Drying Transition of Water Confined between Hydrophobic Pillars
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ABSTRACT: The phase behavior of the water confined between hydrophobic pillars was studied by using a simple thermodynamic theory and the lattice gas Monte Carlo simulation. The drying transition of water with decreasing spacing between pillars is related to the Wenzel (WZ) to Cassie–Baxter (CB) transition of droplet. Our theory agrees with simulation for pillars with heights ranging from 11 to 100 nm. The present theory further predicts that sufficiently large circular pillars cannot sustain a CB state even if the pillars are in contact with each other.

I. INTRODUCTION
A super-hydrophobic surface1−8 has attracted interest due to its numerous applications, such as water repellent glasses,9 self-cleaning clothes,10 and low-drag marine vessels, to name a few.11 The hydrophobicity of a surface is greatly enhanced in the presence of nano- or microscale pillars on it (Figure 1). The hierarchical structure of the pillars on the lotus leaf12,13 gives rise to its unparalleled hydrophobicity. Even a hydrophilic (gold) surface turns to a hydrophobic one by patterning pillars on it.14 A water droplet sitting on top of pillars exists in a Cassie–Baxter (CB) or Wenzel (WZ) state where vapor or liquid, respectively, fills the gap between pillars. An optimal hydrophobic surface induces a CB droplet which has a high contact angle and is easy to roll on a surface.15 However, it is uncertain exactly how the WZ or CB state of droplet depends on the geometry of the pillar and the spacing between them. In principle, the state of the droplet is determined by the competition between the intermolecular cohesion and interfacial energy of the water confined between the pillars: as the interpillar spacing S decreases, the water confined between the pillars reduces its volume and therefore its degree of cohesion. Below a critical value of S, Sc, the confined water is destabilized and evaporates, giving rise to a CB state.16−22 With this view, the WZ to CB transition can be thought of as a drying transition previously studied in the context of protein folding21,23−26 and the capillary evaporation in pores.19,27 Herein, we theoretically study the drying of water confined in an array of square or circular pillars, a prototypical super-hydrophobic surface generated in nano- and micro-electro-mechanical systems (NEMS/MEMS) technology (Figure 1). Using grand canonical Monte Carlo (GCMC) simulation based on the lattice gas model19,27−31 we investigate how the WZ or CB state of droplet depends on the height H and width W of each pillar and S (Figure 1). We present a thermodynamic theory of Sc which agrees with the GCMC simulation.

II. THEORY AND SIMULATION METHOD
We defined ΩV and ΩL as the grand potentials of the vapor and liquid filling the gap between pillars, respectively. In both phases, liquid exists on top of the pillars, z > H. The difference in the grand potentials of the CB and WZ states, ΔΩ, is approximated as

\[ ΔΩ = Ω_V - Ω_L = (∆P)V - (∆γ)A_S + γ_{LV}A_{LV} \]  

where V is the volume of the interpillar gap and A_S is the surface area of the solid in the periodic cell. A_{LV} is the area of the liquid–vapor interface, and ∆P is the pressure of the liquid P_L in excess of the vapor pressure P_V (both have the same

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chemical potential $\mu$). If air flows into the interpillar gap in the CB state, $P_v$ includes the external pressure due to the ambient air. $\gamma_{LV}$ is the liquid–vapor interfacial tension, and $\Delta \gamma$ $\equiv$ $\gamma_{LS}$ $-$ $\gamma_{SV}$ where $\gamma_{LS}$ and $\gamma_{SV}$ are the liquid–solid and vapor–solid interfacial tensions, respectively. In the case of a CB state, there is an extra free energy arising from the solid–liquid–vapor line. This line tension effect can be neglected, however: Note the free energy (per periodic cell) due to the surface tension, $\Omega_{SLV}$, is given by $4\sqrt{\pi}$ $W_{ff}$ and $\pi r^2 W_{ff}$ for square and circular pillars, respectively. In contrast, the free energy due to the surface tension, $\Omega_{LV}$, was estimated by using the experimental line tension value of air $\equiv$ 72.1 mN/m. We then calculated $\Omega_{SLV}$ for square pillars, respectively. The ratio $\Omega_{SLV}$/$\Omega_{LV}$ at $S$ = $S_C$ for each pillar simulated ($H$ = 1.5–100 nm). Therefore, the line tension effect is minor and can be neglected in our theory.

