Morphology Tunable Pinning Force and Evaporation Modes

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We discussed the mechanism of different evaporation modes and PS transition. We established a model based on the pinning force of the contact line and discussed the effect of the morphology of the substrate surface. The pinning force can pin the contact line and force the droplet to evaporate with CCR mode before the contact angle reaches a certain value. At the PS transition point, the contact line begins to shrink, and the evaporation goes into the CCA mode since the pinning force is no longer strong enough. To understand the effect of the substrate morphology and to verify our model, experiments of water droplets evaporating and contact line receding on PDMS spherical cap arrays with different heights were conducted.

1. Theory

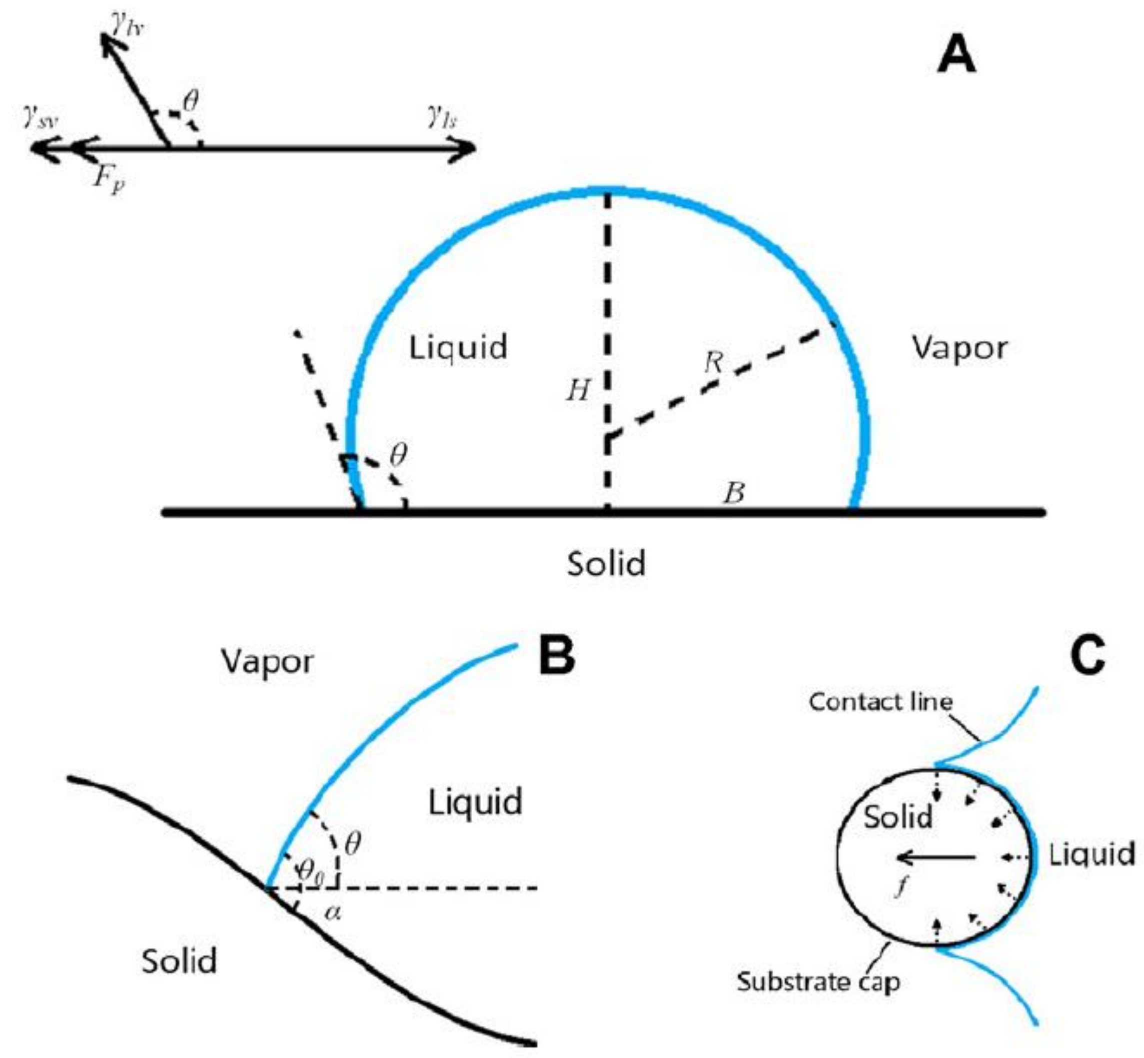


Figure 1. (A) An illustrative graph of a water droplet of spherical cap shape on the substrate and the resolution of force about the contact line. (B) Side view of a droplet on roughness solid, showing the effect of the local tilt surface on the apparent contact angle h. (C) Top view of the contact line following the rim of a substrate cap.

