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Wetting and evaporation phenomena of water droplets on textured surfaces

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When water droplets are placed on a surface, the contact angle depends on the surface conditions, and the subsequent evaporation of the droplets depends on the wetting phenomena. In this study, we investigated the wetting and evaporation of droplets of deionized water from surfaces with various intrinsic contact angles and surface morphologies ($\theta_0 = 34°$, $58°$ and $109°$, $1.00 < f_W < 2.00$, $0.02 < f_{C-B} < 1.00$). For each droplet, the apparent contact angle and radius of the contact line were measured, and the wetting state was visualized with synchrotron X-ray radiography. Comparing between the experimental data and the results of a number of wetting models, the models were experimentally validated. On the basis of the wetting phenomena, the evaporation rate depending on the surface condition is clarified in the experimental ranges.

1. Introduction

Droplet evaporation is important for applications such as inkjet printing [1,2], spray cooling [3,4], deoxyribonucleic acid (DNA)/ribonucleic acid (RNA) microarrays [5,6], and micro-lenses [7,8]. In the absence of an external flow or a temperature difference between the phases, a droplet evaporates due to diffusion, *i.e.*, because of the difference in concentration at the liquid–vapor interface. For a free droplet in air, the droplet evaporates symmetrically, and the evaporation flux at the liquid–vapor interface is uniform. For a droplet on the surface, there are liquid–vapor, liquid–solid, solid–vapor interfaces, and a contact line; the potential field of the concentration can be conventionally described in toroidal form because of the singularity at the contact line. The evaporation flux at the liquid–vapor interfaces is depended on the shape of the droplet evaporation [9,10]. Especially, the evaporation flux is related to the contact angle [11]: the evaporation flux is non-uniform and evaporation is more rapid near the contact line for an acute contact angle, whereas the evaporation flux is more uniform for an obtuse contact angle. Interestingly, the behavior of the contact angle during the droplet evaporation is significantly influenced by the surface wetting conditions. Therefore, to understand the droplet evaporation dynamics, the following wetting phenomena about the contact angle depending on the surface conditions must be studied.

First, to understand the droplet evaporation dynamics, the initial (or apparent) contact angle should be estimated depending on the surface conditions [12]. The surface conditions are determined by the chemical composition and geometrical morphology. The chemical composition determines the intrinsic contact angle, which is the apparent contact angle on an ideal smooth surface; the geometrical morphology is quantified by the roughness ratio, *i.e.*, the ratio of the wetted area to the projected area. On a rough surface, the wetting state of a droplet depends on whether the surface is hydrophilic or hydrophobic. In general, on a hydrophilic rough surface, the surface is fully wetted, *i.e.*, the droplet is in the Wenzel state. On a hydrophobic rough surface, the surface is only partially wetted, *i.e.*, the droplet is in the Cassie–Baxter state. To determine the apparent contact angle on rough surfaces, Wenzel [13] and Cassie–Baxter [14] derived expressions based on Helmholtz free-energy conservation without energy loss at a moving contact line. However, it has been reported that energy loss occurs while the droplet reaches an equilibrium state [15–19]. Recently, Kang–Jacobi [20] proposed a model of the contact angle on a rough surface that accounts for the energy loss. Experimental investigations of the apparent contact angle have also been reported [21–24]; however, these have typically focused

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on hydrophobic rough surfaces for the purpose of developing water-repellent surfaces, and investigations of hydrophilic rough surfaces are lacking. Therefore, fundamental research into wetting phenomena is required to validate the equations that describe the apparent contact angle on hydrophilic and hydrophobic rough surfaces.

Secondly, to understand the droplet evaporation dynamics, the mode transition should be estimated depending on the surface conditions. For a droplet on a surface, evaporation consists of three successive stages, as shown in Fig. 1 [5,25–29]. When the droplet is first placed on a surface, it can be characterized by the initial contact angle and the radius of the contact line. During stage 1, the contact angle decreases and the contact radius remains constant because the contact line of the droplet is pinned. This is known as the constant contact radius (CCR) mode of evaporation. During stage 1, the pinning force at the contact line gradually increases. When the force exceeds the potential energy barrier, stage 2 occurs [30,31]. During stage 2, the contact line of the droplet changes, and the contact radius decreases while the contact angle remains constant (receding contact angle). This stage is known as the constant contact angle (CCA) mode, in which the contact angle remains constant and the contact line shrinks. The difference between the initial and the receding contact angles is referred to as the contact angle hysteresis. Stage 3 occurs when the contact angle and radius decrease simultaneously, and is the final stage of droplet evaporation. In practice, stage 3 is often of relatively short duration compared with the state 1 and 2. The evaporation rate is influenced by the evaporation mode (CCR and CCA). For the reason, it is important to estimate the mode transition from CCR to CCA [32]. In addition, the amount of time that passes during each time is strongly dependent on the surface conditions [33–35]. Therefore, to estimate the evaporation performance, the relation between the mode transition and the surface condition should be quantitatively studied.