The condition, $\Delta \Omega = 0$ at $S$ $\equiv$ $S_C$ gives $S_C$ for square pillars as

$$S_C = \left( \frac{H}{r} \right) \left[ 1 + \frac{4r\Delta \gamma}{((\Delta P)H - \Delta \gamma + \gamma_{LV})} - 1 \right]$$

(2)

$r$ is the aspect ratio, $r$ $=$ $H$/W. Similarly, $S_C$ for circular pillars is given by

$$S_C = \left( \frac{H}{r} \right) \left( \frac{\sqrt{\pi}}{2} \right) \left[ 1 + \frac{4r\Delta \gamma}{((\Delta P)H - \Delta \gamma + \gamma_{LV})} - 1 \right]$$

(3)

In the limit of $H$ $\rightarrow$ 0, both eqs 2 and 3 reduce to $S_C$ $\rightarrow$ 0. In the large $H$ limit, eq 2 approaches a constant independent of $r$

$$S_C \rightarrow \frac{2\Delta \gamma}{\Delta P}$$

(4)

while eq 3 becomes a linear function of $H$

$$S_C \rightarrow \frac{\sqrt{\pi} \Delta \gamma}{2} \left( \frac{1 - \sqrt{\pi} / 2}{\Delta P} \right) \frac{H}{r}$$

(5)

The interpillar gap for circular pillars, unlike for square pillars, is finite at $S$ $=$ 0 and increases in volume with increasing $H$. Consequently, a WZ state is more favored with increasing $H$ and above a threshold value of $H$ (which gives zero value of eq 5), only a WZ state is possible.

In the present GCMS simulation, water molecules reside on the sites of a cubic lattice confined between the pillars and above a flat bottom surface. The lattice spacing $a$ is taken to be the molecular diameter of water, 0.37 nm. A molecule interacts with its nearest neighbor molecules with an attraction energy $\epsilon$ and has its own chemical potential $\mu$. When it is located adjacent to the surfaces of solid, it has a binding energy of $\epsilon_w$. The $\mu$ value for the bulk vapor–liquid phase transition, $\mu_o$, is given by $-3\epsilon$. The relative humidity was defined as $\exp[(\mu - \mu_o)/(k_B T)]$ and set to 105% to mimic an oversaturated vapor. Temperature was fixed at 300 K. The bulk critical temperature for the present lattice gas is exactly given by 1.1288 $e$/k$_B$. Identifying our liquid as water (its critical temperature is 647.3 K) sets $\epsilon$ to be 4.8 kJ/mol. We took $\epsilon_w$ = 0.01e to emulate a hydrophobic surface.

Throughout the present simulation, we fixed $r$ to 2 (a typical aspect ratio in experiments), and $H$ was varied as 1.5, 3, 6, 11, 22, 33, 44, 56, 67, 78, 89, and 100 nm. For a given combination of $H$, $W$, and $S$, we simulated a single pillar in a rectangular parallelepiped box with a size of ($W$ + $S$) $\times$ ($W$ + $S$) $\times$ ($H$ + 18.5 nm) by applying the periodic boundary conditions in the $X$ and $Y$ directions. GCMC moves were performed by using the Glauber single spin-flip algorithm. The initial configuration of the simulation was prepared by setting the occupancy of each lattice site $c_i$ ($i$ $=$ site index) to 1. We also tried an initial configuration similar to the CB state where the interpillar gap ($z$ $\leq$ $H$) is empty ($c_i$ = 0) and the sites above the top of the pillar ($z$ $>$ $H$) are occupied ($c_i$ = 1). We obtained the same results using two different initial configurations. The absence of hysteresis might arise from the fact that the present lattice GCMC performs an extensive sampling of the configuration space. Typically, 100 000 MC moves were tried for each lattice site. In case the density shows significant fluctuation, which is the case where $S$ is close to $S_C$, we increased the number of MC moves up to 400 000 times per site. Therefore, by sampling much more than in a continuous space MC simulation, the present lattice simulation obviates any metastable state and the hysteresis.

