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ARTICLE

Spontaneous Transition of a Water Droplet from Wenzel State to Cassie State: a Molecular Dynamics Simulation Study

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

It is widely accepted that the superhydrophobic state is attributed to the formation of the Cassie state. The Cassie state is mostly metastable, which can be turned into the Wenzel state. Therefore, the superhydrophobic state is generally considered to be unstable. In this study, the wetting behaviors of a water droplet on different pillar surfaces are simulated. The spontaneous transition from the Wenzel state to the Cassie state is achieved, which is significant for the stable existence of the superhydrophobicity. The transition process is analyzed in detail and can be chronologically divided into two stages: the contact area decreases, and the water droplet rises. Moreover, the transition mechanism is studied, which is due to the combined effect of the surrounding pillars and central pillar. The surrounding pillars form a no-wetting gap under the droplet, and the central pillar forces the droplet to move upward. Furthermore, three parameters that may influence the transition are studied: the pillar height, droplet size and hollow size.

Introduction

The superhydrophobicity of a solid surface has attracted much attention for its applications in self-cleaning,¹⁻³ anti-icing,^{4,5} drag reduction,^{6,7} and so on.^{8,9} It is well known that superhydrophobicity has been linked to unique micro- or nanostructures. Water droplets can typically exist in two prominent states on structured surfaces: Wenzel state and Cassie state.¹⁰ The Wenzel¹¹ state is a state in which the water droplet wets the grooves. The Cassie¹² state is a state in which the droplet sits on the peaks of the surface topography. It is widely accepted that the superhydrophobic state is due to the formation of the Cassie state. It has been reported that the Cassie state is always a metastable state, which can be turned into the Wenzel state.¹³ Consequently, it is widely considered that the superhydrophobic state cannot exist stably, which greatly limits the application of the superhydrophobicity.

So far, Quéré et al.¹⁴ and Daub et al.¹⁵ analyzed the stability of Cassie state. The criteria for the stability of Cassie state from them were achieved by analysis of the surface energy, and the transition process between Cassie state and Wenzel state was not involved. That is to say, even if the Cassie state is globally stable from their criteria, the spontaneous transition from Wenzel state to Cassie state still cannot occur when there is an energy barrier between them, which can be proved by the transition that Quéré et al. carried out by an external pressure in their paper. Moreover, in the criteria for stable Cassie state from Quéré et al., some force criteria^{16,17} for entrapped gas existence under a drop were not involved, which were also

necessary for Cassie state. The criteria from Quéré et al. is a necessary condition but not a sufficient condition for a globally stable Cassie state and spontaneous transition from Wenzel state.

To the best of the authors' knowledge, only Zhang et al. reported the transition from Wenzel state to Cassie state.¹⁸ The water model was a layer of liquid film in their simulation, and the solid surface was fully covered by this water film. Their results showed that the transition happened in the liquid-solid interface. If considering the formation of the gas layer under the liquid in actual situations, it is difficult for the transition in Zhang's model to occur owing to no way that gas can go into the space between the solid and the liquid. A superhydrophobic state generally aims for a droplet, which is associated with both the liquid-solid interface and liquid-gas meniscus shape.¹⁹

In this manuscript, wetting behaviors of a water droplet on different pillar-structured surfaces were studied by molecular dynamics (MD) simulation. The aim was to determine whether the transition from the Wenzel state to the Cassie state could occur spontaneously, which would be significant for the steady existence of the superhydrophobic Cassie state. In addition, the parameters that may influence the transition were studied, such as the pillar height, droplet size and hollow size.

