Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials

Atomistic Dewetting Mechanics of Wenzel and Monostable Cassie-Baxter States

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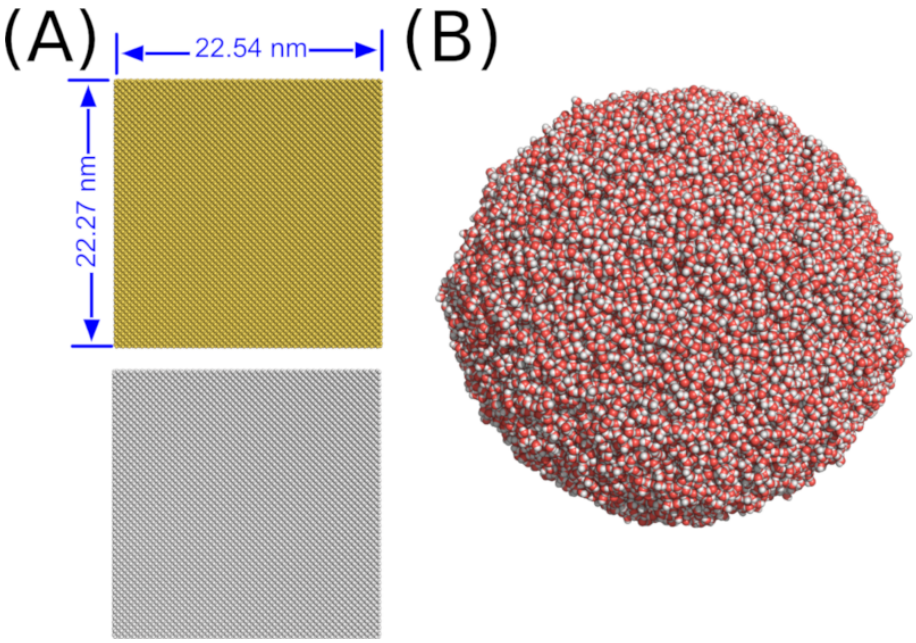
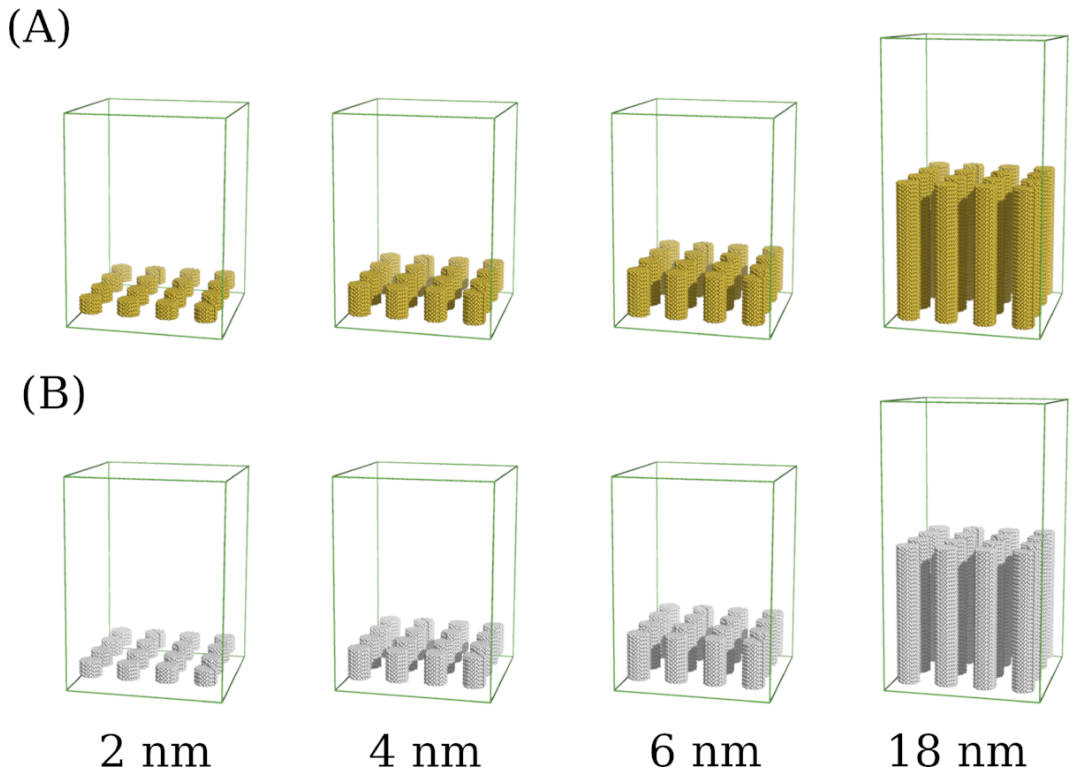
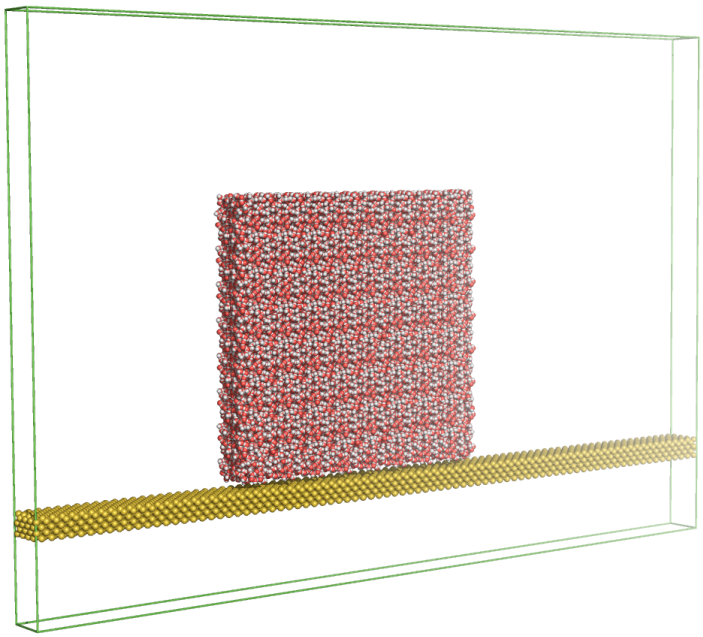
Supplementary Figures