We evaluated $\Delta \gamma$ in eqs 2 and 3 by using the Young equation, $\Delta \gamma$ $=$ $\gamma_{LV}$ $\cos \theta$, where $\theta$ is the intrinsic contact angle of a liquid droplet in contact with a flat surface. $\gamma_{LV}$ was taken to be half of the work of cohesion, the free energy change for the water–quartz interface.

$$\gamma_{LV} \equiv \frac{W_{ff}}{2\pi r^2}$$

(6)

The work of cohesion was approximated as $\epsilon/a^2$ by neglecting the entropic contribution to it. We rewrote $\gamma_{LV}$ in the Young equation as $\gamma_{LS} = \gamma_{LV} + \gamma_{SV} - W_{LS}$ where $W_{LS}$ is the work of adhesion between solid and liquid.

$$\gamma_{LS} \equiv \frac{\epsilon}{a^2}$$

(7)

The zero-temperature approximations for $\gamma_{LV}$ and $W_{LS}$ were shown to be reasonable by Lazar and Leung. Our previous simulation confirmed that entropy is negligible for the capillary force of water confined between a nanoscale tip and a surface. We also used the relation $\Delta P = \rho_i (\mu - \mu_o)$, where $\rho_i$ is the bulk density of liquid (=1/a$^3$). The present $\Delta P$ is 4 MPa, close to the impact pressure on a wind-driven raindrop colliding against a surface (1–20 MPa).

For comparison, we also ran an off-lattice molecular dynamics (MD) simulation by adopting the simple point charge (SPC) model for water: each atom of a water molecule has a partial charge (−0.82 and +0.41 on oxygen and hydrogen atoms, respectively). The partial charges interact via the Coulomb potential

$$U^{C}(r_{ij}) = \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}$$

(8)

where $q_i$ is the charge of atom $i$ and $q_j$ is the vacuum permittivity. $r_{ij}$ is the distance between two atoms $i$ and $j$. Oxygen atoms additionally interact with each other through the Lennard-Jones (LJ) potential

$$U^{LJ}(r_{ij}) = 4 \epsilon_{ij} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{12} - \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{6}$$

(9)

where $\epsilon_{ij}$ and $\sigma_{ij}$ are the LJ energy and length parameters, respectively. The LJ parameters for the oxygen–oxygen interaction are 0.3166 nm ($\sigma_{oo}$) and 0.650 kJ/mol ($\epsilon_{oo}$). The interaction between water and the pillar atom was also described by the LJ potential. The LJ energy parameter $\epsilon_{wa}$ for the water–pillar atom interaction was taken to be $\epsilon_{wa} = 0.01 \epsilon_{ww}$.
which is the same ratio of $\varepsilon_s$ and $\varepsilon$ used in the lattice gas simulation. The LJ length parameter for the water–pillar atom is taken to be the same as $\sigma_{ww}$. We made square pillars out of a simple cubic lattice with a lattice spacing of 0.288 nm. We set $H = 1.152$ nm and $W = 0.576$ nm. The bottom surface is made of four layers. As the initial condition of MD simulation, the liquid water fills in the gap between and above the pillars. By gradually reducing the interpillar gap from 7.2 to 1.44 nm (with a decrement of 0.288 nm), we examined the density of the interpillar gap and checked whether the interpillar gap is in a CB or WZ state. For a given set of $H$, $W$, and $S$, a single pillar was simulated in a parallelepiped box with a size of $(W + S) \times (W + S) \times (H + 17.3$ nm) by applying the periodic boundary conditions. The number of water molecules varied from 301 to 4626 as $S$ changed from 1.44 to 7.2 nm. For equilibration, we ran a constant temperature (NVT) MD run at 300 K for 1 ns. After equilibration, we ran another MD simulation by applying an external pressure of 5.1 MPa on water molecules. To exert a desired pressure of $\Delta P$ on liquid water, we applied an external force of $\Delta P \times (W + S) \times (W + S)$ along the $Z$ direction, and the total external force was uniformly distributed among water molecules. The MD trajectory was propagated using the velocity Verlet algorithm with a 1 fs time step. The atoms constituting pillars were held rigid. The temperature was set to 300 K using the Berendsen thermostat. We used the DL_POLY package to implement the MD methods described above. We collected the 800 snapshots out of a 1 ns long simulation for the purpose of calculation of average quantities.