Methods

In simulations, the strength of the interaction potential between the gas and water is weak. To simplify the model and improve calculation efficiency, the gas molecules are always neglected to study the wetting behavior of the droplet on structured surfaces.^{15,18,19} Therefore, in these simulations,

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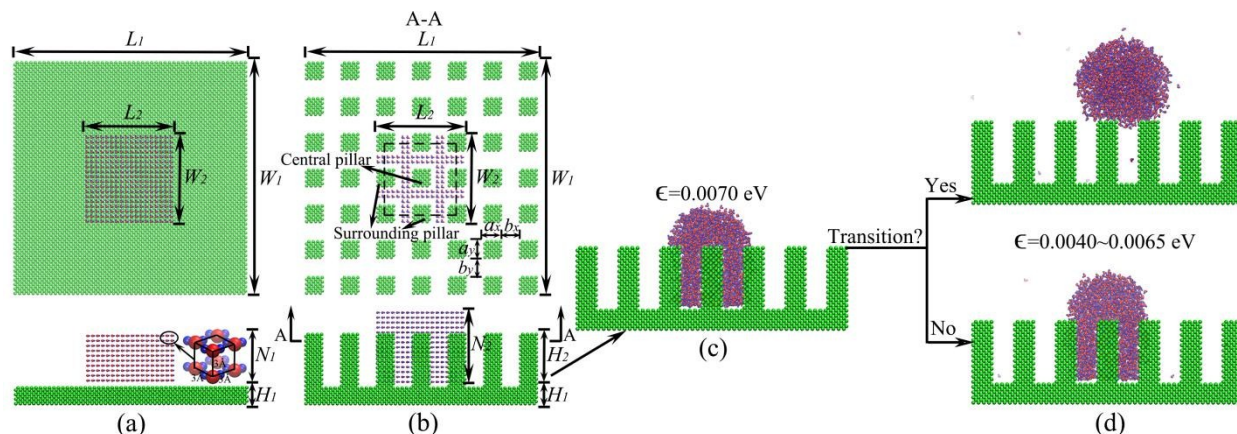


Fig. 1. Initial structures of the ensembles of (a) the flat surface and (b) the pillar surface. (c) Initial Wenzel state of the droplet in the simulation of transition process, which is the equilibrium state of the droplet at the energy parameter of 0.0070 eV. (d) Equilibrium states of the droplet in the simulations of transition process when the energy parameter varies from 0.0040 to 0.0065 eV. Blue, red, and green spheres represent the hydrogen, oxygen, and substrate atoms, respectively.

models with water molecules located on the flat (cf. Fig. 1a) and pillar surfaces (cf. Fig. 1b) were constructed. The water model in this study was the rigid extended simple point charge potential (SPC/E)²⁰. The water molecules were arranged regularly in three-dimensional space, and every molecule was 3 Å away from its nearest-neighbor molecule.²¹ The bottom of the water droplet was 3 Å away from the solid surface. On the flat surfaces, the dimensions of a single layer of water molecules were $54 \times 54 \text{ Å}^2$ (i.e., $L_2 = W_2 = 54 \text{ Å}$), and the number of water-molecule layers, N_1 , was 10. On the pillar surfaces, the water molecules were placed in the hollows between pillars. The number of molecules in a single layer of water was 128, and the number of water-molecule layers, N_2 , was 15. For the model of the solid surface, a cubic diamond structure with the lattice constant, a , equal to 5.43 Å (referenced to the Si crystal and obtained from the Materials Studio package²²) was considered. Two layers of the Si (0 0 1) surface were used to represent the flat surface. The model of the pillar surface consisted of two parts, which were the substrate part and the pillar part.²³ The model of the substrate part was the same as the flat surface with the dimensions $L_1 = W_1 = 141.18 \text{ Å}$ ($26a$) and the height $H_1 = 10.86 \text{ Å}$ ($2a$). The model of the pillar part was cut from the flat surface, in which the pillar dimensions, $a_x = a_y = b_x = b_y$, were 10.86 Å ($2a$), and the height, H_2 , was 32.58 Å ($6a$).