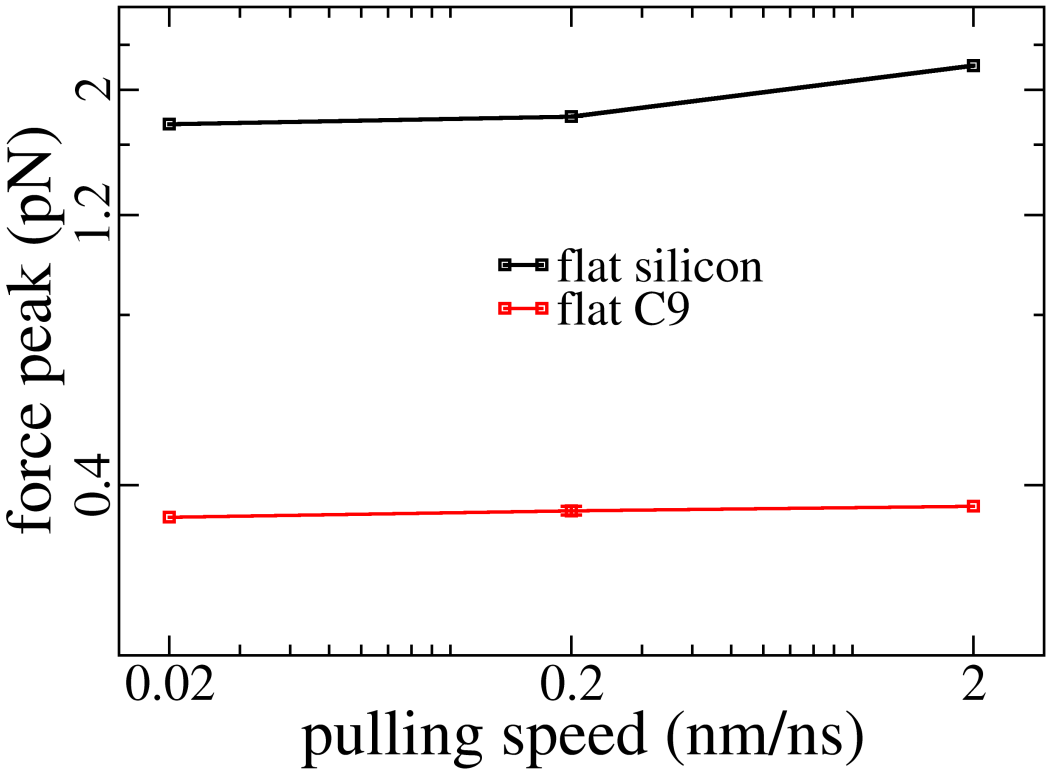
Supplementary Figure S1: **Atomistic models of flat substrates and the water droplet.** (A) top views of the flat silicon and the C9 substrates. Both substrates have the same thickness of 1 nm. The two substrates have the same surface area, as the dimension indicated in the figure. (B) the water droplet model consists of 50066 tip4p water models (200,132 atoms in total).