III. RESULTS AND DISCUSSION

Simulation results are now described. In the case $S > S_C$, the interpillar gap was filled with a liquid, giving rise to a WZ state. A typical snapshot of a WZ state is shown in Figure 2a and b for the square and circular pillars, respectively. There are empty sites among liquid sites due to thermal fluctuation, and they can further form clusters (made of 2–8 sites) near the pillar walls. When averaged over GCMC snapshots, however, these empty sites are erased and the interpillar gap is full of a liquid. At an inter pillar gap evaporated as the simulation proceeded. The evaporation started from the bottom ($z = 0$) but stopped at the top of the pillar ($z = H$), giving a liquid atop pillar ($z > H$). Such a CB state is shown in Figure 2c and d for the square and circular pillars, respectively.

We checked the water density in the interpillar gap, $\rho_f$, defined as the average occupancy of sites, $\langle \rho_f \rangle$, with $z \leq H$. Figure 3 plots $\rho_f$ vs $S$ for square and circular pillars with different $H$s. A value of $\rho_f$ close to 1 (0) indicates that the interpillar gap is in the WZ (CB) state. The abrupt drop in $\rho_f$ near a critical value of $S(S_C)$ is characteristic of a first-order drying transition. The rounded transition (the smooth increase of $\rho_f$ from near 0.2 to 1) for $H = 1.5$ nm presumably arises from the small inter pillar gap in this case (that is, due to a finite size of gap, the first-order transition disappears and the transition becomes supercritical). The $\rho_f$ for $H = 6$ nm is near 0.3 and 0.4 for the square and circular pillars, respectively. These states, intermediate between typical CB and WZ states, are called partially dry states by taking 0.5 to be the borderline value distinguishing a WZ (wet) state from a CB (dry) state. The states having $\rho_f$ near 0.65 for $H = 100$ nm are called partially wet states. Note also the states with $\rho_f$ close to 0.48 and 0.66 for the square and circular pillars with $H = 1.5$ nm, respectively. All of these intermediate states have large fluctuations in density.

Figure 4a and b shows the density profile $\langle \rho \rangle$ for the circular pillar with $H = 6$ nm and $S = 5.92$ nm. Figure 4a shows the density is low near the pillar wall, but it increases with increasing distance from the wall. In Figure 4b, the liquid on top of the pillar penetrated down into the interpillar gap. This is similar to the metastable droplet immersed into the inter pillar gap reported in the lattice Boltzmann study. Figure 4c and d plots the density profile for the partially wet state for the highest circular pillar with $S = 4.81$ nm. Figure 4c shows that a liquid forms along the diagonal ($x = y$) direction where liquid is least confined, while the liquid evaporated along the $X$ and $Y$ axes, where the confinement is greatest. Figure 4d shows that evaporation partly occurs at the intersection of the pillar wall and bottom surface.