The intermolecular interactions were calculated as follows. The electrostatic interaction was modeled by using the Coulomb's law, whereas the dispersion and repulsion forces were obtained by using the Lennard–Jones (L–J) potential²⁰ for $r_{ij} < r_c$,

$$U_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{c q_i q_j}{\epsilon_{ij} r_{ij}}, \quad r_{ij} < r_c \quad (1)$$

where i and j are oxygen (O), hydrogen (H) and substrate (S) atoms. q_i and q_j are the charges of the atoms. σ_{ij} and ϵ_{ij} are the distance where the interatomic potential is zero and the depth of the potential well, respectively. r_{ij} is the distance

between two atoms, and r_c is the cutoff equal to 15 Å (i.e., $U_{ij} = 0$, when $r_{ij} > 15 \text{ Å}$). The mixed-atom interatomic potentials were obtained through the Lorentz-Berthelot mixing rules²⁴,

$$\sigma_{ij} = 1/2(\sigma_{ii} + \sigma_{jj}) \quad (2)$$

$$\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2} \quad (3)$$

The values of ϵ_{ii} for O, H and Si are 0.006748, 0 and 0.0175 eV, and the corresponding values of σ_{ii} are 3.166, 0 and 3.826 Å.^{21,25} According to Eq. 2, the values of ϵ_{O-S} and σ_{O-S} were calculated to be 0.010867 eV and 3.496 Å. A water droplet on the surface with these parameters was simulated, and the contact angle was 70°. In MD simulations, two types of models can be employed to study the wetting behaviors on surfaces with different chemical compositions. One model is based on a real solid surface, in which its real lattice structure and the corresponding potential parameter are used.^{26, 27} In this case, different models need to be established for different materials to obtain the results of different surfaces. Because of the limit of real material types, it is difficult to construct a series of real surfaces with a continuous change from hydrophilicity to hydrophobicity in theoretical research. The other model is based on a virtual solid surface with a certain lattice structure.^{28,29} To construct surfaces with different hydrophobic properties, the interaction potential energy parameters between the surface and water vary artificially. The latter model is more convenient and efficient for building surfaces that range from hydrophilic to hydrophobic. Werder et al.²¹ demonstrated that the contact angle of the flat surface increased as the interaction energy parameter ϵ_{ij} decreased. To study the wetting behavior of a water droplet on surfaces ranging from hydrophilic to hydrophobic one, the value of ϵ_{O-S} was decreased and σ_{O-S} was fixed. When the energy parameter ϵ_{O-S} equaled 0.0070 eV or 0.0040 eV, the contact angle of the flat surface was 100° or 129°. To construct the surfaces with contact angles from 100° to 129°, seven different values of the energy parameter ϵ_{O-S} (0.0070, 0.0065, 0.0060, 0.0055, 0.0050, 0.0045, and 0.0040 eV) were chosen.

The equilibrium state of the droplet on the pillar surface at the energy parameter of 0.0070 eV was Wenzel state. To

determine whether the transition from the Wenzel state to the Cassie state could occur spontaneously, this Wenzel state ($\epsilon_{O-S}=0.0070$ eV) was served as initial state of the simulations in which energy parameter varied from 0.0040 to 0.0065 eV.

All simulations were carried out with the LAMMPS MD package³⁰. The water droplet was in the NVT (fixed number, volume, and temperature) ensemble at $T = 300$ K. The total simulation time was 1 ns, and the integration time step was 1 fs. The SHAKE algorithm³¹ was used to keep the O–H distance fixed at 1 Å and the H–O–H angle at 109.47°. The lateral size of the solid surface was approximately three times the length of the water cube, and the effect of the surface edge on the behavior of the droplet was negligible. The PPPM method was applied to minimize the error in the long-range terms. The length of the simulation cell was seven times the length of the water cube, and the influence of molecules in duplicate domains on the behavior of the droplet could be ignored. The atoms in the solid surface were fixed at their initial positions and represented an inert wall. The water temperature remained stable at 300 K during the production run, and the deviation was less than 5.0 K.