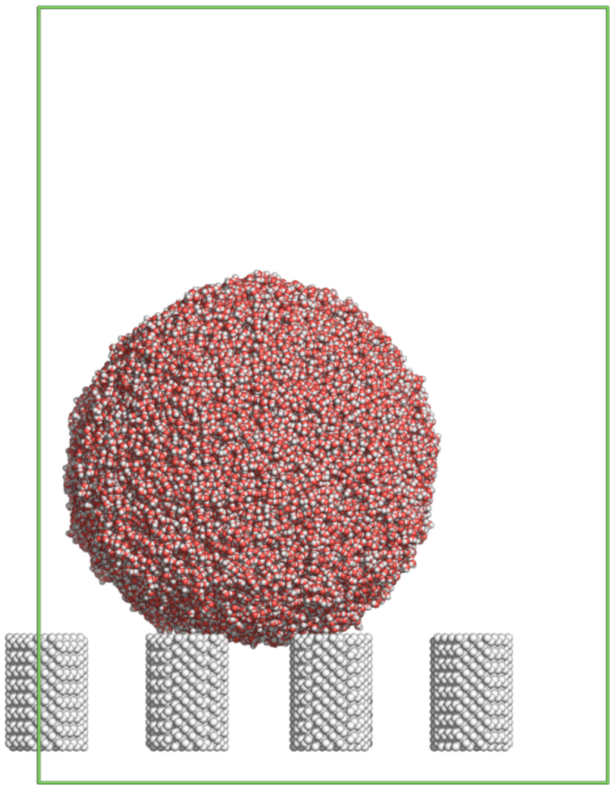
Supplementary Figure S2: **Nanopillars.** (A) periodic silicon nanopillars (gold) in simulation boxes. (B) periodic C9 nanopillars (grey) in simulation boxes. All the simulation box are periodic and shown in green. The heights of the nanopillars are given in the figure.



