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Directional motion of evaporating droplets on gradient surfaces

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Evaporation of sessile water droplets on surfaces with wettability gradients was studied. The wettability gradient was generated by fabricating non-uniformly distributed cylindrical micropillars on silicon surfaces. During the evaporation, it was found that the center of mass of the droplet moved either in or against the direction of the wettability gradient, depending on the configuration of the micropillars. An energy-based theoretical criterion was derived to predict the moving direction. The theoretical predictions agreed well with the experimental observations. The results provide a parametric design basis to control the contact line dynamics and directional transport of evaporating droplets.

Droplet evaporation on surfaces has various applications in drying problems such as ink-jet printing, pesticide spraying, chemical or biological detection, and DNA microarray spotting technology. Controlling evaporating droplets via substrate morphology, wetting properties, and evaporation rate allows efficient deposition of sample molecules in these applications. For example, sample molecules in droplets can be enriched to the specific sensing area with minimal loss by virtue of localization during the evaporation of diluted solutions on specially designed surfaces. Such evaporation-assisted manipulation of droplets to the targeted locations is very important for bio/chemical sensing applications. Previously, droplet evaporation has been widely investigated on hydrophilic, hydrophobic, or superhydrophobic surfaces. The evaporation process is largely determined by the surface tensions between the liquid, solid, and vapor phase through the evolution of the contact angle (CA) and contact line (CL) of the droplets. In terms of the change of the CA and CL, the evaporation process can be divided into three modes: the constant contact line (CCL) mode, in which the CL remains unchanged while the CA decreases; the constant contact angle (CCA) mode, in which the CA retains its initial value while the contact area shrinks; and the mixed mode, in which both the contact area and CA decrease. However, most of these studies were performed on uniform surfaces and the evaporation process shows a symmetric stick-slip motion of the CL towards the center of the droplet in all directions. Therefore, on uniform surfaces, it is impossible to relocate droplets through self-evaporation. If the evaporating droplets can be guided in certain directions and transported to a desired location, it will benefit many evaporation-assisted applications including chemical sensing, bio-detection, and spotting of DNA microarray.

In this letter, we study the evaporation of droplets on surfaces with wettability gradients, generated by fabricating micropillars of varying densities on silicon surfaces. It is observed that the center of the CL of an evaporating droplet moves along the wettability gradient. The moving direction can be controlled in or against the gradient direction by varying the configuration of the micropillars. This phenomenon is explained by comparing the excess free energy during evaporation and the energy barrier required to overcome the adhesion for the receding of the CL. Based on the energy analysis of the surfaces, we developed a theoretical model that can be utilized to quantitatively guide the design of gradient surfaces for controlled droplet evaporation applications.

We performed droplet evaporation experiments on a surface with micropillars of uniform pillar diameter but varying pillar-to-pillar spacing. The surface was fabricated by standard photolithography and deep reactive ion etching on silicon substrates followed by surface treatment using Perfluorodecyltriethoxysilane, which yields an intrinsic static contact angle of ~110° on a flat surface. As shown in Fig. 1(a), the micropillar diameter \(a\) is 10 \(\mu m\) and height \(h\) is 20 \(\mu m\). The micropillars of varying densities on silicon surfaces. It is observed that the center of the CL of an evaporating droplet moves along the wettability gradient. The moving direction can be controlled in or against the gradient direction by varying the configuration of the micropillars. This phenomenon is explained by comparing the excess free energy during evaporation and the energy barrier required to overcome the adhesion for the receding of the CL. Based on the energy analysis of the surfaces, we developed a theoretical model that can be utilized to quantitatively guide the design of gradient surfaces for controlled droplet evaporation applications.

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center-to-center spacing $s$ varies from 10 to 70 $\mu$m. As a result, the solid fraction $\varphi = (a^2\pi)/(4s^2)$ ranges from 0.786 to 0.012 and the static CA varies from 121° to 170°. We recorded the entire evaporation process of a 7 $\mu$l de-ionized water droplet placed on the surfaces by a CMOS digital camera. Figure 2(a) shows the snapshots of an evaporating droplet. Different from that on uniform surfaces, the evaporation of the droplet on the gradient surface demonstrated asymmetric behavior. On the relatively wetting side, where the static CA is lower (higher solid fraction), the CL pinned strongly. However, on the high CA side, the CL experienced a repeated pinning and depinning from one pillar to another, moving toward the lower CA side (in the direction of wettability gradient). The changes of the CA and contact diameter are shown in Fig. 2(c). It is seen that the evaporation changed quickly from the CCL mode to the CCA mode, in which the contact area shrank stepwisely as the CL moved over the micropillars.

