Monte Carlo Study on the Wetting Behavior of a Surface Texturized with Domed Pillars

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ABSTRACT: A lattice gas Monte Carlo simulation was performed to examine the wetting properties of a surface texturized with nanometer-sized, dome-shaped pillars. The vapor and liquid phases of the gap between the pillars were related to the Wenzel and Cassie-Baxter states of a macroscopic water droplet resting on top of the pillars. We studied the effects of the pillar size by systematically varying its height from 6 to 53 nm for a fixed ratio of the height to its width. With increasing interpillar spacing or pressure, the liquid on top of the domed pillars penetrated smoothly down into the gap between the pillars. This wetting transition contrasts with that observed for the gap between rectangular or cylindrical pillars, where a liquid abruptly fills in the interpinlar gap at a critical interpinlar spacing or pressure. The pressure between the domed pillars was more susceptible to the intrusion of the bulk liquid on top of the pillars, due to the open geometry of the gap between the domed pillars. Also, the liquid penetrating into the gap between the domed pillars was locally more fluctuating in density and compressible than that penetrating into the gap between square or cylindrical pillars. This enhanced density fluctuation however was local and did not propagate into the bulk liquid sitting on top of the pillars. Simple analytic expressions of the critical spacing and pressure at which the wetting transition occurs for the domed pillars were derived using continuum theory. These continuum results agreed reasonably well with the present molecular simulations, even for pillars as small as a few nanometers in width.

I. INTRODUCTION

Superhydrophobic surfaces have attracted considerable attention primarily because of their wide potential applications, such as water harvesting, impermeable textiles, anti-fogging, bioadhesion, and self-cleaning materials (e.g., paint and windows). A superhydrophobic surface provides not only a high contact angle (150°) but also enhanced surface mobility to a water droplet deposited on it. A superhydrophobic surface is typically constructed by patterning micro- or nanometer sized pillars on a flat surface. Although the contact angle of a droplet on a flat surface barely exceeds 120°, the texturizing of a surface with micro- or nanopillars drastically enhances the surface hydrophobicity.

The mobility of a water droplet placed on a pillared surface depends critically on whether it is impaled by the pillars. A water droplet impaled by the pillars is in the Wenzel (WZ) state, and the interpillar gap in this case is filled with the liquid (Figure 1(a)). In contrast, the droplet is in the Cassie-Baxter (CB) state when the interpillar gap is in the vapor phase. A water droplet in the WZ state is immobile with a contact angle lower than it would be if it was in the CB state (Figure 1(b)). Therefore, it is desirable to have a pillared surface that preferentially induces the CB state of a droplet. The rising question is exactly how the size, shape, and pitch of the pillars influence the CB or WZ states of a droplet. Another interesting issue is how the CB or WZ state is affected by the pressure of the liquid droplet deposited on the top of the pillars. The pressure of a liquid droplet varies as a result of partial evaporation (shrinking) of the droplet, vibration of the surface, impact against a surface, and the application of a hydraulic pressure. A desirable superhydrophobic surface should have a high threshold for the pressure needed to fill the interpinlar gap with a liquid.

Precise control of the size, shape, and pitch of the pillars is possible with the assistance of micro- and nano-electro-mechanical (MEMS and NEMS) technology. Nevertheless, finding an optimal pillared surface by systematically varying the surface geometry can be both time-consuming and expensive. In this respect, theory and computer simulations can be helpful for prescreening the candidate surface geometries and providing guidelines for designing the optimal hydrophobic surfaces. Thus far, previous studies have focused mainly on periodic arrays of rectangular or cylindrical pillars. On the other hand, lotus leaves, which are the most venerable superhydrophobic surface, have minute papillae (pillar-like protrusions) similar to the domes on their surfaces.