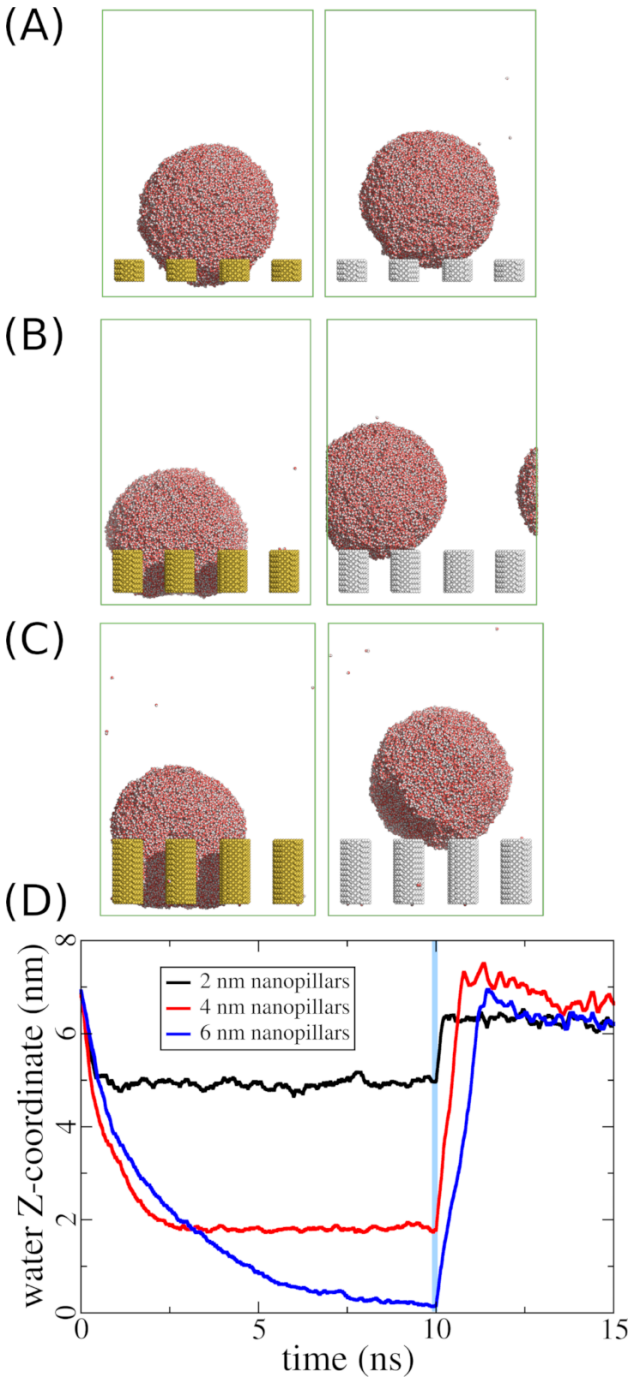
Supplementary Figure S3: **Initial system snapshot of the slab water droplet on silicon surface.** The the water slab has the same thickness as the substrate stripe and the periodic simulation box.



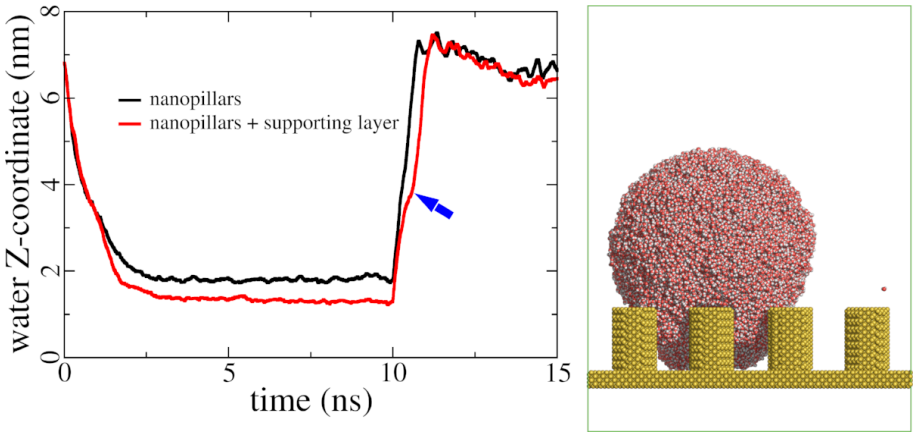
Supplementary Figure S4: **Pulling-rate dependancy of the highest force observed in the force profiles.** The highest force observed in each force profiles were obtained from detaching water droplets from flat surfaces of silicon and C9. The data points at 0.2 nm/ns is the mean value from 5 independent simulations, with error bars showing standard deviations. Each data point at 2 and 0.02 nm/ns was obtained from 1 simulation.