We also conducted experiments on a surface with varying pillar diameters (4-20 $\mu$m) and spacings (5-76 $\mu$m), as shown in Fig. 1(b). The solid fraction $\varphi$ and static CA for these surfaces range from 0.503 to 0.054 and 124° to 163°. Surprisingly, we observed the CL receding from the lower static CA to the higher static CA (against the direction of wettability gradient), which is opposite to the direction of the previous experiment. In Fig. 2(b), it is seen that the droplet gradually receded from the region of lower static CA whereas the CL at the higher CA side remained stationary. Figure 2(d) shows the variations of the CA and contact diameter during evaporation, which follow similar fashion to that in Fig. 2(c).

To understand the distinct directional motion of the droplets, it is necessary to explore the variation of the surface energy of the droplet during evaporation. Figure 3 shows the schematic of the model for droplet evaporation on a gradient surface, where, to be general, the pillar diameter $a$ increases gradually from the left to the right side and the pillar spacing $s$ also varies in location. The solid fraction of the surface $\varphi$ and static CA change in the horizontal direction accordingly. Since the droplet size is small, it is reasonable to assume that the spherical droplet cap create nearly equal CAs on both sides. The Gibbs free energy $G$ for the droplet can be written as

$$G = \gamma_h A + \varphi\pi r^2(\gamma_d - \gamma_h) + (1 - \varphi)\pi r^2\gamma_h,$$

(1)
where $\gamma_{lv}$, $\gamma_{as}$, and $\gamma_{sv}$ are the surface tensions at the liquid-vapor, solid-liquid, and solid-vapor interfaces, respectively, $A$ is the area of the liquid-vapor interface of the spherical cap, and $r$ is the radius of the contact area. Using Young’s equation, $\gamma_{sl} - \gamma_{sv} = -\cos \theta \gamma_{lv}$.

Equation (1) can be written as

$$G = \pi r^2 \gamma_{lv} \left[ \frac{2}{1 + \cos \theta} + 1 - \varphi(\cos \theta + 1) \right].$$

(2)

In Eqs. (1) and (2), the CA $\theta$ and solid fraction $\varphi$ are the average of that at points $L$ and $R$ (Fig. 3). Since the droplet evaporation is slow, the CL receding is assumed in a quasi-steady-state process. All the free energy equations are derived in their equilibrium forms. When a droplet evaporates, the CL reduces and deviates from that of the initial equilibrium state $\theta_0$, which will be discussed later. The corresponding excess free energy per unit length of the CL has been shown dependent on the deviation of the CA $\delta \theta = \theta - \theta_0$.

$$\delta G = \frac{r \gamma_{lv}}{2(1 + \cos \theta_0)} (\delta \theta)^2.$$  

(3)

On the other hand, the CL experiences a series of stick-slip motions during the evaporation. The threshold for the CL to transit from stick to slip is the adhesion work between the liquid and solid for a distance between two adjacent micropillars. Figure 3 illustrates the gradual receding of the CL. A hypothetical route of the CL movement is composed of two steps. The CL separates from the pillar where it sat on previously and then jumps to the adjacent pillar (see inset of Fig. 3). For the CL to move, the droplet has to overcome an energy barrier required to separate a liquid-solid interface into a liquid-vapor and a solid-vapor interface. For a Cassie droplet on a micropillar surface, the energy barrier $G$ is given by

$$U = s \varphi [\gamma_{lv} - (\gamma_{sl} - \gamma_{sv})] = \frac{a^2 \pi}{4s} (1 + \cos \theta) \gamma_{lv}.$$  

(4)

During the evaporation, $\delta \theta$ increases and the excess free energy $\delta G$ increases greatly as it is proportional to $(\delta \theta)^2$. When $\delta G$ surpasses the energy barrier $U$, the CL will move. Therefore, the CL would start to move from the lower energy barrier side. Once the CL moves, the excess free energy is released and the droplet resumes another equilibrium state. Then the evaporation process repeats another cycle of stick-slip motion. For a gradient surface where the energy barrier on one side is always lower than the other one, the CL always slips from one side, resulting in a directional motion of receding.