Herein, the hydrophobicity of a surface texturized with periodic domed pillars was investigated theoretically. Pre-

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viosously, the pressure required for a liquid to fill in the gaps between domed pillars was estimated theoretically to be 12–15 kPa. Carbone and Mangialardi examined theoretically how the surface geometry and pressure affect the WZ and CB states of a sinusoidal surface corrugation. Exstrand and Zhang et al. reported that secondary structures on top of the domed pillars further enhance the hydrophobicity of a domed surface. Unfortunately, these previous theoretical studies relied heavily on the continuum picture of water, neglecting the fact that a water droplet is a collection of discrete molecules. Therefore, they had inherent difficulties in delivering the underlying molecular details. The present study used a molecular approach to examine the wettabiliy of a surface textured with nanometer-sized domed pillars (6–53 nm in height): Monte Carlo (MC) simulations based on the lattice gas (LG) model were performed. The present LG model is coarse-grained, but it does capture the phase behavior of a liquid confined in a nanoscale boundary. For example, the LG model is fully consistent with an atomistic simulation on the drying transition for a carbon nanotube immersed in water. In addition, the LG simulation successfully explained the capillary condensation of water between an atomic force microscope tip and a surface.

The present MC simulation focused on the phase behavior of a fluid confined between the domed pillars (see Figure 2(a)). For comparison, the surfaces texturized with rectangular and cylindrical pillars were also simulated (Figure 2(b,c)). The liquid and vapor phases of the gap between the pillars were related to the WZ and CB states of a macroscopic water droplet resting on top of the pillars. The wetting transition, where a liquid fills up the gap between the pillar walls, was investigated by increasing the interpillar spacing or pressure systematically. In the wetting transition, a liquid penetrates continuously down into the gap between the domed pillars, which is in contrast to the abrupt filling of a liquid found for the rectangular and cylindrical pillars. Using a continuum theory, we also derived an analytic formula for the critical spacing and pressure, where a wetting transition occurs. The continuum results agreed reasonably with the LGMC simulations.

II. MOLECULAR SIMULATION METHOD AND CONTINUUM THEORY

In the present LG model, a water molecule occupies a cubic lattice site above a pillared surface. A molecule interacts with its six nearest neighbors through an attraction energy, $\varepsilon$, and has its own chemical potential, $\mu$. If a molecule is located at a site next to the pillared surface, it experiences a surface binding energy, $\varepsilon_S$. The $\mu$ value for the bulk vapor—liquid phase transition, $\mu_C$, is given exactly by $-3\varepsilon$ in this model. The relative humidity of the system is defined as $\exp\left[\frac{(\mu - \mu_C)}{(k_B T)}\right]$, which is exact in the ideal gas limit. The bulk critical temperature, $T_C$, for the lattice gas is given by $1.128\varepsilon/k_B$. The relative humidity was set to 105% to emulate an oversaturated vapor. Identifying the liquid as water, $\varepsilon$ was set to 4.8 kJ mol$^{-1}$ ($T_C$ of water is 647.3 K), and the lattice spacing, $l$, was set to 0.37 nm (the approximate molecular diameter of water). The surface binding energy was set to $\varepsilon_S = 0.01\varepsilon$. Temperature was fixed to 300 K. The Glauber single spin flip was used for the MC move. 100 000 MC moves were attempted for every lattice site. When the density fluctuated considerably, the number of MC moves was increased to more than 400 000 per site. Owing to this extensive sampling (possible for the present LG model), any metastable state and the resulting hysteresis in the vapor—liquid phase transition of the interpillar gap could be obviated. The initial configuration of the simulation was prepared by setting the occupancy of each lattice site to 1.
which is similar to the WZ state. The initial condition, where all lattice sites are empty, was also attempted, and no difference was found.