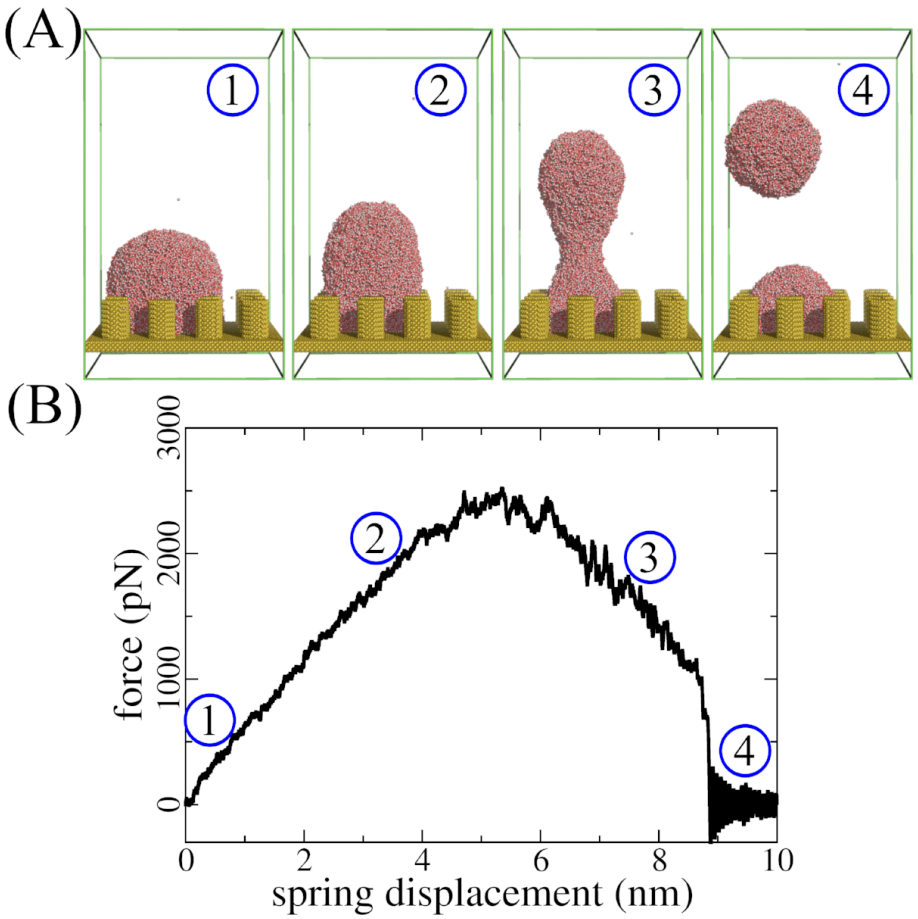
Supplementary Figure S5: **Representative snapshot of the water droplet on 4 nm C9 nanopillars at the monostable CB wetting state.**



