was chosen for parameterizing substrates with low surface energy. For the sake of simplicity, the substrates with C9 atoms used the same atomistic structures of the silicon substrates, and served as counterparts for comparing water adhering mechanics. The  $\varepsilon$  value of the C9 atoms, 0.29288 kJ/mol/nm<sup>2</sup>, was borrowed from the fusion carbon number 9 that only connects to other carbon atoms in naphthalene molecule in OPLS force field 54.

Flat substrates and nanopillars were then modelled using the two atom types, as shown in Fig. 1. Two periodic flat substrates of silicon and C9 atoms were built with the (100) surface for water adhesion. Both the two flat substrates had a thickness of 1.0 nm and a surface area of  $22.27 \times 22.54$  nm<sup>2</sup>, as shown in Fig. 1(A) and Suppl.Fig. S1(A). Each substrate consisted of 28224 atoms. Cylinder nanopillars with (100) surface on their tops were constructed with the two atoms types, silicon and C9. All the nanopillars had the same radius (*l*) of 1.5 nm. As examples shown in Fig. 1(B) and Suppl.Fig. S2, periodic nanopillar arrays were created with nanopillars of the same height (*h*) and inter-space distance (*d*) for varied nanoscale surface topographies (see below). It was the purpose of this study to realize the WZ state on silicon nanopillars, and the monostable of CB state on C9 nanopillars.

**Table 1** Van der Waals parameters of radius ( $\sigma$ ) and energy well depth ( $\varepsilon$ ) used for two substrate atom types.

atom type	σ (nm)	$\varepsilon$ (kJ/mol/nm <sup>2</sup> )
silicon	0.33855	2.44704
C9	0.33855	0.29288

There are a number of transferable water models available for building aqueous environment<sup>55</sup>. It was not our intention to compare the detailed difference of adhesion mechanics of these models, but rather the general water adhesion mechanics. We here only chose one of the 4-site water model, tip4p, for modeling water droplets in this study<sup>55</sup>. A spherical water droplet consisting of 50066 tip4p water molecules (200,264 atoms) were used for wetting and dewetting simulations. The water droplet had a diameter of ~14.5 nm, as the snapshot shown in Suppl.Fig. S1(B), which reach the biggest system size our computers can handle. In order to enable a fast water absorption in the simulations, the water droplets were positioned as close as possible to the substrates, nanopillars and flat surfaces, initially and at the same time without atomic overlap.



**Fig.** 1 Atomistic models and simulation setup this study. (A) top view of the flat silicon substrate. (B) silicon nanopillars with uniform height of 2 nm. (C) a slab of water droplet on flat silicon substrate for determining intrinsic water contact angle. (D) schematic simulation setup of pulling a water droplet from silicon nanopillars. (B) and (C) share the same coordinate system indicated in (D). Periodic simulation boxes are shown in green.

#### Simulations

In order to follow the design principle of nanotopographies for realizing the Wenzel and the monostable CB wetting states given in Eqn. (1) and (2), the equilibrium CA on flat silicon( $\theta_E$ ) and receding CA ( $\theta_r$ ) on flat C9 substrates should be first determined. It was known that the CA's of nanoscale water droplets in MD simulation systems were system-size dependent because of the nonnegligible line tension at the three-phase contact line<sup>56</sup>. In order to avoid building multiple systems with varied water droplet sizes for determining the macroscopic CA's by extrapolation, we here followed another approach of using thin slab of water droplets in a periodic simulation box for evaluating the water CA's on the two flat substrates 57. As a system snapshot shown in Fig. 1(C) and simulation details given below, the contact line at the threephase area was straight and thus was free of curvature line tension found in dome-shaped water droplets. The CA can then be evaluated by fitting the projection of water slab on the y-z plane of the simulation box. It was found that the CA value obtained in this way was comparable to experimental results<sup>57</sup>.