The coordinate system was chosen, where the surface normal directs toward the Z axis and the base surface lies at \( z = 0 \) (top of the pillar lies at \( z = H \), see Figure 2). The width \( W \) of a rectangular or cylindrical pillar refers to its lateral (in the X or Y direction) width. The \( W \) of a domed pillar represents the lateral width at its bottom. Each domed pillar was taken to be a prolate spheroid where the vertical axis (along the Z axis) is \( H \) in radius and the two equatorial (along the X and Y axes) are \( W \) in diameter. The surface of a domed pillar in the MC simulation was taken to be the collection of the lattice points nearest to the ellipsoid described by \((x^2 + y^2)/(W/2)^2 + z^2/H^2 = 1 \) (\( z > 0 \)). The interpillar spacing \( S \) stands for the wall-to-wall distance for rectangular and cylindrical pillars. The \( S \) for domed pillars corresponds to the distance between the bottoms of neighboring domed pillars. Throughout the simulation, the aspect ratio, \( \alpha = H/W \), was fixed to 2, which is a typical value for a pillared surface generated experimentally. As long and slender pillars are difficult to construct and vulnerable to damage, most commonly manufactured are pillars with aspect ratios on the order of one.\(^{18,20,34,36}\) The pillar height, \( H \), was varied from 5.92 to 53.28 nm (with 5.92 nm increments). For a given combination of \( H \), \( W \), and \( S \), a single pillar was simulated in a rectangular parallelepiped box with a size of \((W + S) \times (W + S) \times (H + 18.5 \text{ nm})\). The periodic array of pillars was emulated by applying the periodic boundary conditions along the \( X \) and \( Y \) directions.

The continuum theory for the wetting (CB to WZ) transition was derived as follows. For both WZ and CB states, it was assumed that a bulk liquid occupies the space above the pillar tops. Focusing on the gap between the pillar walls, it was assumed that a bulk liquid occupies the space above the transition was derived as follows. For both WZ and CB states, the critical spacing where the transition between the WZ and CB states occurs,

\[
S_C = \left( \frac{H}{\alpha} \right) \left[ \frac{\sqrt{\pi}}{6} \right] \left[ \frac{1}{PH} \left[ \frac{PH + \gamma(\cos \theta + 1)}{PH + \gamma(\cos \theta + 1)} - 1 \right] \right] \left[ \frac{4 \gamma \cos \theta}{\{PH + \gamma(\cos \theta + 1)\}} - 1 \right]
\]

(1)

where \( K = (1 - 1/(4 \alpha^2))^{1/2} \). \( P \) is the pressure of a liquid in excess of the vapor pressure (both have the same chemical potential \( \mu \)). When air flows in and out of the interpillar gap in the CB state (open system), the vapor pressure includes the external pressure due to ambient air.\(^{37}\) \( \gamma \) is the liquid–vapor interfacial tension, and \( \theta \) is the intrinsic contact angle (that of a macroscopic droplet on a flat surface). Similarly, for periodic rectangular pillars replicated on a square grid

\[
S_C = \left( \frac{H}{\alpha} \right) \left[ \frac{\sqrt{\pi}}{6} \right] \left[ \frac{1}{PH} \left[ \frac{PH + \gamma(\cos \theta + 1)}{PH + \gamma(\cos \theta + 1)} - 1 \right] \right] \left[ \frac{4 \gamma \cos \theta}{\{PH + \gamma(\cos \theta + 1)\}} - 1 \right]
\]

(2)

and \( S_C \) for the periodic cylindrical pillars is given by

\[
S_C = \left( \frac{H}{\alpha} \right) \left[ \frac{\sqrt{\pi}}{6} \right] \left[ \frac{1}{PH} \left[ \frac{PH + \gamma(\cos \theta + 1)}{PH + \gamma(\cos \theta + 1)} - 1 \right] \right] \left[ \frac{4 \gamma \cos \theta}{\{PH + \gamma(\cos \theta + 1)\}} - 1 \right]
\]

(3)

Consider several limiting cases. In the limit of \( H \to 0 \), eqs 1–3 all reduce to \( S_C \to 0 \). As a liquid on top of extremely short (\( H \to 0 \)) pillars easily fills in the gap between the pillars, the interpillar gap can be dry by reducing \( S \) to zero. In the opposite limit of \( H \to \infty \), eq 2 approaches a constant as follows

\[
S_C \to -\frac{2 \gamma \cos \theta}{P}
\]

(4)

In contrast, the \( S_C \) values for the cylindrical and domed pillars become linearly decreasing functions of \( H \), which are expressed as

\[
S_C \to -\frac{\gamma}{2 \alpha} \left[ \frac{\sqrt{\pi}}{6} \right] \left[ \frac{\cos \theta + 1}{P} \right] - \left( 1 - \frac{\sqrt{\pi}}{2} \right) \left( \frac{H}{\alpha} \right)
\]