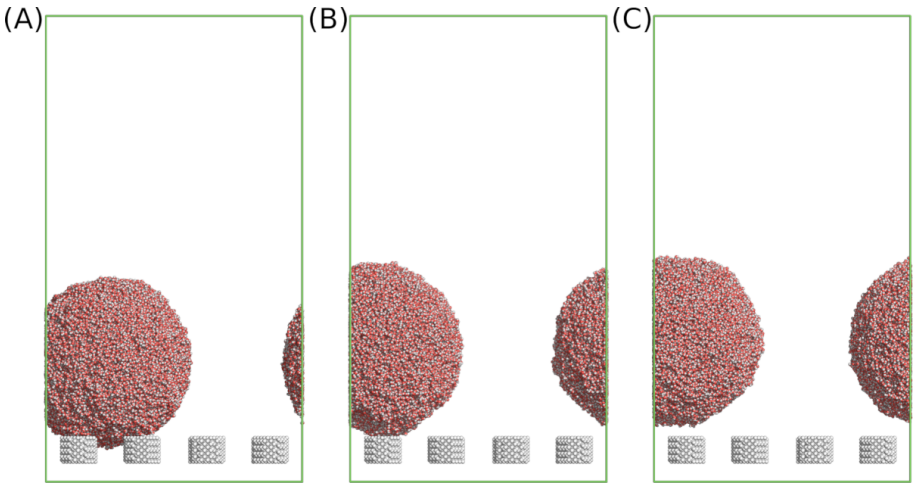
Supplementary Figure S6: **Wetting of the water droplet on the silicon nanopillars and spontaneous transition to the monostable CB state on the C9 nanopillars.** (A) the water droplet at the WZ state on silicon nanopillars of 2 nm (left), and at monostable CB state after spontaneous transition. (B) and (C) snapshots showing same wetting states in (A) for nanopillars with heights of 4 nm and 6 nm, respectively. (D) the Z-coordinates of the center of mass (COM) of the water droplets in wetting and spontaneous transition simulations on different nanopillars. The heights of the nanopillars in each simulation system were indicated as legends.



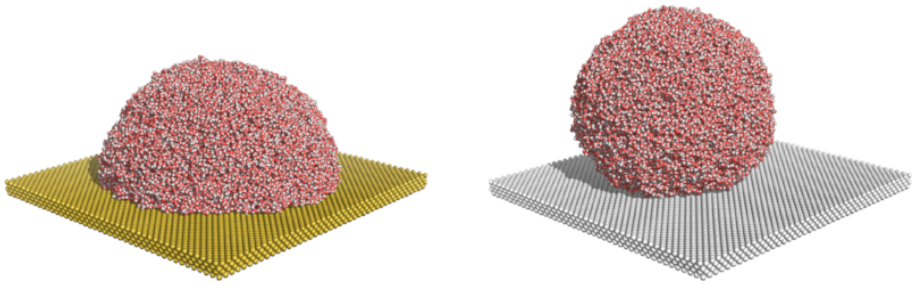
Supplementary Figure S7: **Spontaneous transition from the WZ to the monostable CB state on nanopillars with and without underneath supporting layer.** A supporting silicon atom layer with thickness of 1 nm was first added to the underneath of silicon nanopillars with heights of 4 nm, as the system snapshot shown on the right. The water droplet was let to adsorbed onto these nanopillars for 10 ns. The substrate atoms were then switched at 10 ns to be C9 for probing spontaneous wetting transition. Comparing to the nanopillars without a supporting atom layer, the water droplet adsorbed further onto the substrate and had a lower COM coordinate at the final adsorbed state. A supporting layer can slightly slow down the wetting transition process, as indicated by the blue arrow in the plot and the system snapshot shown on the right.