For probing the equilibrium CA's ( $\theta_E$ ), a slab of water droplet contained 17448 water molecules (69792 atoms, including dummy atoms) was let to adsorb onto two periodic strips of silicon and the C9 substrates, as the initial and final adsorped system snapshots shown in Suppl.Fig. S3 and Fig. 1(C), respectively. The two substrates consisted of 6720 atoms and had the same geometry, namely a thickness of ~1.2 nm, a width of ~2.2 nm and a length of ~45.6 nm. We note that the water droplets and the simulation systems are much larger than the ones used in former studies<sup>29–31</sup>. The periodic simulation boxes had the same dimensions to the substrates on *x* and *y* direction but 30 nm on *z* direction, as shown in Fig. 1(C), which guaranteed no interaction between the water droplets and their periodic images under the non-bonded cutoff scheme of 1 nm in all the simulations.

All the simulations, including equilibration for calculating CA's and the following force-probe MD simulations, were carried out using the package GROMACS 5.0.7<sup>58</sup>. Before carrying out MD simulations, all the atomistic structures were energy minimized utilizing the steepest descent algorithm to remove any possible close atom contacts in the simulation systems. The nonbonded interaction cutoff distance in all the systems was set to be 1.0 nm. To account for the long-range electrostatic interactions, the particle-Eward method was applied in all simulations<sup>59</sup>. The LINC algorithm was employed to constrian bond vibration in the water molecules for enabling a longer time step of 0.002 ps<sup>60</sup>. All the substrates were fixed in position in the systems during the simulations. All the simulations were performed in the NVT ensemble at a temperature of 255 K, which is higher than the melting temperature of the tip4p water model<sup>61,62</sup>. The Nosè-Hoover coupling method was used to maintain the temperature of the water droplets with a coupling time constant of 0.4  $ps^{63,64}$ . During all simulations, atomic trajectories of the systems were collected every 5 ps for analysis.

The slab of water droplets were then let to freely adsorb onto the substrates in equilibration simulations of 50 ns. It was found that the water droplet was able to achieve stable  $\theta_E$  in 20 ns. The last 20 ns of the equilibration simulation on silicon was then used to calculate the average  $\theta_E$ . The  $\theta_E$  of the slab water droplet on the silicon substrate was found to be  $55.2\pm5.1^{\circ}$ . In order to obtain the receding CA's ( $\theta_r$ ) of water on the C9 substrate, the system snapshot of slab water droplets adsorption on C9 substrate at 50 ns simulation time was subjected to shearing force using the force-probe MD simulation method<sup>65</sup>. Similar to a former study on ice adhesion<sup>66</sup>, the center of mass (COM) of the slab water droplets was attached a virtual harmonic spring with a force constant of 500 kJ/mol/nm<sup>2</sup> in the simulations. Shear force was applied on the slap of water droplets by pulling the virtual spring at constant rate parallel to the C9 substrate surface along the y direction of the simulation box. Given the large atom number in the simulation systems, a spring pulling rate of 0.2 nm/ns was chosen in the shearing simulations and also the following dewetting simulations. The length of the shearing simulations was 50 ns, with last 40 ns being used for calculating the  $\theta_r$ . The  $\theta_r$  of the water droplet on the C9 substrate was found to be  $126.8\pm5.4^{\circ}$ . The values of  $\theta_E$  and  $\theta_r$  obtained were then used as references for selecting different heights (h) and inter-space distance (d) of nanopillars for realizing the WZ and the monostable CB states on silicon and C9 nanopillars, respectively.