Denote Fp as the pinning force and introduce it to the Cassie- Baxter equation:

$$F = ((1-\phi)\gamma_{lv} + \gamma_{lv}\cos\theta - r_\phi\phi(\gamma_{sv} - \gamma_{ls})) - F_p$$

At the PS-transition point:

$$\cos\theta_c = -(1-\phi) + r_\phi\phi\frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}} + \frac{F_{pc}}{\gamma_{lv}} = \cos(\theta_i) + \frac{F_{pc}}{\gamma_{lv}}$$

As shown in figure 1, affected by the local tilt:

$$\theta = \theta_0 - \alpha$$

This is equivalent to a force f (per unit length) dragging the contact line and leading to the hysteresis.

$$f = \gamma_{lv}(\cos(\theta) - \cos(\theta_0)) = \gamma_{lv}(\cos(\theta_0 - \alpha) - \cos(\theta_0))$$

From geometry, the following relation can be easily obtained:

$$\bar{f} = \frac{2}{\pi}f$$

$$\alpha = \arccos\left(1 - \frac{h}{r}\right)$$

$$\phi_l = \frac{b}{r} = \sqrt{2\frac{h}{r} - \left(\frac{h}{r}\right)^2}$$

The surface of our substrate (PDMS) is a kind of polymer, containing roughness in molecular scale, leading to the hysteresis which is denoted as F0. With above discussion, the total hysteresis of the substrate surface can be described as

