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Direct Geometric Observation of an Agar Gel Droplet on a Multipillar Surface

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We successfully determined the three-dimensional structure of agar gel droplets on multipillared surfaces. The contact angle, length of penetration of the agar gel into the interspace between pillars, and curvature of the bottom surface of the droplets were changed with respect to changes in the volume and concentration of the aqueous agar solution and the distance between the surface-bound pillars.

Analyzing wettability on multipillared surfaces is important for understanding wetting on biological rough surfaces and designing super-water-repellent surfaces.[1–8] Usually, the contact angle on a multipillared surface is described by the Cassie–Baxter (CB) equation, while the intermediate state between the Wenzel and CB states sometimes can be seen, where the criteria for the formation of such intermediate states are still unclear. In relation to this, we theoretically discussed the existence of an energy barrier for the process of droplet penetration into a cylindrical defect.[9] To understand the criteria, it is essential to directly observe the geometry of the penetrating component. However, there are few studies providing a three-dimensional analysis of liquid droplets on multipillared surfaces owing to problems associated with the liquid itself and the small size of the droplets. To address these problems, we used an agar sol solution instead of water to obtain a steady droplet with mm-sized pillars of a multipillared surface after gelation. Here we demonstrate a method that enables the three-dimensional observation of agar gel droplets on hydrophobic multipillared surfaces by microscope (Figure 1).[10–12]

Figure 2 shows a side view of a 10-μL agar gel droplet (3 wt % aqueous agar solution) mounted at the center of three equilateral triangularly aligned cylindrical pillars with the distance between pillars (d) of 0.5 mm at the temperature (T) of 25 °C. Before gelation, the droplet slightly penetrated into the interspace. The contact angle (θ) of a hemispherical agar gel droplet (the upper part) was $93.1 \pm 0.7°$. The length of penetration into the space (l) was 0.87 ± 0.08 mm, and the curvature radius of the bottom surface (R) was 1.02 ± 0.40 mm.

The effect of the volume of the aqueous agar solution (v) on the three-dimensional geometry was evaluated at the agar concentration (c) of 3 wt % ($d = 0.5$ mm). Figure 3 shows the dependence of θ, l, and R on v. The angle θ increased from 93.1 ± 0.7 to $123.6 \pm 2.7°$ with increasing v from 10 to 50 μL. The length l was approximately 0.9 mm when v ranged from 10 to 30 μL, but it decreased when v exceeded 40 μL. The radius R was also approximately 0.9 mm in the same volume range (v = 10–30 μL), but it increased as v increased from 40 to 50 μL. On the other hand, in the case of the water droplet, θ increased from 110.8 ± 2.1 to $125.7 \pm 1.5°$, and l decreased from 0.44 ± 0.02 to 0.31 ± 0.05 mm when v increased from 10 to 50 μL.

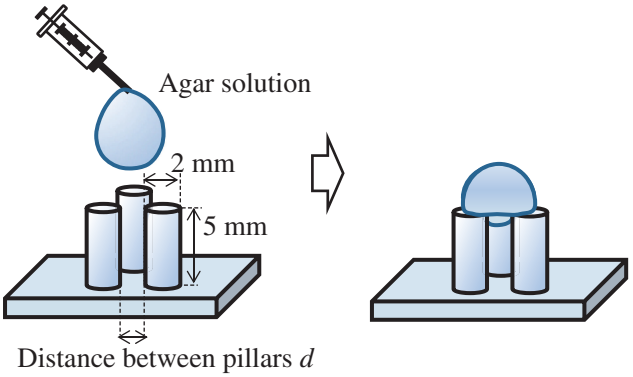

Figure 1. Method for the preparation of agar gel droplets. Agar solution was put on multipillar surfaces.