The WZ wetting state was expected on the silicon nanopillars, given that the  $\theta_E$  was found to be  $55.2\pm5.1^\circ$  and  $-cos(\theta_E)$  being negative. However, realizing the monostable CB state on the C9 nanopillars was as challenging as in the former experimental study<sup>38</sup>. The  $\theta_r$  on the C9 substrate was  $126.8\pm5.4^\circ$ , and thus  $-cos(\theta_r) = 0.60$ . For the sake of simplicity and at the same time following the conditions given in Eqn.(1) and (2), the inter-space distance (*d*) was kept to be 4 nm in all the periodic nanopillar arrays, while only the height of nanopillars varied between  $2\sim18$  nm in this study, as shown Suppl.Fig. S2. As the parameter sets of the nanopillar geometry given in Table. 2, one

can see that the monostable CB wetting state can be expected the C9 nanopillar systems of different heights. The nanopillars used in this study contained atom number ranging from 12246 to 110376, as all the atomistic structures shown in Suppl.Fig. S2. It should be noted that it is the purpose of this study to model the nanopillars without an underneath supporting flat layer, but separating into nanopillars and flat surfaces. In such a way, it should be easier for clarifying the contribution of the two in dewetting mechanics. Dewetting on the nanopillars in this study thus was comparable to dewetting water droplets trapped in nanopillars but not touching the supporting layer of the nanopillars in the former studies<sup>31</sup>. Nevertheless, dewetting simulations of water droplets at the WZ state and touching the nanopillar supporting solid layer was provided in the supporting materials, serving as comparison for notifying the differences in water adhering mechanics.

**Table 2** Geometry of periodic cylinder nanopillars chosen for realizing the WZ and the monostable CB states. The pillar radius (*l*) and spacing distance (*d*) determine the surface fraction  $(f = \pi l^2/(l+d)^2)$ , and with pillar height (*h*) determine the roughness factor  $(r = 1 + 2\pi rh/(r+d)^2)$ .

<i>h</i> (nm)	<i>l</i> (nm)	<i>d</i> (nm)	f	r	(1-f)/(r-f)
2	1.5	4	0.23	1.62	0.55
4	1.5	4	0.23	2.25	0.38
6	1.5	4	0.23	2.87	0.29
18	1.5	4	0.23	6.61	0.12

Adsorption of water droplets onto individual substrates were carried out by equilibration simulation up to 50 ns, using the same simulation parameters in determining equilibrium water CA's above. The final system snapshots of the water droplets on their substrates, nanopillars and flat surfaces, were adopted for performing force-probe MD simulations<sup>65</sup>. As depicted in Fig. 1 (D), pulling force was applied onto the water droplets by the displacement between the spring and the COM of the water droplets. Force-probe MD simulation for accessing water adhesion mechanics used the same simulation parameters in determing receding CAs, with additional pulling force on the z direction of the simulation box. In order to accomodate the moving virtual spring, the simulation boxes in the z direction were enlarged to ensure dewetting events. 5 independent detaching simulations were carried out for each system, with simulation length depending on the water adhesion strength. It should be noted that the wetting behavior and adhesion mechanics are intrinsic properties of water, yet the absolute value of force obtained in our force-probe simulation can be sensitive to the spring pulling rate. It had been reported that force increased logarithmically with pulling loading rate<sup>67</sup>, and was observed in studies using similar approaches<sup>66,68,69</sup>. In order to clarify this pulling rate dependancy, detaching water droplets from flat silicon and C9 surfaces with pulling rate of 2 nm/ns and 0.02 nm/ns to compare with pulling rate of 0.2 nm/ns used in this study, as shown in Suppl.Fig. S4. For detaching the water droplet from the flat silicon substrate using the low pulling rate of 0.02 nm/ns, it took simulation time of more than 500 ns for an individual simulation. In total, we accumulated simulation trajectories of  ${\sim}5~\mu s$  for this study.