Results and discussion

In this section, the simulation results of a water droplet on the flat and pillar surfaces with different energy parameters are first discussed, including the contact angles and wetting states. Second, from the simulation results of the wetting states, a transition from the Wenzel state to the Cassie state is found. The transition behavior of the water droplet during the transition process is then analyzed. Third, the transition mechanism and the factors influencing the transition are presented.

Results of a Water Droplet on Different Surfaces.

From the MD simulation trajectories, the 3D coordinates of every atom at each moment could be obtained. To extract the contact angle of the flat surface from the coordinates, a two-step procedure was adopted (cf. Fig. 2b). First, in accordance with the x and z coordinates, a graph of atomic positions was drawn at a moment in time in the x – z plane. Second, a circular fit through these points was extrapolated to the solid surface where the contact angle, ϑ , was measured. To reduce the deviation, after an equilibrium time of 0.6 ns, the angles at five times (0.6, 0.7, 0.8, 0.9 and 1.0 ns) were obtained. The average

value of the angles at these five times was chosen as the contact angle of this model, and the deviation was calculated. According to this method, the results showed that the contact angles of the flat surfaces with seven different energy parameters ranged from 100° to 129° (cf. Fig. 2c).

Equilibrium Wenzel state on the pillar surfaces with the energy parameter of 0.0070 eV was obtained. To achieve the transition from this Wenzel state to the Cassie state, this Wenzel state was used as the initial state, and simulations with decreased energy parameters (from 0.0040 to 0.0065 eV) were carried out. The simulation results are summarized in Table 1. The results indicated that, for Case 1 or 2, the state of the water droplet remained in the Wenzel state. For Case 3, 4, 5, or 6, however, the state of the water droplet changed to the Cassie state. Therefore, spontaneous transitions from the Wenzel state to the Cassie state were achieved on the pillar surfaces when the contact angles with their flat surfaces were equal to or greater than 115°. Quéré et al. concluded that if the contact angle on a flat surface ϑ is larger than the threshold value ϑ_c between the Cassie state and the Wenzel state, the energy of the Cassie state was lower than that of the Wenzel state. The threshold value ϑ_c was given by

$$\cos \theta_c = (\phi_s - 1)/(r - \phi_s) \quad (4)$$

where ϕ_s is the ratio of the area of the solid in contact with the liquid S_l over the apparent surface area of the solid S_s in Cassie state (ϕ_s is dimensionless and smaller than unity). r is the ratio of the actual contact area S_c over the apparent surface area of the solid S_s in Wenzel state (r is dimensionless and larger than unity). Based on the behavior of the water droplet in contact with the pillars in Fig. 2d, the values of areas were calculated as

$$S_l = 4a^2 \quad (5)$$

$$S_s = 16\pi a^2 \quad (6)$$

$$S_c = 16H_2a + 16\pi a^2 \quad (7)$$

where a is the lattice constant of the solid and equals 5.43 Å. H_2 is the height of the pillars and equals 32.58 Å. The values of ϕ_s and r were calculated to be 0.08 and 2.91. According to the Eq. 4, ϑ_c was achieved to be 109°. Therefore, the energy of the Cassie state was lower than that of the Wenzel state when the contact angle on a flat surface was larger than 109°, which was a necessary condition but not a sufficient condition for the occurrence of the spontaneous transition.