The top of Figure 5 shows $S_C$ vs $H$. The $S_C$ values for the circular pillars were smaller than those for the square pillars. For the same $S$ value, a liquid is less confined between circular

![Figure 3](image-url)

**Figure 3.** Density of water confined between pillars vs the interpillar spacing $S$. For $H$s ranging from 1.5 to 100 nm, $\rho_f$ was plotted vs $S$ for the square (top) and circular (bottom) pillars. The lines are drawn for a visual guide. The standard deviations are drawn as error bars.
pills than between square pillars, because of the concave gap between the circular pillars when viewed from the top (Figure 1d). Consequently, a smaller $S_C$ is required for circular pillars than for square pillars. With increasing $H$, $S_C$ increases for square pillars, but for circular pillars, $S_C$ first increases and then decreases. Overall, the theory agrees sensibly with the GCMC simulation. It is not clear why the present continuum theory agrees with the lattice gas simulation which explicitly considers the discrete nature of the molecule. Interestingly, a similar agreement was found in the MD simulation on the drying transition of water confined between two hydrophobic plates. On the other hand, the $S_C$ from theory approaches zero as $H$ comes near zero but the $S_C$ of simulation approaches a finite value. The relative deviation of the theoretical $S_C$ from that of the simulation increased with decreasing $H$, ranging from 0.5 to 29%. The deviation for $H < 11$ nm exceeded 10% and reached up to 29% for the smallest pillars. The small circular pillars of $H = 1.5$ and 3 nm actually appear as diamonds in the present cubic lattice. We checked if the discrepancy between simulation and theory for these small pillars arises from the poor representation of circular pillars in the cubic lattice. To do so, we derived a theory for diamond-shaped pillars following the same procedure for circular or square pillars shown above. This theory, drawn as the dotted line in the inset of Figure 5 (top), again deviated from simulation. Therefore, the deviation could be ascribed to the failure of thermodynamics in describing the small-sized systems.

In the bottom of Figure 5, the theoretical predictions were shown by extending the range of $H$ up to 250 nm. The $S_C$ for square pillars slowly converges to 14.2 nm with increasing $H$. The $S_C$ value for the circular pillars reaches a maximum at $H = 33$ nm and then decreases with further increases in $H$. $S_C$ reached zero at $H = 207$ nm for circular pillars, and no CB state existed for pillars taller than that. As discussed above, with increasing $H$, the finite interpillar gap at $S = 0$ increases in volume and the WZ state becomes more favorable. Above a critical value of $H$, only a WZ state is possible.

Although it is shown above that the effect of line tension should be small, the shift of $S_C$ to a new value $S'_C$ due to the line tension can be estimated as follows. First, note the line tension changes the grand potential as $\Delta \Omega = \Delta \Omega + \Omega_{SLV}$, and $S'_C$ must satisfy $\Delta \Omega'(S'_C) = 0$. The Taylor expansion gives $S'_C \approx S_C - \Omega_{SLV}/\partial \Delta \Omega/\partial S_{L-S=C}$. For the square pillars, $S'_C$ is given by

$$S'_C = S_C - \frac{2\Omega_{SLV}}{((\Delta P)H - \Delta \gamma + \gamma_{SLV})(\partial S_{C} + H)}$$

(8)

For the circular pillars, $S'_C$ is given by

$$S'_C = S_C - \frac{\pi H_{SLV}}{2((\Delta P)H - \Delta \gamma + \gamma_{SLV})(\partial S_{C} + H)}$$

(9)

These $S'_C$ values are evaluated by using the experimental line tension of air–water–quartz, $\gamma_{SLV} \approx 3 \times 10^{-11} J/m^2$, and are drawn as dot-dashed and dotted lines in the bottom of Figure 5. The deviation of $S'_C$ from $S_C$ is small, especially pillars with $H$s above 100 nm. The line tension however might play an important role in determining the rate of transition from the WZ to CB state (the present work however focuses on the
equilibrium thermodynamics for the WZ and CB states). For example, Sharma and Debenedetti have reported the line tension is important in the capillary evaporation rate of water confined between two circular disks.