The pulling forces on the water droplets were collected every 5 ps in the course of the force-probe MD simulations for quantifying the atomistic adhesion mechanics of water on nanopillars and the flat surfaces. Specifically, the contact area,  $A_{contact}$ , of the water droplets and their substrates were calculated by the accessible surface areas <sup>70,71</sup>:

$$A_{contact} = 0.5 \times (SA_{droplet} + SA_{substrate} - SA_{system}), \qquad (4)$$

where  $SA_{droplet}$ ,  $SA_{substrate}$  and  $SA_{system}$  are accessible surface areas of the water droplet, the substrate and the whole system, respectively. The water adhering stress was obtained by normalizing the force observed in the dewetting simulations by the contact area:

$$\sigma_d = F_{detach} / A_{contact}.$$
 (5)

Here the subscript d denoted that the stress was a dynamic quantity changing during the dewetting process.

# **Results and discussion**

The results included firstly the realization of the two wetting states on the designed nanopillars, and secondly water droplets dewetting mechanics under force from nanopillars and flat surfaces.

#### Wetting states on nanopillars

The water droplets were able to fast adsorb onto the silicon and C9 pillars nanopillars, given that they were placed close to the top of the nanopillars initially. After adsorbing, the droplets maintained at the CB state on all the C9 nanopillars during 20 ns equilibration simulations, as an example snapshot shown in Suppl.Fig. S5. This result was expected by the design of the C9 nanopillars followed by Eqn. 1. Yet the CB state on the C9 nanopillars was not neccessarily monostable, unless the evidence of spontaneous transition from the WZ to CB state of a water droplet on the C9 nanopillars was observed.

The droplet continued to invade into the inter-space of the pillars after adsorbing onto the tops of the silicon nanopillars. The detailed dynamics of this process on the 18 nm height silicon nanopillars was shwon as example in Fig. 2. As can be seen by the Z-coordinates of its COM migration trajectory shown in 2(B), the droplet gradually moved into the nanopillars in ~20 ns, and reached a stable position with almost all the body of the droplet in the inter-space of the nanopillars. With another 20 ns simulation time, the droplet stayed at the same postion without further migration, and had a very small potion of water molecules remained above the top of the pillars (middle, Fig. 2(A)). Such small potion of water molecules were found to be critically importantly for enabling the transition from the WZ to the CB state<sup>31</sup>.

The system snapshot of the droplet final state at 40 ns simulation time in the silicon nanopillars was taken to probe the spontaneous transition from the WZ to CB state. Specifically, the simulation was carried on with atomic properties of silicon nanopillars being switched to C9 without changing any other simulation parameters. As depicted by the droplet COM Z-coordinates af-



**Fig. 2** Water invasion into 18 nm silicon nanopillars and spontaneous transition to monostable CB states on C9 nanopillars. (A) snapshots of the simulation system from left to right showing water droplet above the silicon nanopillars initially, the final stable adsorbed water droplet in the nanopillars, and the droplet at monostable CB state on the C9 nanopillars, respectively. Periodic simulation boxes are shown in green. (B) The Z-coordinate of the COM of the droplet in the simulation. 0 in the Z-coordinate corresponds to the top of the nanopillars. The mutation point of silicon to C9 is indicated by a blue bar in the plot. The circled numbers indicate the same corresponding positions of the coordinate and the snapshot in the simulation trajectory.

ter switching to C9 nanopillars (Fig. 2(B)), the droplet promptly gained velocity and moved upward along the pillars. It took the droplet  $\sim$ 6 ns to fully run out the inter-space of the nanopillars and reached the CB state found on all other C9 pillars, with migration dynamics similar to former studies  $^{29-31}$ . Because the water droplet used in this study is much larger that the ones in former studies, the droplet migrated with contact of multiple nanopillars at all time rather than only along a single nanopillars<sup>30</sup>. Comparing to sub-nanosecond spontaneous transition time found in former studies<sup>30,31</sup>, the water droplet took relatively longer time to complete the WZ to CB transition, which can be attributed to the much larger droplet size. The same result of spontaneous transition was observed in all the other systems with nanopillars of 2 nm, 4 nm and 6 nm heights, as shown in Suppl.Fig. S6. Because of the relatively shorter pillar heights and thus smaller inter-pillar space, only part of the whole water droplet invaded into these nanopillar, which led to shorter time to reach the final equilibrium WZ state and shorter spontaneous transition time to the CB state. In all these simulations, the spontaneous transitions were obtained without any external energy input, which was the same phenomenon observed in experiments<sup>38</sup>. The addition of a solid supporting silicon layer underneath the silicon nanopillars did not alter the results. As shown by Suppl.Fig. S7, the nanopillar supporting layer resulted in almost negligible delay in the transition from the WZ to the CB state. These results confirmed that the CB state on all the C9 pillars was monostable, and the success of the nanopillar geometry design in this study. Here it should be noted that it is not the purpose of this study to probe the energy landscape of water wetting transition on nanoscale topographies, but rather realization of two wetting states for studying water adhesion mechanics.