Equation (4) suggests that the energy barrier depends on the configuration of the micropillars. By changing the pillar diameter and spacing, the energy barrier can be freely tuned. In this sense, the moving direction of an evaporating droplet can be controlled either in or against the wettability gradient. Considering that the CA at large solid fraction $\varphi$ side is small, it can be derived from Eq. (4) that a criterion for evaporating droplets to move against the wettability gradient (from low to high CA), satisfying the conditions $U_L < U_R$ and $\varphi_L > \varphi_R$, is given by

$$\frac{a^2}{k} \left\langle \frac{a_L}{a_R} \right\rangle^2 < \frac{s_L}{s_R}.$$  

(5)

If Eq. (5) is not satisfied, the droplets will move from high to low CA (in the direction of wettability gradient). This criterion is illustrated in the $a_l/a_R$ versus $s_l/s_R$ diagram (Fig. 4), indicating the CL receding direction in relation to the static CA gradient by three regions, I, II, and III). In regions I and III, the CL moves in/opposite the direction of wettability/CA gradient, while in region II, the CL moves against/in the direction of the wettability/CA gradient.

To verify the criterion of Eq. (5), additional surfaces with various micropillar configurations were fabricated. These surfaces have gradually varying pillar diameters and center-to-center spacings. Table I summarizes the geometric parameters of the as-fabricated surfaces. Droplet evaporation experiments were performed on these surfaces under the same experimental conditions. The droplets receded unidirectionally either in or against the direction of the wettability gradient. As indicated in Fig. 4, the results of the CL receding directions on all the surfaces tested are in excellent agreement with the theoretical predictions.
In summary, we investigated droplet evaporation on surfaces with wettability gradients. Interestingly, we found that the droplets could fashion strikingly different CL receding motion following or against the wettability gradient depending on the competition of the energy barrier for dewetting along the wettability gradient. A criterion based on the free energy of the droplet and the energy barrier for the stepwise motion of the CL was developed to predict the moving direction of the CL. Experiments showed that the directional motion of the CL agreed well with the theoretical predictions. Our findings reveal that controlling surface roughness (wettability) can be harnessed to precisely manipulate droplet transport during evaporation.

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<table>
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<tr>
<th>Surface No.</th>
<th>Pillar diameter $a$ (μm)</th>
<th>Center-to-center spacing $s$ (μm)</th>
<th>Solid fraction $\varphi$</th>
<th>CL receding (in/against the direction of wettability gradient)</th>
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<tr>
<td>1</td>
<td>10</td>
<td>10,12,14,16,18,20,22,24,26,28,30,32</td>
<td>0.786-0.077</td>
<td>in</td>
</tr>
<tr>
<td>2</td>
<td>6,7,8,9,10,11,12,13,14,15</td>
<td>8,11,16,21,26,32,39,46,54,62</td>
<td>0.442-0.046</td>
<td>in</td>
</tr>
<tr>
<td>3</td>
<td>5,6,7,8,9,10,11,12,13,14,15,16</td>
<td>7,9,11,14,18,22,26,30,35,40,46,52</td>
<td>0.401-0.074</td>
<td>against</td>
</tr>
<tr>
<td>4</td>
<td>20,22,24,26,28,30,32,34,36,38,40</td>
<td>23,5,26,28,5,31,33,5,36,38,5,41,43,5,46,48,5</td>
<td>0.569-0.534</td>
<td>against</td>
</tr>
<tr>
<td>5</td>
<td>6,8,10,12,14,16,18,20,22,24,26,28</td>
<td>30,31,32,33,34,35,36,37,38,39,40,41</td>
<td>0.031-0.366</td>
<td>in</td>
</tr>
<tr>
<td>6</td>
<td>8,10,12,14,16,18,20,22,24,26,28,30</td>
<td>60</td>
<td>0.014-0.196</td>
<td>in</td>
</tr>
<tr>
<td>7</td>
<td>7,8,9,10,11,12,13,14,15,16,17,18</td>
<td>49,48,47,46,45,44,43,42,41,40,39,38</td>
<td>0.016-0.176</td>
<td>in</td>
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TABLE I. Parameters of the surfaces.