(5)

and

\[
S_C \to -\frac{\gamma}{2 \alpha} \left[ \frac{\sqrt{\pi}}{6} \right] \left[ \frac{\cos \theta + 1}{P} \right] + \frac{3 \gamma \cos \theta \{ \arcsin(K)/K \}}{P} - \left( 1 - \frac{\sqrt{\pi}}{2} \right) \left( \frac{H}{\alpha} \right)
\]

(6)

respectively. Equations 5 and 6 predict that \( S_C \) decays to zero at a sufficiently large \( H \), \( H_T \). In other words, a water droplet deposited on cylindrical or domed pillars cannot be in the dry (CB) state for \( H > H_T \). The threshold \( H_T \) values for cylindrical and domed pillars, respectively, are given by

\[
H_T = \left\{ \frac{\alpha \gamma \cos \theta}{(1/4 - 1/\pi)} \right\} \left[ \left( \frac{1}{P} \right) \right]
\]

(7)

and

\[
H_T = \left\{ \frac{3 \gamma [2 \cos \theta + 1] + \pi \alpha \cos \theta \{ \arcsin(K)/K \}}{(\pi - 6)} \right\} \left[ \left( \frac{1}{P} \right) \right]
\]

(8)

The absence of a dry (CB) state can be understood as follows. Unlike rectangular pillars, the interpillar gap does not vanish by making \( S = 0 \) for the cylindrical or domed pillars. With increasing \( H \), the liquid confined between the cylindrical or domed pillars at \( S = 0 \) increases in both volume and contact area with the pillar walls. It turns out the increase in volume is faster than the increase in surface area.\(^{38}\) Consequently, the cohesion of a liquid dominates the liquid–solid interface effect. Above \( H_T \), the WZ state is always more stable than the CB state. Note however that the absence of a CB state for the present cylindrical and domed pillars is only valid for the case where the aspect ratio \( \alpha \) is fixed. In other cases such as one where \( H \) increases with \( W \) fixed (therefore, \( \alpha \) increases), the WZ state will not always be more stable than the CB state.

Consider the case of increasing pressure for a fixed combination of \( H \), \( W \), and \( S \). \( P \) can be increased, for example, by the collision of a droplet against a surface, by reducing the size of a droplet (due to evaporation), and by applying an external pressure. If the \( P \) value of the dry interpillar gap is increased continuously, the initially dry interpillar gap will switch to a wet (WZ) state above a critical pressure, \( P_C \). The analytic expression of \( P_C \) can be obtained using a similar
procedure for deriving \( S_C \). The \( P_C \) for rectangular pillars can be expressed as

\[
P_C = -\frac{4H\gamma \cos \theta}{aS^2} + 2HS - \frac{\gamma(\cos \theta + 1)}{H}
\]

For cylindrical pillars, \( P_C \) is

\[
P_C = -\frac{\pi H\alpha \gamma \cos \theta}{(aS)^2 + 2(aS)H + (1 - \pi/4)H^2} - \frac{\gamma(\cos \theta + 1)}{H}
\]

In the case of the domed pillars, \( P_C \) is expressed as

\[
P_C = -\frac{\pi H\alpha \gamma \cos \theta(\arcsin(K)/K)}{2((aS)^2 + 2(aS)H + (1 - \pi/6)H^2)} - \frac{\pi H\gamma(\cos \theta + 1)}{H}
\]

In the limit, \( H \to 0 \), the \( P_C \)'s in eqs 9–11 all reduce to zero, indicating that no excess pressure is needed to make the CB to WZ (wetting) transition for very short pillars. In the limit of very tall pillars (\( H \to \infty \)), the \( P_C \) for the rectangular pillars approaches a constant

\[
P_C \to -\frac{2\gamma \cos \theta}{S}
\]

In contrast, the \( P_C \)'s for the cylindrical and domed pillars become negative in the limit, \( H \to \infty \). This limiting behavior is similar to the absence of a CB state for cylindrical and domed pillars for large \( Hs \). Here, as \( H \to \infty \), the volume of the interpillar gap increases more rapidly than the liquid–solid interfacial area of the interpillar gap. Therefore, the cohesion of the liquid dominates the liquid–solid interfacial effect, and the WZ state is preferred over the CB state.