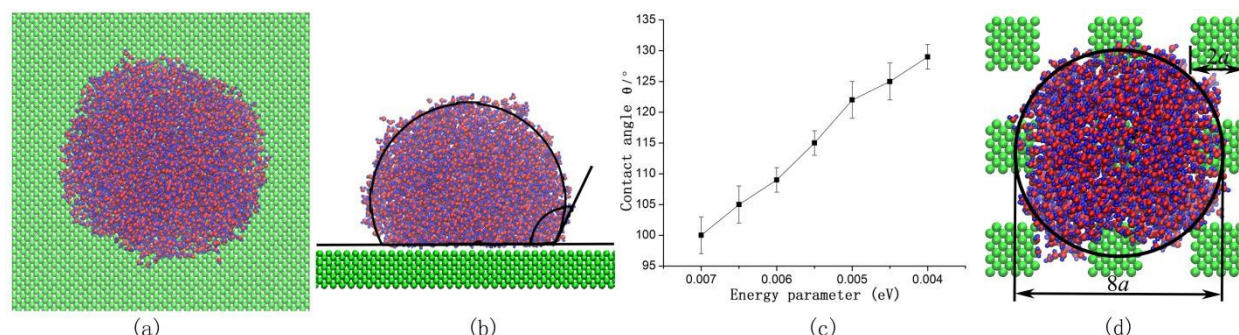


Fig. 2. Measurement of the contact angle of the flat surface: (a) top view, (b) side view, and (c) contact angle variation with the energy parameter. (d) Top view of the water droplet on the pillar surface.

Table 1. Simulation results of a water droplet on pillar surfaces with different energy parameters

Case	Energy parameter (eV)	Contact angle ($^{\circ}$)	Initial state	Equilibrium state	Transition?
1	0.0065	105	Wenzel	Wenzel	No
2	0.0060	109	Wenzel	Wenzel	No
3	0.0055	115	Wenzel	Cassie	Yes
4	0.0050	122	Wenzel	Cassie	Yes
5	0.0045	125	Wenzel	Cassie	Yes
6	0.0040	129	Wenzel	Cassie	Yes

Transition Behavior of a Water Droplet during Transition Process.

To the best of our knowledge, the transition was also simulated by Zhang et al.¹⁸ On the basis of Zhang's model, similar models were constructed (cf. Fig. 3ai). To construct the fully wet state, the interaction parameter ϵ_{ij} was set to be 0.0070 eV. After the simulation at 0.0070 eV for 1 ns, the equilibrium state of the droplet was fully wet state (cf. Fig. 3aai). The initial state of the simulations at 0.0050 and 0.0055 eV was this wet state. At each energy parameter, simulations with two different boundaries of simulation cells were carried out (cf. Fig. 3c), which were based on our model and Zhang's model, separately. In Zhang's model, the periodic boundaries in the lateral direction were employed. The boundary of the simulation cell in our model was larger than that in Zhang's model, and the water-gas interface in lateral direction was free. Therefore, in our model, a droplet could be formed, and the effect of both liquid-solid and liquid-gas interface was considered. When the interaction parameter was 0.0050 eV, the results showed that transitions occurred in both models (cf. Fig. 3b). In our model, the transition occurred at 0.40 ns (cf. Fig. 3bi), which was about one-fortieth of the time in Zhang's

model (15.85 ns in Fig. 3bii). When the interaction parameter was increased to 0.0055 eV, however, transitions only occurred in our models, and Zhang's model was still fully wetted after 30 ns (cf. Fig. 3c). Therefore, it could be concluded that our model that considered the effect of both liquid-solid and liquid-gas interface was more accurate. Furthermore, when considering the effect of the gas under the liquid, it was difficult for the transition in Zhang's model to occur owing to the negative pressure. In our model, however, the gas under the droplet could flow freely to the outside, and the outside gas could also flow into the area under the droplet. The pressure of the outside environment was equal to that of the area under the droplet. Therefore, the effect of the gas under the droplet on the transition could be ignored in our model, and the transition could occur in actual situations.

To find out how this transition occurred, a more detailed observation was made. Snapshots of the transition process from the Wenzel state to the Cassie state for Case 4 are shown in Fig. 4. In this transition process, the wetting behavior of the water droplet could be chronologically divided into two stages.