#### Dewetting mechanics on nanopillars

The water droplets on the silicon and C9 nanopillars were subjected to pulling force for accessing nanoscale dewetting mechanics from the WZ and the monostable CB states, as schematic simulation setup depicted in Fig. 1(D). It is known that external energy is needed to dewet water droplets at the WZ state  $^{31,33-37}$ . In the current simulation scheme, higher force was expected to dewet the water droplets at the WZ state in the silicon nanopillars than at monostable CB state on the C9 ones. It was indeed the case when compared the force profiles obtained in the dewetting process on silicon and C9 nanopillars with the same heights, as exemplified by the 2 nm height nanopillars shown in Fig. 3. The water droplets were found to slide out of the silicon nanopillars under increasing pulling force at the first stage of dewetting (Fig. 3(A)). Interestingly, the water droplet remained to adhere to the tops of the silicon nanopillars, which resulted in obvious intermediate states before the droplet being fully detached from the substrate. As can be seen in Fig. 3(B), the intermediate states during the dewetting were marked by short plateaus in the last section of the force profile. These intermediate states corresponded to water adhering on different number of nanopillars at the top surface, and could be regarded as CB wetting states under force. It was surprising that the force profile obtained in non-equilibrium pulling could signify these intermediate states, which was only possible with the sufficiently slow pulling rate in the simulation and the net kinetic energy of the whole water droplet was lower than the adhering potential at these states. As discussed in the Methods section, this result revealed the detailed effect of nanopillars in dewetting nanomechanics. Such effect could be difficult to uncover if the nanopillars has a supporting solid layer, especially in cases that the supporting layer is as hydrophilic as silicon. As shown in Suppl.Fig. S8, the strong interactions between silicon and the water molecules stop the droplet being fully dewetting from the nanopillars with an underneath supporting atom layer. Instead, the water droplet broke into two smaller droplets under pulling force in all five independent simulations, leaving one of which firmly adsorbed on the substrate in the WZ state.

Comparing to their counterparts, it required much lower force to detach water droplets from the C9 nanopillars of different heights, as shwon by Fig. 3(B). Because the water droplets on all the C9 nanopillars were at monostable CB state, the maximal pulling force observed in the detaching force profiles were lower. The water droplets were found to quickly decrease their anchoring points, number of C9 nanopillars tops, and then being detached from the substrate, as example snapshots shown in Suppl.Fig. S9.

The adhering stress of the water droplets on silicon nanopillars



**Fig. 3** Dewetting on silicon nanopillars of 2 nm height. (A) representative subsequent snapshots of the simulation system at different stage of dewetting. (B) force profiles obtained in dewetting on silicon (black) and C9 nanopillars (red). The periodic simulation box is shown in green. (C) dynamic adhering stress of the water droplet on on silicon (black) and C9 nanopillars (red). The circled numbers in (A) and (B) indicate the same corresponding positions of the force profile and the snapshot in the simulation trajectory.