To compare the results with the LGMC simulation, the continuum theory above requires the values of thermodynamic parameters, \( \theta, \gamma, \) and \( P \), which are assigned as follows. The \( \gamma \) value can be taken to be half of the work of cohesion, the free energy change, where two unit areas of liquid are separated.\(^{39} \) If entropy (zero temperature approximation) is neglected, the work of cohesion in the present LGMC simulation is given by \( \epsilon/\ell^2 \). The resulting \( \gamma \) value is 29.1 mN m\(^{-1} \). Using the approximation, \( \gamma = \epsilon (1 + \cos \theta)/2 \), the intrinsic contact angle, \( \theta, \) of the present LG model is given by \( \theta = 168^\circ \). The approximation, \( P = \rho_0 (\mu - \mu_C) \), where \( \rho_0 \) is the bulk density of the liquid (\( = 1/\ell^2 \)), was also used. The resulting \( P \) value was 4 MPa, which is close to the impact pressure on a wind-driven raindrop colliding with a surface (1–20 MPa).\(^{16} \) These parameters of the continuum theory were determined without any adjustment to impose agreement between theory and the LGMC simulation, but instead through reasonable assessment.

### III. RESULTS AND DISCUSSION

The density of water confined between the pillar walls, \( \langle \rho \rangle \), which is defined as the average occupancy of sites in the interpillar gap, \( z \leq H \), was first inspected. \( \langle \rho \rangle \) was plotted as a function of \( S \) for the rectangular, cylindrical, and domed pillars in Figure 3. Different \( Hs \) were simulated by fixing the aspect ratio, \( \alpha = H/W \), to 2. A value of \( \langle \rho \rangle \approx 1 \) (0) indicates that the interpillar gap is in a liquid (vapor) state. In the cases of rectangular (Figure 3(a)) and cylindrical (Figure 3(b)) pillars, \( \langle \rho \rangle \) jumps from a vapor value to a liquid one at a critical value of spacing, \( S_C \), with increasing \( S \). This discontinuity in the density indicates the first-order nature of the vapor–liquid (wetting) transition. For the smallest \( H \) (≈5.92 nm), however, the jump in \( \langle \rho \rangle \) is rounded, and the density increases rather smoothly from a vapor to a liquid value. This does not mean that the fluid is supercritical but instead signifies that the liquid on top of the pillars (such as those shown in Figure 2) penetrates down steadily into the gap between the pillars (\( z \leq H \)). The liquid–vapor interface always exists in the present simulation.

As shown in Figure 3(c), the \( \langle \rho \rangle \) vs \( S \) curve always shows a smooth transition from a liquid to a vapor for domed pillars, regardless of \( H \). This behavior differs from the abrupt leap in \( \langle \rho \rangle \) observed for rectangular and cylindrical pillars. The rounded change in \( \langle \rho \rangle \) arises again from the fact that a liquid penetrates continuously down into the gap between the domed pillars. Note also in Figure 3(c) that the densities at \( S = 0 \) for domed pillars are considerably higher than those of the cylindrical or rectangular pillars, particularly for large pillars of \( H > 18 \) nm. For the largest domed pillars simulated (\( H = 53.28 \) nm), \( \langle \rho \rangle = 0.52 \) at \( S = 0 \). If \( \langle \rho \rangle = 0.5 \) is taken to be the borderline value of the liquid and vapor densities, this value corresponds to a state lying between a liquid and vapor (closer to a liquid). Such an intermediate state arises from the partial penetration of a liquid into the interpillar gap illustrated in Figure 4. Figures 4(a–c) present snapshots taken at three different \( S \) values of the domed pillars with \( H = 53.28 \) nm. Even at \( S = 0 \), a liquid substantially penetrates down into the interpillar gap (Figure 4(a)), giving rise to an intermediate state with \( \langle \rho \rangle = 0.52 \). As the interpillar spacing increases to 5.18 nm (Figure 4(b)), the liquid permeates further down into the interpillar gap by more than one-half of \( H \). The \( \langle \rho \rangle \) value in this case was 0.71. This state is another intermediate state closer to a liquid. For \( S = 10.36 \) nm, the interpillar gap is in the WZ state (Figure 4(c)), giving a \( \langle \rho \rangle \) value of 0.97. For comparison, MC