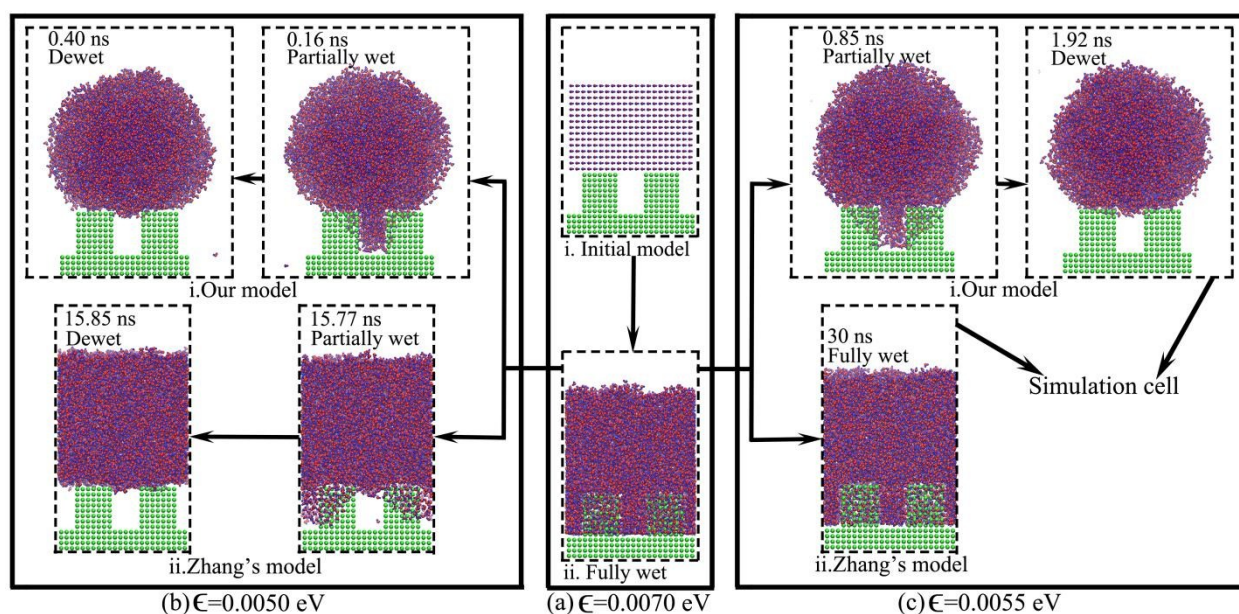


Fig. 3. Snapshots of the initial model and fully wet state when the energy parameter (a) $\epsilon=0.0070$ eV, and the transition behavior in our model and Zhang's model when the energy parameter (b) $\epsilon=0.0050$ eV, and (c) $\epsilon=0.0055$ eV. Blue, red, and green spheres represent the hydrogen, oxygen, and substrate atoms, respectively. Black dotted lines represent the boundaries of the simulation cells.

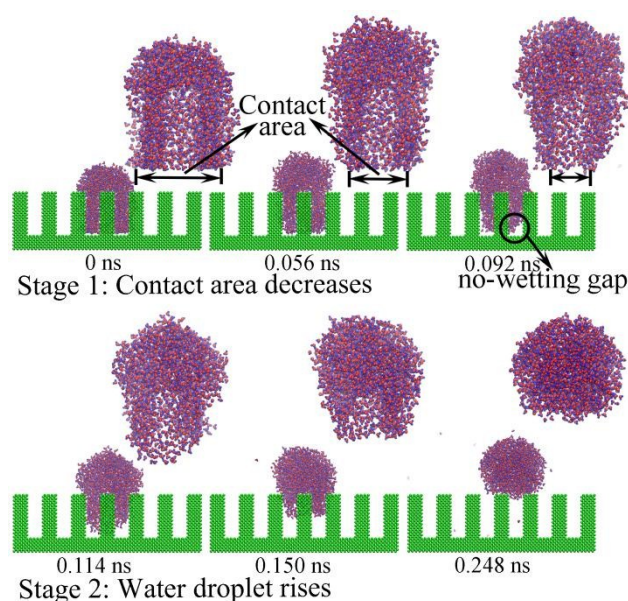


Fig. 4. Snapshots of the transition process from the Wenzel state to the Cassie state. Magnified figures of the water droplets without pillars are shown in the upper right of each snapshot.