Let us delve into the absence of a CB state for large circular pillars. As mentioned in the Introduction, $S_C$ is determined by the interplay of the cohesion and interface energies of liquid confined between pillars. Consider the change in the grand potential for the WZ to CB transition, $\Delta \Omega = \Omega_C - \Omega_S$, given by eq 1. There, $\Delta \Omega$ increases by $(\Delta P)V$ because creating a cavity of volume $V$ costs a decrease in the cohesion energy of liquid. $\Delta \Omega$ also increases by $\gamma_{LV}A_{LV}$ due to making the new interface between liquid and vapor. In addition to these two unfavorable terms in $\Delta \Omega$ which are against the WZ to CB transition, there is a favorable term, $-(\Delta \gamma)A_S$, arising from replacing the liquid–pillar interface by the vapor–pillar interface. These three terms of $\Delta \Omega$, along with $\Delta \Omega$, are plotted vs $S$ for different $H$s in Figure 6. Except for $H = 300$ nm, the favorable term $-(\Delta \gamma)A_S$

Figure 6. Change of the grand potential involved in the WZ to CB transition, $\Delta \Omega$. By varying $H$ from 5 to 300 nm, we plot $\Delta \Omega$ (solid line) and its projection into $(\Delta P)V$ (lines with up triangles), $\gamma_{LV}A_{LV}$ (lines with squares), and $-(\Delta \gamma)A_S$ (lines with down triangles). Drawn as a circle in each panel is the point at which $\Delta \Omega$ changes from a negative to positive value as $S$ increases from 0. All the panels have the same axis labels as those in the lower left panel.

dominates at small values of $S$, giving rise to a negative $\Delta \Omega$. As $S$ increases, $(\Delta P)V$ and $\gamma_{LV}A_{LV}$ take over, making $\Delta \Omega$ positive. Therefore, the exact location of $S_C$, drawn as circles in Figure 6, is determined by the relative magnitudes of these favorable and unfavorable terms. As $H$ increases from 5 to 300 nm, each of these three terms increases its magnitude. For pillars with small $H$ (= 5, 10, 30 nm), the decrease in $-(\Delta \gamma)A_S$ (drawn as the lines with down triangles) with increasing $S$ is faster than the increase of the unfavorable two terms. This gives an increasing $S_C$ with increasing $H$ (the circle in each panel shifts to the right as $H$ increases from 5 to 30 nm). For $H \geq 50$ nm, however, the increase in $(\Delta P)V$ (drawn as the lines with up triangles) with increasing $S$ becomes faster than the decrease in $-(\Delta \gamma)A_S$. Consequently, $S_C$ now decreases with increasing $H$ from 50 to 100 nm. Note $(\Delta P)V$ does not vanish at $S = 0$, and this offset increases as $H$ rises. For $H$ of 300 nm, this offset is so large that $\Delta \Omega$ is positive no matter how small $S$ is. There is then no transition from the WZ to CB state. In contrast, $(\Delta P)V$ at $S = 0$ vanishes for square pillars. It might seem counterintuitive that increasing the pillar size suppresses the drying transition for circular pillars. As shown above, however, the drying is determined by the subtle interplay between the cohesion and interface energies of liquid confined in the interpillar gap, not simply by the size of pillar. Note also this decreasing $S_C$ with increasing $H$ for circular pillars was confirmed by the lattice gas simulation.

The present theory predicted a CB state is not allowed for circular pillars with $H \geq 207$ nm (bottom of Figure 5). There, we assumed a very high pressure for the water droplet, which is relevant to the case where the droplet collides with high speed against a pillared surface. For a static droplet sitting on a pillared surface, we can estimate $\Delta P = P_s - P_v$ as follows. If a water droplet of 1 mm in radius is considered, we can use the Young–Laplace equation, $\Delta P = 2\gamma_{LV}/R$, where $\gamma_{LV}$ is the surface tension of water (72.1 mN/m) and $R$ is the radius of droplet. Then, we get $\Delta P = 144$ Pa for such a static droplet. Further assuming the same contact angle and the aspect ratio $r = H/W$ used above, we evaluate the $S_C$ values from our theory. As shown in Figure 7, the $S_C$ vs $H$ curve shows the same qualitative behavior as found for the droplet with a high pressure (Figure 5). Quantitatively, however, now the CB state for circular pillars can exist up to $H = 14$ nm. This means a CB state exists for typical pillars generated by NEMS/MEMS experiments (which ranges up to 100 $\mu$m). Moreover, $S_C$ now increases with increasing $H$ for both square and circular pillars up in the typical range of $H$s produced in NEMS or MEMS technology. The present lattice gas model, although qualitative in nature, has captured the essential features of the phase behavior of nanoconfined liquids;

Figure 7. Size dependence of the drying transition predicted for a static droplet sitting on a pillared surface. We have drawn the theoretical predictions, eqs 2 and 3, for a static water droplet with a radius of 1 mm sitting on top of square and circular pillars as solid and broken lines, respectively.