in the dewetting process was complicated. The force observed before the water droplets finishing migrating to the top of the nanopillars was a combination of shearing force and normal adhering force, because the water droplet were experiencing friction force from the sides of and adhering force from the tops of the nanopillars at the same time. The force reduced to only normal adhering force when the water droplets fully pulled out of the inter-pillar space and at the intermediate states before being detached. In order to quantify the adhering stress, the detailed difference between shearing and normal adhering force was disregarded. As indicated by Eqn. (4), the adhering stress ( $\sigma_d$ ) was obtained by normalizing the the total force observed at any time point of the simulation by the total contact area between the water droplet and the nanopillars including the side and top areas. As shown in Fig. 3(C), the water droplet adhering stress during the dewetting process from both wetting states featured a steady increase, and an abrupt jump resulted from droplet detachment. Although the adhering stress showed a linear increase pattern indicating the gradual migrating of the water droplet out the silicon nanopillar inter-space, it did not clearly resolve the intermediate CB states before droplet detachment.

When comparing all the nanopillars, the dewetting force profiles were similar on C9 nanopillars, given that all the water droplets were sitting on the tops of the pillars initially. In contrast, the dewetting force profiles deviated on different silicon nanopillars, because the droplets at WZ wetting state were at varied depth in the silicon nanopillars inter-space (Fig. 2 and Suppl.Fig. S6). The percentage of water molecules trapped in the inter-space of different nanopillars ranged from 5.6~99.2%, as given in Table 3. As shown in Fig. 4, all of the dewetting force profiles on silicon nanopillars featured an initial increase for enabling the droplet migration, and intermediate states where droplet adhered to the top of nanopillars before detachment. The highest force values observed for dewetting from nanopillars of 2 nm was more than 50% lower than from the other three systems (Table. 3). As can be seen in Fig. 4(A) and Table. 3, the percentage of water droplet initially trapped in the inter-space of nanopillars of 4 nm was only 30%, the highest force (1.69 $\pm$ 0.01 nN) in dewetting was already close to the peak value of 1.85±0.02 nN for dewetting on nanopillars of 18 nm with 99.2% of the water droplet in the pillar inter-space. This result indicated that the highest force required for dewetting a droplet even with less than 50% of its volume in the inter-space of nanopillars could be as high as the critical force value for dewetting a full water droplet in the inter-space of nanopillars.



**Fig. 4** Representative force and adhering stress profiles of water droplets on silicon nanopillars of different heights. Corresponding force and adhering stress profiles obtained from the same simulation trajectory and system in (A) and (B), respectively, share the same color. The heights of the silicon nanopillars are shown as legends. (A) and (B) share the same X-coordinate and legends.

The water droplets on taller nanopillars took more time to slide along the nanopillars from the WZ to CB state, and resulted high force plateaus especially on the 18 nm silicon pillars. As shown in Fig. 4(A) (blue curve), the force profile obtained from dewetting on 18 nm height silicon nanopillars demonstrated an outstanding flat portion at high force value. Such high force plateau was a signature of high energy input in the dewetting simulation. By integrating the pulling force on the dewetting pathway, the

mechanical energy input for dewetting the water droplets on all nanopillars were given in Table. 3. The energy needed for dewetting on the 18 nm nanopillars was one order of magnitude higher than its other three counterparts. Such high energy input signified high energy barrier for wetting transition, and agreed with former studies results that the energy barrier between the WZ to CB state can be as high as 10  $K_BT$ , where  $K_B$  is the Boltzmann constant and T is the temperature<sup>31</sup>. The adhering stress profiles on all silicon nanopillars shared a similar pattern, namely a linear increase at the early dewetting stage, higher stress at intermediate CB states and followed by a abrupt jump due to droplet detachment. It is worth noting here again that the absolute value of force obtained in the simulation was dependent on the pulling rate<sup>66–69</sup>, but the dewetting mechanics of a water droplet either from the silicon and C9 nanopillars should be intrinsic to water and the wetting states.