**Figure 3. Density of water confined between the pillar walls (\( \rho \)) vs the interpillar spacing S.** For \( Hs \) ranging from 5.92 to 53.28 nm, the \( \langle \rho \rangle \) from the MC simulation is plotted as a function of \( S \) for the rectangular (a), cylindrical (b), and domed (c) pillars. The lines are merely drawn for a visual guide. The aspect ratio was fixed to 2 throughout. The axis labels in (a) and (b) are the same as shown in (c).
snapshots of the rectangular (Figures 4(d−f)) and cylindrical (Figures 4(g−i)) pillars were obtained. Here, we cannot find any intermediate state, where a liquid penetrates almost halfway down into the interpillar gap. The liquid on top of the pillars either slightly (Figures 4(e and h)) or completely (Figures 4(f and i)) enters the interpillar gap. This is manifested by the abrupt jump in density shown in Figures 3(a and b).

Even in the WZ state, a small vapor pocket exists at the corner, where the pillar wall and base surface are encountered, regardless of the shape of the pillar (see Figures 4(c, f, and i)). Consequently, the densities shown in Figure 3 do not quite reach 1. Figure 5 shows the top view of the vapor pocket developed near the bottom of the pillar. Drawn are cross-sectional snapshots taken along the direction parallel to the XY plane at three different heights, \( z = 0.37 \) (a, d, and g), 0.74 (b, e, and h), and 0.96 nm (c, f, and i). The vapor pockets of the domed (a−c) and cylindrical (g−i) pillars were annular and almost identical in shape. On the other hand, the vapor pockets of the rectangular pillars were anisotropic and exhibited 4-fold rotational symmetry: they were thicker along the X and Y axes where the confinement between the neighboring pillar walls is maximal. Along the diagonal direction, however, the confinement between the pillar walls was minimal, and the vapor pocket was consequently thin. Regardless of the pillar shape, the vapor pocket shrinks and vanishes as its height increases and approaches the top of the pillar.

The penetration of a liquid down into the interpillar gap was studied quantitatively as follows. For a given MC snapshot, the lowest \( z \) position of those molecules belonging to the liquid on top of the pillars, \( z_{\text{min}} \), was determined. The molecules detached from the liquid on top of the pillars were not included in calculating \( z_{\text{min}} \). Therefore, \( z_{\text{min}} \) denotes the bottom of the liquid as those minimum points of the liquid shown in Figures 4(a−c). The degree of penetration \( d \) was defined as \( d = (H - z_{\text{min}})/H \). The zero and one values of \( d \) represent no and complete penetration of the bottom of liquid into the interpillar gap, respectively. The average of \( d \), \( \langle d \rangle \), was calculated by averaging over the MC snapshots (the fluctuation of \( d \) was negligible). \( \langle d \rangle \) is drawn as a function of \( S \) for various pillar heights simulated in this study (Figure 6). The \( \langle d \rangle - S \) curve is...
qualitatively similar to the $\langle \rho \rangle - S$ curve. In the case of the rectangular and cylindrical pillars, the bottom of the liquid barely reaches 0.26 of $H$ before it touches the bottom of the pillars ($\langle d \rangle = 1$). Therefore, there is no intermediate state where the liquid penetrates halfway down into the gap between the pillars. Even for the smallest rectangular and cylindrical pillars, the bottom of the liquid never reaches more than 0.49 of $H$. On the other hand, for the domed pillars, the liquid smears continuously into the interpillar gap until it touches the bottom surface. Hence, the penetration of the liquid for the domed pillars profoundly differs from those of liquids penetrating into the rectangular and cylindrical pillars.