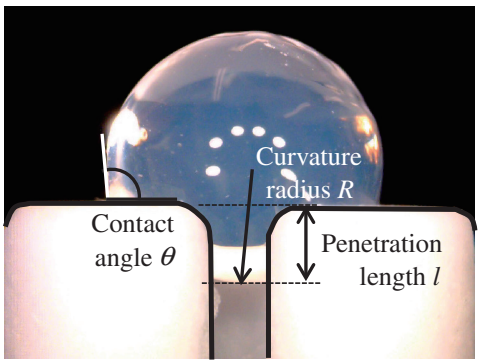

Figure 2. Photograph of an agar gel droplet on multipillar: $T = 25$ °C $v = 10$ μL, $c = 3$ wt % and $d = 0.5$ mm. $\theta = 93.1$ degree.

The effect of the distance d was evaluated under the following conditions: $c = 3$ wt %, $T = 25$ °C, and $v = 10$ μL. The contact angle θ decreased from 93.1 ± 0.7 to $25.0 \pm 2.1°$ as d increased from 0.5 to 1.5 mm and was approximately 0 degrees when d was 2.0 mm (Figure S1[14]). The length l increased from 0.87 ± 0.07 to 2.51 ± 0.09 mm as d increased from 0.5 to 1.5 mm. The curvature radius R was approximately 1.2 mm when d was 0.5–2.0 mm. On the other hand, in the case of the water droplet, θ decreased from 110.8 ± 2.1 to $30.5 \pm 1.1°$ as d increased from 0.5 to 1.5 mm, while it was approximately 0 degrees when d was 2.0 mm. The length l increased from 0.44 ± 0.02 to 2.43 ± 0.04 mm as d increased from 0.5 to 1.5 mm.

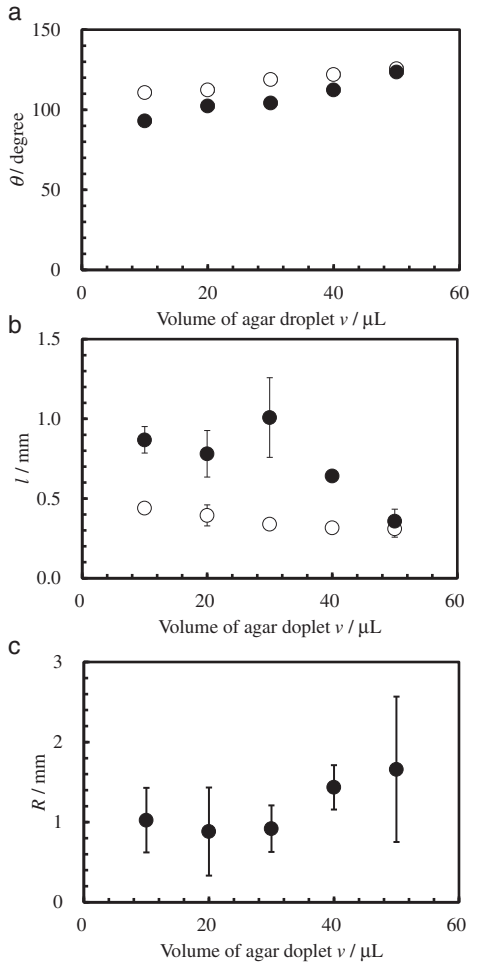

Figure 3. Effects of the volume of agar gel droplets (●) and water (○) on (a) contact angle θ, (b) penetration length l, and (c) curvature radius of air–liquid interface R. $T = 25\,^{\circ}\mathrm{C}$, $c =$ 3 wt %, and $d = 0.5$ mm.

The effect of c on the three-dimensional geometry was evaluated under the following conditions: $T = 25\,^{\circ}\mathrm{C}$, $v = 10\,\mu\mathrm{L}$, and $d = 0.5$ mm. We could observe the geometry of the agar gel droplets only when c was 1–3 wt % (the mechanical strength of the agar gel was not sufficiently good to separate it from the pillar surfaces when c was 0.5 wt %, while the agar gel surfaces were rough when c was 4 wt %). The contact angle θ of a 1–4 wt % aqueous agar solution droplet was approximately 93°, which was lower than that of water droplets (110.8°), as shown in Figure S2.[14] On the other hand, the length of penetration l of a 1–4 wt % aqueous agar solution droplet was greater than 1 mm, which was greater than that of water droplets (0.44 mm). The curvature radius R was approximately 0.8 mm when c was 1–4 wt %.