**Table 3** Force and mechanical energy in dewetting water droplets at WZ state from nanopillars of different heights. The height of nanopillars (h), percentage of water droplets (%) in the inter-space of nanopillars, the highest pulling force (F) observed in dewetting and the energy input (E) for dewetting are given in the table.

%	F (nN)	E (10 <sup>3</sup> kJ/mol)	
5.6	$1.08{\pm}0.02$	$2.07{\pm}0.04$	
30.0	$1.69{\pm}0.01$	$5.15{\pm}0.02$	
45.3	$1.77{\pm}0.02$	$6.76 {\pm} 0.03$	
99.2	$1.85{\pm}0.02$	$15.50{\pm}0.06$	
	% 5.6 30.0 45.3 99.2	%         F (nN)           5.6         1.08±0.02           30.0         1.69±0.01           45.3         1.77±0.02           99.2         1.85±0.02	

#### Dewetting on flat surfaces

Dewetting simulation of the water droplets from flat silicon and C9 substrates were performed for comparing the adhering mechanics obtained on nanopillars above. The same simulation parameters and spring pulling rate were used in flat surface dewetting. Because the flat silicon surface had much higher surface energy than its C9 counterpart, the water droplet was more adsorbed onto the silicon surface and thus had a lower CA, as simulation snapshots shown in Suppl.Fig. S10. After equilibration simulation of 50 ns, the same size of water droplets were stably adsorbed onto the two flat substrates. The interaction potential of the droplet with the silicon surface ( $\sim$ -1.48×10<sup>4</sup> kJ/mol) was about 2 orders of magnitude lower than with the C9 surface ( $\sim$ -7.14×10<sup>2</sup> kJ/mol).

Given the strong adsorption potential of the droplet on flat silicon surface, high pulling force and spring pulling distance were expected to detach the water droplet. As example snapshots shown in Fig. 5(A), the water droplet showed a shape changing from dome-shape at the beginning of the dewetting process, to bulb-like under high pulling force, and finally spherical after detaching from the silicon surface. The water droplet was fully detached from the silicon flat surface in all 5 independent simulations. The pulling force observed correspondingly showed an interesting feature during the dewetting process. As depicted in Fig. 5(B), the pulling force first steadily increased to a highest peak, and then slowly decreased again to a much lower value before a sudden drop indicating droplet detachment. The detaching



Fig. 5 Dewetting on flat surfaces. (A) example subsequent system snapshots of dewetting a water droplet from flat silicon surface. (B) force profiles of dewetting on flat silicon (black) and C9 (red) surfaces. (C) adhering stress of the water droplet on flat silicon (black) and C9 (red) surfaces in dewetting. The circled numbers in (A) and (B) indicate the same corresponding positions of the force profile and the snapshot in the simulation trajectory.

of water droplets from surface of high energy was thus markedly different from rupture of rigid molecular stucture like proteins or ice, where the pulling force first steadily increased to a highest value and then was directly followed by a sharp stucture broken down<sup>66,68,72</sup>. The detaching process of the water droplet from the flat C9 surface is less dramatic. The pulling force increases to a short plateau and then suddenly drops to zero because of droplet detachment (Fig. 5(B)). The highest force peak observed in the force profile was one order of magnitude lower than its counterpart. Because of smaller contact area and lower attraction between the droplet and the C9 surface, the droplet maintained almost identically spherical before and after detachment from the substrate.

The adhering stress,  $\sigma_d$ , of the water droplets on flat surfaces was purely resulted from normal adhering force. Similar to what was observed in dewetting from silicon nanopillars, the adhering stress obtained from dewetting from flat silicon surface also showed a linear increase as shown in Fig. 5(C), even at the second half of the dewetting simulation where the pulling force was starting to decrease (Fig. 5). Before the detachment event of the water droplet, the adhering stress showed obvious fluctuation at high value, followed by final jump because of the fast decrease in the already very small contact area. The detaching stress profile observed on flat C9 surface only featured the same sharp increase during the detachment of the water droplet.