$$F_{pc} = \phi_l\bar{f} + F_0$$

2. Material

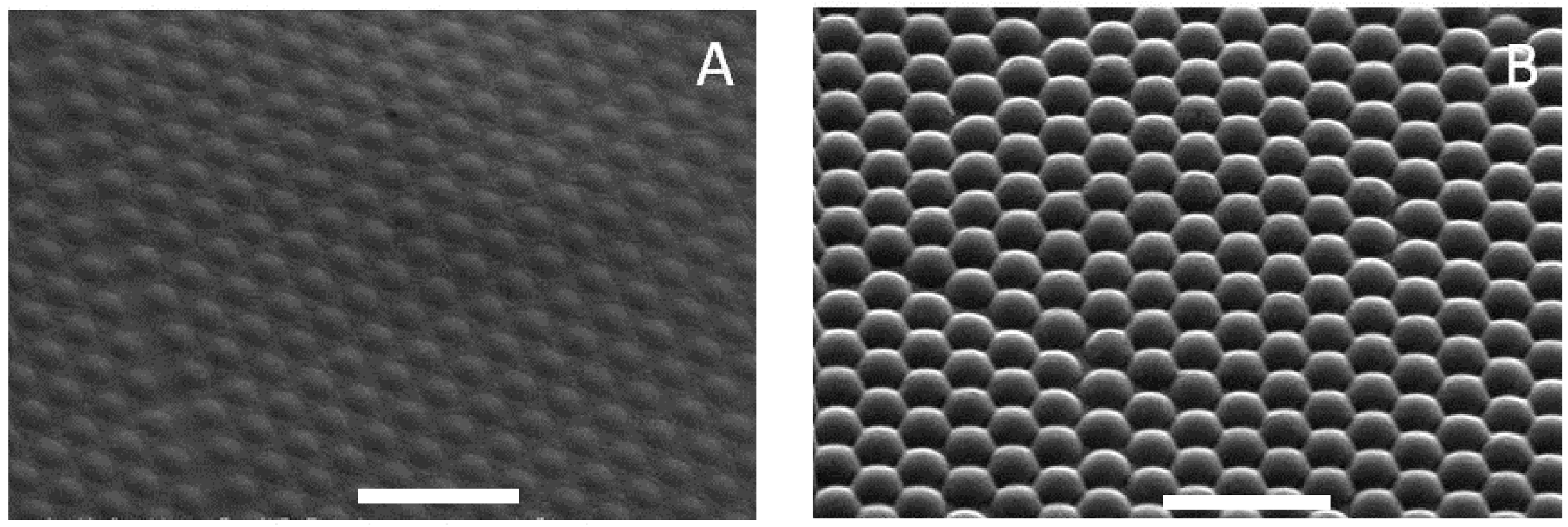
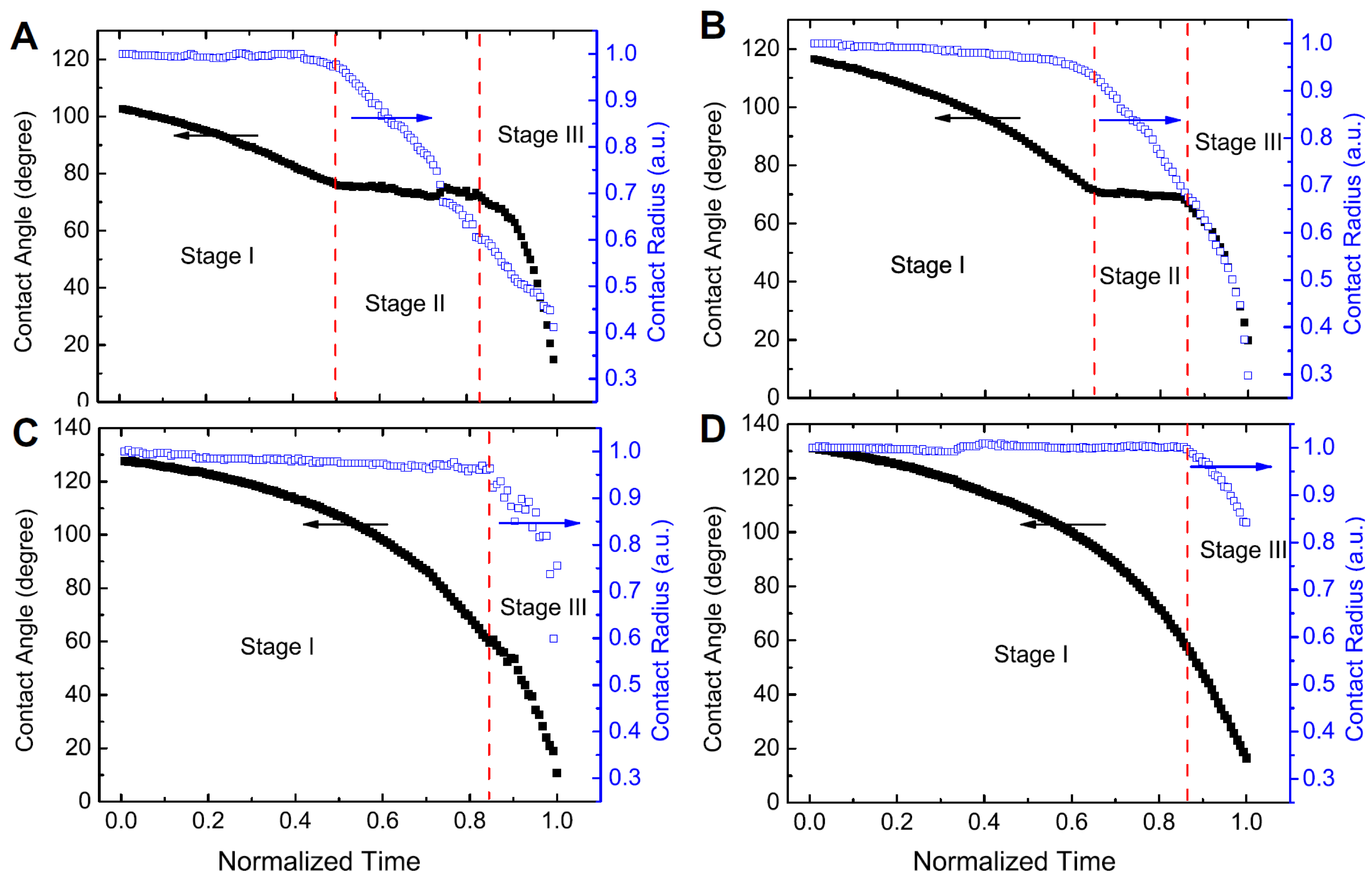


Figure 2. SEM images of PDMS spherical cap arrays. (A) h=0.2r, where h is the height of the spherical caps, (B) h=r. Scale bar: 5 μm.

The evaporation experiments were carried out on PDMS (polydimethylsiloxane) surfaces with microstructures.