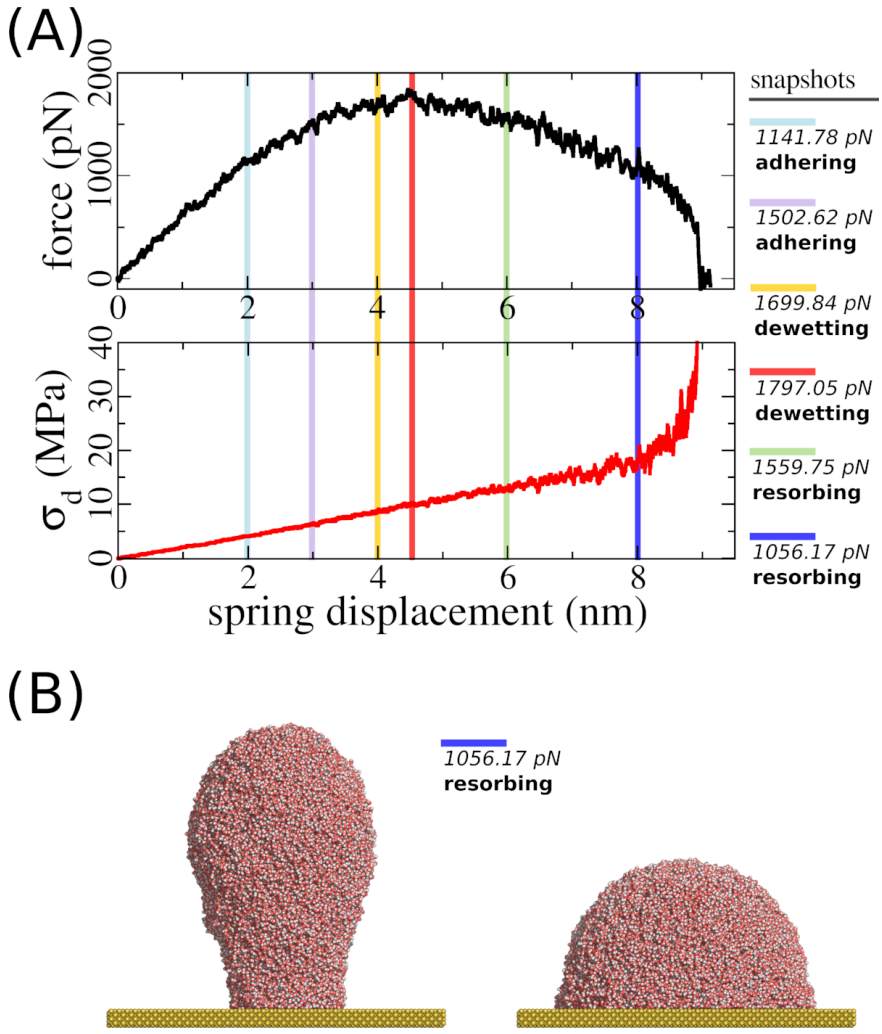
Supplementary Figure S8: **Dewetting on the silicon nanopillars with an underneath supporting atom layer.** The water droplet was initially fully absorbed onto silicon nanopillars with heights of 4 nm and with an underneath supporting silicon atom layer with thickness of 1 nm. Because of strong interactions between the silicon atoms and the water molecules, the droplet broke into two parts under pulling force in the couse of all five independent dewetting simulations. (A) System snapshots of one example dewetting simulations. (B) Representative dewetting force profile. Circled numbers indicate the same corresponding positions in the simulation trajectory of the snapshots and the force profile.



Supplementary Figure S9: **Dewetting of a water droplet at monostable CB state.** Snapshots of the simulation system at the beginning, middle and end of the dewetting process are shown in (A), (B) and (C), respectively.



Supplementary Figure S10: **Water droplets on flat silicon and C9 surfaces.** Silicon atoms are colored in gold and C9 in grey.



Supplementary Figure S11: **Force-clamp MD simulations at different dewetting stages.** System snapshots were first taken in the course of dewetting on flat silicon surface at 255 K. The pulling force on the water droplet in each system snapshot was maintained constant in these simulations. (A) Six snapshots were taken for these force-clamp MD simulations. Their corresponding positions in the simulation trajectory were marked in the dewetting force profile by color bars. The constant pulling force applied on the water droplets were given as legends on the left. The final water droplet morphologies, adhering, detaching or resorbing, were also given in the legends. (B) Water droplet resorbing, exemplied by the simulation with constant pulling force of 1056.17 pN. The initial and final snapshots of this simulation system were given on the left and right, respectively. It is clear that there are two forces resisting the droplet detachment, namely droplet shape deformation (increasing droplet surface area) and water-substrate adhesion (decreasing contact area). With the constant loading of the pulling force (force-probe MD simulation), there was an upper-bound of pulling force that over-power the two forces and led to water droplet detachment. In this study, this upper-bound force value was close to the highest force value found in the force profile. The droplet detachment event was not depended on the pulling distance because of the fluid property of the water molecules. The droplet can relax under constant force (force-clamp MD simulation), and allowed water molecules to move back to the hydrophilic Si substrate, which resulted in the whole droplet resorbing back to the substrate.