In order to further investigate the adhering mechanics of the water droplets on the flat silicon surface, snapshots of the simulation system were first taken before, close to and after the highest force peak, as well as right before the droplet detachment. These system snapshots at different detaching states were subjected directly to force-clamp MD simulations<sup>65</sup>, in which the pulling forces at each point were held constant without changing any simulation parameters. Each force-clamp simulation lasted 50 ns as long as detachment event of the water droplet did not

occur. As details shown in Suppl.Fig. S11, detachment event of the water droplet only occured under high constant pulling forces very close to the peak value. Otherwise the water droplet remained adhering to the silicon substrate under lower forces. Remarkably, resorption events of the water droplet were observed in the system snapshots after the highest force peak and close to droplet detachment (Suppl.Fig. S11(B)). There were two forces resisting the droplet detachment, namely droplet shape deformation (increasing droplet surface area) and water-substrate adhesion (decreasing substrate contact area). The results showed that there was an upper-bound of pulling force that over-power the two forces and leads to water droplet detachment, and this upper-bound was close to the highest force value found in the force profile. The droplet detachment event was not fully depended on the pulling distance because of the fluid property of the water molecules. The water droplet was able to resorb back to the flat substrate under constant force despite of only a very small contact area with the substrate. Because the SI substrate is hydrophilic ( $\theta_E = 55.2 \pm 5.1^\circ$ ), individual water molecules in the droplet favor moving closer to the substrate (increasing substrate contact area) without constant loading (net energy input to compensate the decreasing interaction between water and the substrate), which led to droplet resorption.

# Conclusion

Theoreticl understanding of water wetting is generally on continuum mechanics scale, and based on Young's equation<sup>13</sup>. Nanoscale water dewetting mechanics, especially the dynamic process on nano-topographies, is difficult to study by empirical and analytical approaches. Here, atomistic modeling and molecular dynamics simulations with pulling force were employed to reveal the details of adhering mechanics of a water droplet on nanopillars and flat surfaces with varied surface energy. It is important to quantify and distinguish the fluid dewetting mechanics of water droplets at the WZ and the newly discovered monostable CB states, which can supply basis for multiscale studies, for instance finite element analysis, on dewetting phenomena. It is interesting to find that the pulling force observed during the dewetting can resolve the intermediate CB states of a water droplet. Generally, high value of stress was observed at high loading of pulling force during the failure of a molecular structure or a solid interface <sup>66,68</sup>. The change of droplet shape during the dewetting process can have an interesting effect on water adhering stress, namely the highest stress is not corresponding to the highest pulling force, but rather right before the droplet detachment event under much lower force value.

The results of this work detailed the mechanical effects of surface nanoscale topographies, nanopillar and flat surface, on water adhesion separately. It should be noted that the detaching mechanics of water droplets from the SI nanopillars is relevant to wetting state where droplets are trapped in the nanopillars without touching the supporting base of the nanopillars, a situation can occur when the diameter of the droplet is smaller than the height of the nanopillar<sup>31</sup>. Such results could also apply to experiment system when hydrophilic nanopillars on highly hydrophobic base. This study on water adhering mechanics compensate studies by analytical approaches and experiments in surface wettabilities, and fulfills a missing theoretical piece in understanding water adhesion. This study mainly considered single value of nanopillar separation distance and cylinder pillars. It is suggested that other nanoscale roughness parameters, such as different nanopillar geometries, had significant effects on water adhesion interfacial energy<sup>73</sup>. Further modeling and simulations are still needed for revealing such effects in the future dewetting studies.

## Acknowledgments

The authors gratefully acknowledge the support from the Research Council of Norway through the FRINATEK project Towards Design of Super-Low Ice Adhesion Surfaces (SLICE, 250990). The computational resources were provided by Norwegian Metacenter for Computational Science (NOTUR NN9110k and NN9391k).

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