This study examined how the critical spacing, $S_C$, for the wetting transition depends on the pillar height, $H$. Figure 7 presents $S_C$ as a function of $H$ from the LGMC simulation.
(symbols) and the continuum theory (lines) drawn for rectangular (solid line and squares), cylindrical (broken line and circles), and domed (dotted line and triangles) pillars. To calculate $S_C$ from the simulation, each $\langle \rho \rangle - S$ curve shown in Figure 3 was checked. $S_C$ was taken to be the $S$ value, whose incremental changes $\langle \rho \rangle$ from less than half to above half ($S_C = 0$ means such an $S$ value does not exist). The $S_C$ values of the rectangular pillars are always larger than those for the cylindrical and domed pillars. This originates from the fact that at the same $S$ value the liquid confined between the rectangular pillars has a volume smaller than that of the cylindrical or domed pillars (see Figure 2). To provide the same liquid volume in the interpillar gap, the $S$ value for the rectangular pillars should be larger than those of the cylindrical and domed pillars. Consequently, the $S_C$ values of the rectangular pillars are larger than those of the cylindrical and domed pillars. For a given $S$ value, the $S_C$ value for the domed pillars was the smallest because the interpillar gap was largest for domed pillars.

According to continuum theory, the $S_C$ value for rectangular pillars should increase and converge to 14.3 nm with increasing $H$. In contrast, for cylindrical and domed pillars, $S_C$ first increases, reaches a maximum, and then decreases (this decrease was not observed clearly for the current range of $H$s for cylindrical pillars because the decrease in $S_C$ is slow). Above a threshold $H$, $S_C$ becomes negative, meaning that the droplet resting on the cylindrical or domed pillars always remains in the WZ state. As explained in Section II, the interpillar gap for the cylindrical and domed pillars does not vanish by making $S = 0$. As the pillar height increases at $S = 0$, the increase in volume between the pillar walls is faster than that in the liquid—solid interface area. Consequently, the cohesion of liquid scaling with the volume takes over the liquid—solid interfacial effect for sufficiently large $H$s. Therefore, the WZ state is always more stable than the CB state for $H > H_T$. Using eqs 7 and 8, $H_T$ values of 209.2 and 63.9 nm were obtained for the cylindrical and domed pillars, respectively. The LGMC simulation of $S_C$ overall agrees with the continuum theory, particularly for the rectangular pillars. The mismatch between the simulation and theory becomes relatively large for small $H$s, presumably due to the limitation of the continuum picture of the fluid confined in small systems. The discrepancy might also arise from the cubic lattice representation of the small curved pillars. The $S_C$ from the continuum theory was calculated by using the zero temperature approximation for the surface tension. To assess the effects of finite temperature, we calculated the critical spacing by decreasing the surface tension. The theoretical $S_C$ decreased with reducing the surface tension, regardless of the shape of pillar (see the Supporting Information). As the theoretical $S_C$ is generally smaller than that from the simulation (see Figure 7), the theory is expected to deviate more from the simulation if finite temperature is considered.

This study investigated how the pressure of a liquid, $P$, affects the CB or WZ state of the liquid confined between the pillars. Figure 8 plots $\langle \rho \rangle$ as a function of $P$ for the three types of pillars with different $H$s. Here, the interpillar spacing $S$ was fixed to 5.92 nm. As $P$ was increased from 1 to 10 MPa, $\langle \rho \rangle$ increased from a vapor density ($<0.5$) to a liquid one ($>0.5$) in all the cases studied. For the rectangular and cylindrical pillars, with increasing pressure, $\langle \rho \rangle$ jumped from a vapor density to a liquid one at a near critical value, $P_C$. This jump in density was smoothed for the smallest rectangular and cylindrical pillars due to the finite size effects, as observed in the $\langle \rho \rangle$ vs $S$ plot (Figure 3). In contrast, the $\langle \rho \rangle$ for the domed pillars, regardless of $H$, increased gradually without a jump in its value, owing to the gradual invasion of liquid down into the interpillar gap. Here again, the surfaces covered with domed pillars were qualitatively different from those with rectangular and cylindrical pillars.