Stage 1: the contact area between the substrate and the water droplet decreased owing to the hydrophobicity of the substrate at the bottom and side of the pillars. This phenomenon was attributed to the force at the liquid–solid interface. Meanwhile, a no-wetting gap at the lower parts of some pillars (marked in Fig. 4), whose sides contacted the droplet, was formed. Stage 2: an upward force for the droplet could be induced because of the existence of the no-wetting gap and the contractive tendency of the partial droplet surface above the pillars. This force resulted in the transition from the Wenzel state to the Cassie state. After the equilibrium state became the Cassie state, it remained in the Cassie state.

Transition Mechanism and the Factors Influencing the Transition.

In these two stages, the droplet started to move upward by the actions of the surrounding pillars and central pillar (marked in Fig. 1). To analyze this phenomenon, two other simulations (cf. Fig. 5) were carried out. One model with the

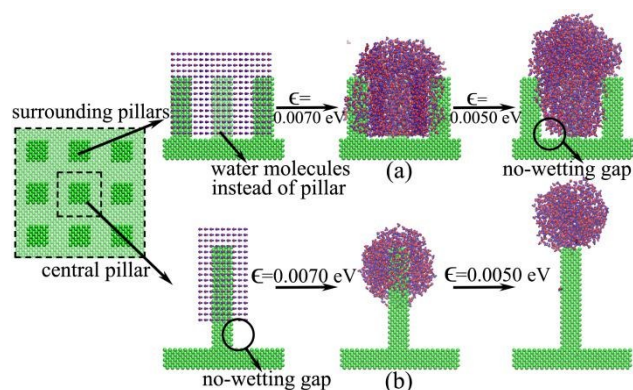


Fig. 5. Equilibrium processes of a water droplet for different models with (a) surrounding pillars and (b) a central pillar.

water droplet on a surface lacking a central pillar was simulated (cf. Fig. 5a) to study the role of the surrounding pillars. In this model, water molecules instead of the pillar were placed in the vacant position. The results showed that the contact area between the substrate and the water droplet decreased, and a no-wetting gap formed, which resulted from the effect of the side of the surrounding pillars. At this moment, the transition did not occur without the effect of the central pillar. Then, another model with the water droplet surrounding a single pillar was simulated (cf. Fig. 5b) to study the role of the central pillars. In this model, there was a no-wetting gap at the lower part of the pillar initially. The results demonstrated that the central pillar forced the droplet to move upward, which resulted in the transition to the Cassie state.

To determine whether the equilibrium state would be affected by the pillar height, droplet size, and hollow size, models with different dimension parameters were simulated (cf. Table 2). For each case, the simulation process was similar to that in Fig. 1b, 1c and 1d, which has two steps. First, the Wenzel state of the droplet was obtained by using a larger energy parameter (0.0070 eV). Second, this Wenzel state was served as the initial state of the subsequent simulations at the energy parameter of 0.0050 eV. The results for different pillar heights indicated that transitions from the Wenzel state to the Cassie state were achieved for all five surfaces. It could be concluded that the transition was not affected by the pillar height as the height increased from 21.72 to 48.87 Å. Similar results were also reported by Lundgren et al.²³, who examined variations in the contact angle with the height of the pillars by MD simulation. They concluded that the contact angles were independent of the pillar height when the height exceeded 15 Å. When the transition occurred on the pillar with the height of 21.72 Å, it was easier to take place when the pillar height increased, which could be induced by the three-phase contact line pinning effect^{32,33}. The contact line pinning effect slows down the droplet to spread in the direction that is perpendicular to the pillars. The sizes of the contact line increased as the pillar height increased, which resulted in the increase of the pinning effect. Meanwhile, the size of the droplet remained unchanged. Therefore, the ability of the droplet to spread in the direction that was parallel to the pillars (from Wenzel state to Cassie state) increased when the pillar height increased. The results for different droplet sizes demonstrated that the transitions from the Wenzel state to the Cassie state were achieved when the sizes were larger. It could be concluded that the transition was affected by the droplet size as the size varied from 3 to 11 layers. When the size ranged from 3 to 7 layers, the top of the droplet was below the top of the pillars. In these cases, it was difficult for the transition to occur. This conclusion corresponded to the finds of Koishi et al.³⁴, who simulated the equilibrium states of a water cube, which was placed at two initial positions: an upper position not fully embedded by the pillars and a lower position where the entire water cube was embedded in the groove region. They found that the droplet at a lower position