Here we discuss the mechanism for the changes in the three-dimensional geometry in terms of v, d, and c. We focus on the pinning effect on the multipillared surface. This effect involves a discontinuous change in the contact angle on nonuniform surfaces due to the energy barrier at the edges; that is, at the edges, the spreading of a liquid is inhibited, and the contact angle changes from θ_{eq} to $\theta_{eq} + \alpha$, where θ_{eq} is the contact angle of the liquid droplet on a flat substrate and α is the angle of the edge.[13] This effect causes the changes to l and θ. The penetration of a liquid into the interspace between pillars, which is induced by gravity and capillary forces, is inhibited by the pinning effect.[9] The contact angle θ decreased as d increased because an increase in d weakens the pinning effect at the edges of multipillared surfaces. In supporting information, we discuss a possible scenario based on pinning effect.

In summary, we demonstrate a method for determining the three-dimensional structure of agar gel droplets on hydrophobic multipillared surfaces. For example, the contact angle θ and the curvature radius R increased with increasing v, while the length of penetration l decreased. These changes for θ, l, and R are caused by the pinning effect at the edges of the pillar systems. Other than water and aqueous agar solutions, the wetting behavior of some oils was observed on the multipillar surface: silicone oil and 2-propanol were spread on the pillar surface completely, while 85 wt % of aqueous glycerol solution formed a droplet with 99.9 degree of contact angle. The present method is useful for understanding the wetting or penetration behavior of liquids on rough surfaces.

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References and Notes

1 Y. Nonomura, Y. Morita, T. Hikima, E. Seino, S. Chida, H. Mayama, *Langmuir* **2010**, *26*, 16150.
2 Y. Nonomura, S. Chida, E. Seino, H. Mayama, *Langmuir* **2012**, *28*, 3799.
3 J. Bico, C. Marzolin, D. Quéré, *Europhys. Lett.* **1999**, *47*, 220.
4 Z. Yoshimitsu, A. Nakajima, T. Watanabe, K. Hashimoto, *Langmuir* **2002**, *18*, 5818.
5 R. D. Narhe, D. A. Beysens, *Langmuir* **2007**, *23*, 6486.
6 N. A. Patankar, *Langmuir* **2010**, *26*, 8941.
7 T.-S. Wong, C.-M. Ho, *Langmuir* **2009**, *25*, 12851.
8 Q.-S. Zheng, Y. Yu, Z.-H. Zhao, *Langmuir* **2005**, *21*, 12207.
9 H. Mayama, Y. Nonomura, *Langmuir* **2011**, *27*, 3550.
10 Multipillared silicon elastomers were made of RTV rubber from Shin-Etsu Chemical Co. The composition and elasticity were as follows: KE-26/CAT-RM/CAT-24 (100:1:4.5, Shin-Etsu Chemical Co., Tokyo, Japan) and 10500 N mm^{-2}. The diameter and height of the cylindrical pillars and d were 2, 5, and 0.5–2.0 mm, respectively.
11 An aqueous agar solution was dropped in the center of three pillars under the following conditions: temperature (T), 25 °C; agar concentration (c), 1–4 wt %; agar solution volume (v), 10–50 μL. The contact angle of the agar gel droplets on the multipillared surfaces (θ) and the length of penetration into the interspace of the pillars (l) were estimated with a DM-501 contact angle meter (Kyowa Inter Science) and Dino-Lite digital microscope, AM-3FI (AnMo Electronics Corp.), respectively.
12 Agar gel droplets on multipillared surfaces were demounted to observe the bottom surfaces of the droplets with an optical microscope, XTP-11 (Nikon Co.). Contours were lined in the step of 50 μm. The curvature radius (R) of the bottom surfaces of the agar gel droplets was calculated on the basis of the cross-section profiles of these contours.
13 P.-G. de Gennes, F. Brochard-Wyart, D. Quéré, *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*, Springer, New York, **2004**.
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