3. Results and Discussion



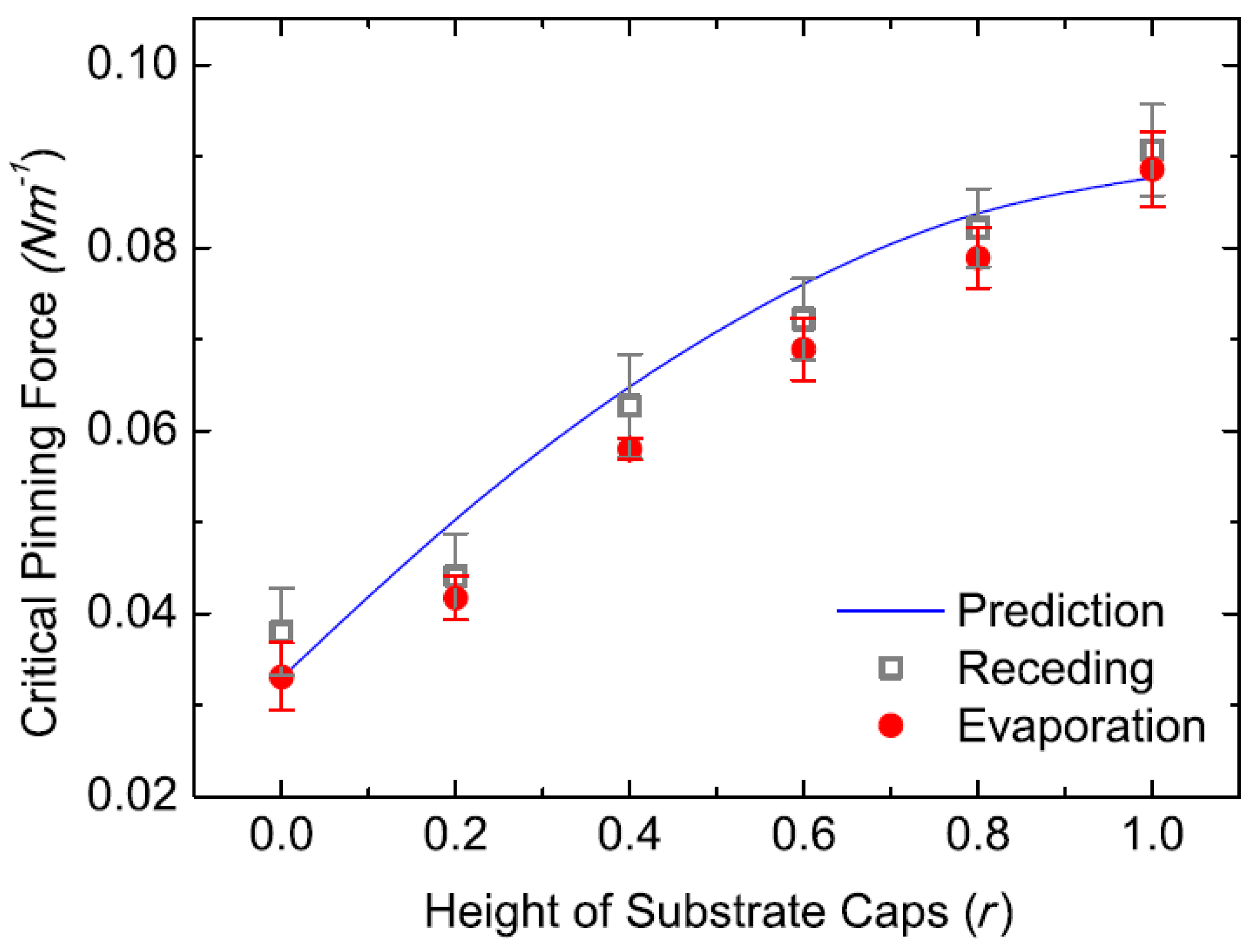


Figure 3. The contact radii (blue open) and the contact angles (black closed) of water droplets evaporating on PDMS substrates with spherical cap arrays of different cap heights (A 0, B 0.4r, C 0.8r, D r).

Figure 4. Measured critical pinning forces of water droplets evaporating (red circles) and contact line receding (gray squares) on the PDMS substrates with spherical cap arrays of different cap heights and their prediction (blue line) calculated from the theory section.

References

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[2] X. L. Zhu et al., *Nano Research* 3 (11) (2010) 807.
[3] M.E. Abdelsalam et al., *Langmuir* 21 (2005) 1753.