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calculation reproduced the typical magnitude of the capillary force exerted on an atomic force microscope tip and its humidity dependence.\textsuperscript{28} By introducing extra spin variables in the present two-state ($c_i = 0, 1$) lattice gas model, such as in the multistate Potts model,\textsuperscript{46} we might be able to consider the orientation of water molecules. Even a glassy behavior of a confined liquid has been reproduced by imposing kinetic constraints (in the Monte Carlo move)\textsuperscript{46} or an asymmetric interaction in the lattice gas model.\textsuperscript{47}

An off-lattice simulation adopting realistic intermolecular potential functions might reveal the tetrahedral hydrogen bond network and the alignment of electric dipoles of water along the surface normal.\textsuperscript{1, 48, 39} Inclusion of a long-ranged electrostatic interaction between water molecules will facilitate condensation but hinder drying of water. The resulting $S_C$ will be presumably lower than that predicted in the present lattice model employing the nearest neighbor interaction. This prediction is indeed confirmed by our off-lattice MD simulation. In Figure 8a, we show a typical MD snapshot of the CB state for $H = 1.152$ nm, $r = 2$, and $S = 2.016$ nm. An external pressure of 5.1 MPa was applied to water. Plotted in Figure 8b is the mass density of water confined between pillars, $\rho_{m}$ (drawn as squares), calculated from the MD simulation. As $S$ increases from 1.44 to 7.2 nm, $\rho_{m}$ smoothly increases from 0.04 to 0.68 g/cm$^3$. The half of the maximum $\rho_{m}$ is taken to be the borderline value for the WZ and CB states. According to this criterion, $S_C$ (circled in the figure) is found to be 3.168 nm. Also drawn as circles in Figure 8b is the $\rho_{m}$ vs $S$ from the lattice gas simulation by using $\Delta P = 5.1$ MPa. Here $S_C$ is found to be 4.608 nm. Therefore, the $S_C$ from the off-lattice MD simulation is smaller than that from the lattice simulation by 1.44 nm. The present thermodynamic theory predicts $S_C$ to be 3.946 nm, which is in the middle of those from the MD and lattice GCMC simulations. Overall, the $S_C$ from the lattice gas simulation reasonably agrees with that from the MD simulation. Further MD simulations to demonstrate the decreasing $S_C$ for circular pillars are too time-consuming and beyond the scope of the present work. Instead, we note that the present lattice gas simulation, which nearly quantitatively agrees with a fully atomistic MD simulation, does show the decreasing $S_C$ behavior for circular pillars. Therefore, this conclusion should be valid for MD simulations as well.

IV. CONCLUSION

We studied the WZ or CB state of a water droplet on an array of pillars by focusing on the drying behavior of the water confined between pillars. Using a molecular GCMC simulation, we examined how the drying depends on the shape (square or circular) and size of each pillar and the gap between pillars. Our simulation revealed that the liquid atop pillars can penetrate down into the interpillar gap, and the interpillar gap for an array of circular pillars can be dried partially along the direction where the wall-to-wall distance between pillars is shortest. We presented a thermodynamic theory for the critical spacing between pillars which gives a WZ to CB transition, $S_C$. Our theory agreed with the GCMC simulation. As the pillar grew in size for square pillars, $S_C$ increased and converged to a constant value. For circular pillars, however, $S_C$ showed a turnover behavior with increasing pillar size, such that sufficiently large circular pillars cannot sustain a CB state.

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Notes

The authors declare no competing financial interest.

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