The slope of the $\langle \rho \rangle$ vs $P$ curve indicates how susceptible the density is to the increase in pressure. This density susceptibility $d\langle \rho \rangle/dP$, shown in Figure 9, was sharply peaked at $P_C$ for the rectangular and cylindrical pillars. In contrast, the susceptibilities of the domed pillars had small broadened peaks. The susceptibility is related to the fluctuation of density, $(\langle \delta \rho \rangle^2) \equiv \langle \rho^2 \rangle - \langle \rho \rangle^2$, where $\langle \rho^2 \rangle$ is the ensemble average of the density squared. From the statistical mechanical relation, $(\langle \delta \rho \rangle^2) = (k_BT/N)(\partial \langle \rho \rangle/\partial P)$, where $N$ is the number of total sites of the interpillar gap, we can derive $\partial \langle \rho \rangle/\partial P = (N/k_BT)(\langle \delta \rho \rangle^2)$.
by using the approximation, \( du = (1/\rho_b)dp \). Therefore, the density susceptibility is proportional to the fluctuation in the density of the interpillar gap. The density fluctuation in turn is proportional to the isothermal compressibility, \( \kappa \), because of the relation \( \langle (\delta \rho)^2 \rangle = \langle (\rho)^2 \rangle k_B T / V \kappa \).\(^{40}\) Note in Figure 9 that the susceptibilities of the domed pillars at low pressures are larger than those of the rectangular and cylindrical pillars. Therefore, the local density fluctuation and compressibility at low pressure are relatively large for domed pillars. The enhanced fluctuation or compressibility did not propagate into the bulk liquid sitting on top of the pillars however.

Of special interest is the critical pressure, \( P_C \), needed to fill the dry (CB) interpillar gap with liquid.\(^{36,41,42}\) In Figure 10, the \( P_C \) from theory and simulation were plotted as a function of the pillar height, \( H \). The interpillar spacing is fixed to 5.92 nm. The simulated \( P_C \) values are drawn as squares, circles, and triangles, respectively, for rectangular, cylindrical, and domed pillars. The theoretical \( P_C \) values for the rectangular, cylindrical, and domed pillars are drawn as solid, broken, and dotted lines, respectively.

Extensive efforts have been made to understand precisely how the hydrophobicity of a pillared surface is influenced by the height and width of a pillar and the spacing between pillars. Previous theoretical investigations relied too much on the continuum picture of water and lacked the molecular details underlying the hydrophobicity. Using a Monte Carlo simulation based on the lattice gas model, this study examined the phase behavior of water confined in the gap between pillars. The dry and wet phases of the interpillar gap, respectively, were related to the Cassie–Baxter and Wenzel states of a macroscopic droplet deposited on the pillared surface. We studied the pillar size effects by systematically varying its height from 6 to 53 nm for a fixed ratio of the height to its width (\( \approx 2 \)). The present molecular model of water was coarse grained but still captured the essence of a confined liquid. An extensive range of sizes and shapes of the pillars could be studied using this simplistic model. The periodic arrays of the domed pillars were simulated to shed light on the origin of the unparalleled hydrophobicity of a lotus leaf. As the interpillar spacing or the pressure of liquid increases, the liquid on top of the domed pillars penetrated smoothly down into the interpillar gap. This contrasted with the phase behavior observed for the rectangular and cylindrical pillars where the liquid abruptly fills in the gap between the pillars as the interpillar spacing or pressure reaches a critical value. The gap between the domed pillars was more susceptible to the intrusion of the bulk liquid on top of the pillars, due to the open geometry of the gap between the domed pillars. Also, the liquid penetrating into the gap between the domed pillars was locally more fluctuating in density and compressible than that penetrating into the gap between square or cylindrical pillars. This enhanced density fluctuation however was local and did not propagate into the bulk liquid sitting on top of the pillars. Using continuum theory, a simple analytic formula was derived for the critical spacing and pressure at which the transition between the WZ and CB states occurs. The critical spacing and pressure from continuum theory showed reasonable agreement with the present molecular simulation results.

**Figure 10.** Critical pressure, \( P_C \), as a function of the pillar height, \( H \). The interpillar spacing is fixed to 5.92 nm. The simulated \( P_C \) values are drawn as squares, circles, and triangles, respectively, for rectangular, cylindrical, and domed pillars. The theoretical \( P_C \) values for the rectangular, cylindrical, and domed pillars are drawn as solid, broken, and dotted lines, respectively.

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■ ASSOCIATED CONTENT

Supporting Information

Derivation of the continuum theory for $S_c$ and $P_c$. The effect of finite temperature on $S_c$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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