Table 2. Dimension parameters for the water droplet and pillar structures

Influencing factor	H_2 (Å)	N_2	$b_x = b_y$ (Å)	$a_x = a_y$ (Å)	Transition?
Pillar height	48.87	15	10.86	10.86	Yes
	43.44	15	10.86	10.86	Yes
	38.01	15	10.86	10.86	Yes
	32.58	15	10.86	10.86	Yes
	21.72	15	10.86	10.86	Yes
Droplet size	38.01	11	10.86	10.86	Yes
	38.01	9	10.86	10.86	Yes
	38.01	7	10.86	10.86	No
	38.01	5	10.86	10.86	No
	38.01	3	10.86	10.86	No
Hollow size	27.15	5	9	10.86	Yes
	27.15	5	10.86	10.86	Yes
	27.15	5	12	10.86	Yes
	27.15	5	14	10.86	Yes
	27.15	5	16	10.86	No
	27.15	5	18	10.86	No

had difficulty reaching the top of the pillars. This conclusion could also be explained by the contact line pinning effect. The size of the contact line decreased as the layer of the droplet decreased to below the top of the pillars, which reduced the ability of the droplet to spread in the direction that was parallel to the pillars. Therefore, it was difficult for the transition to occur when the top of the droplet was below the top of the pillars. The results for different hollow sizes demonstrated that the transitions from the Wenzel state to the Cassie state were achieved when the hollow sizes were smaller. It could be concluded that the transition was also affected by the hollow size as the hollow size increased from 9 to 18 Å. The possibility that the transition occurred decreased as the hollow size increased, which agreed with the simulation results of Sharma et al.³⁵, who simulated the behavior of water confined between hydrophobic surfaces and found that a hydrophobic surface dewetted as the surface separation decreased. Similarly, this conclusion could be explained by the contact line pinning effect. The sizes of the contact lines were the same because the sizes of pillars remained unchanged. Therefore, the abilities of the droplet to spread in the direction that was parallel to the pillars were the same when the hollow size varied. However, the sizes of the droplet confined between the pillars increased when the hollow size increased, which reduced the probability of the droplet to spread in the direction that was parallel to the pillars. Therefore, it was difficult for the transition to occur when the hollow size increased.

Conclusions

The transition of a water droplet from the Wenzel state to the Cassie state was investigated in this study. The results showed

that spontaneous transitions were achieved on pillar surfaces when their corresponding flat-surface contact angles were equal to or greater than 115°. The transition process of the water droplet was analyzed, and the wetting behavior could be chronologically divided into two stages: the contact area decreased, and the water droplet rose. Furthermore, three parameters that could influence the transition were studied: the pillar height, droplet size and hollow size. The results showed that the transition was not affected by the pillar height when the height ranged from 21.72 to 48.87 Å. However, it was affected by the droplet size and hollow size. The possibility that the transition occurred decreased as the droplet size decreased or the hollow size increased.

Acknowledgements

This work was supported by the National Natural Science Foundation of China Project under grant nos. 51375253 and 51321092. The authors also acknowledge the support of this work from the Tsinghua National Laboratory for Information Science and Technology, China.

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