In this study, we investigated the wetting and evaporation of water droplets for various surface condition. To investigate the initial contact angle, the apparent contact angle was measured on the surfaces with the various wetting conditions. And the wetting state of each droplet was visualized with synchrotron X-ray radiography. Comparing between the existing wetting model [13,14,20] and experimental data, the wetting models were experimentally validated. To investigate the mode transition, the contact angle and contact radius of each droplet were also measured during evaporation. The relation between the surface condition and mode transition is experimentally investigated. On the basis of the study about the initial contact angle and mode transition, the evaporation performance is analyzed depending on the surface conditions.

2. Experiment setup

2.1. Preparation of the surfaces

A 20×20 mm section of silicon wafer (with an intrinsic contact angle $\theta_0 = 58^\circ$) was used as a reference. The surface properties were modified using self-assembled monolayers (SAMs) to create various intrinsic contact angles on smooth surfaces. The silicon surfaces were coated using hydrophilic mercapto-propyl-trimethocy-silane (MPTS) and hydrophobic heptadecafluoro-1, 1, 2, 2-tetra hydrodecyltrichlorosilane (HDFS). As shown in Fig. 2a, the intrinsic contact angle was 34° on the MPTS-coated surface and 109° on the HDFS-coated surface.

To investigate the effects of the surface geometry, micro-textured surfaces were fabricated using conventional photolithography and dry-etching processes, as shown in Fig. 2b. The morphology of the surface was defined according to the roughness ratio f, which is the ratio of the wetted area A_{wetted} to the projected area $A_{\text{projected}}$. The concept of a unit cell can be used to define the roughness ratio, because the arrangement of the micro-pillars is periodic (see Fig. 2b). Therefore, the roughness ratio can be defined geometrically based on the pillar diameter d, pillar height h, and pitch between pillars p. The dimensions of the micro-pillars of each fabricated surface were measured using a 3D-profiler and a high-resolution field-emission scanning electron microscope (FE-SEM). When a droplet is in the Wenzel state (W), the liquid fills the space between the micro-pillars. However, dry etching commonly results in scalloping at the sides of the micro-pillars, which enlarges the wetted area. Therefore, for Wenzel droplets, we used the correction coefficient 'c' to correct for this effect [36], *i.e.*, the roughness ratio of a Wenzel droplet is given by

$$f_W = \frac{A_{\text{wetted}}}{A_{\text{projected}}}\bigg|_{\text{unit cell}} = \frac{(p^2 + c \cdot \pi dh)}{p^2} = 1 + c\frac{\pi dh}{p^2} = 1 + \frac{\pi}{2}\frac{\pi dh}{p^2}, \quad (1)$$

When a droplet is in the Cassie–Baxter state (C–B), the liquid of the droplet cannot penetrate between the micro-pillars, so the roughness ratio is defined as:

$$f_{C-B} = \frac{A_{\text{wetted}}}{A_{\text{projected}}}\bigg|_{\text{unit cell}} = \frac{\pi d^2}{4p^2}. \quad (2)$$

In this study, the geometry of the micro-pillars was varied to analyze of the effects of the morphology on the wetting and evaporation phenomena. Four micro-pillar diameters were investigated (15 μm, 45 μm, 75 μm, and 105 μm), together with three intervals between the micro-pillars (25 μm, 55 μm, and 85 μm), giving thirteen geometries (including the flat surface), as listed in Table 1. These combinations were applied to the three different chemical compositions (bare silicon, hydrophilic MPTS SAM, and hydrophobic HDFS SAM), giving a total of 39 surfaces.

2.2. Experimental setup

Wetting and evaporation phenomena are very sensitive to the experimental environment. For this reason, all experiments were carried out at a constant temperature of 22 °C ± 1 °C and a relative humidity of 42% ± 1%; these conditions were maintained using a thermo-hygrostat. A micropipette was used to place 6.3-μl droplets of deionized water on the surfaces. As shown in Fig. 3, the history of a droplet contains both wetting and evaporation processes. During the wetting process, a droplet placed on the test section reaches mechanical equilibrium with an initial contact angle and radius. The initial parameters were measured, and subsequently, during evaporation, the contact angle and droplet diameter were measured every 20 s. The experimental parameters were measured using the automatic goniometer (SDLab-200TEZD, FEMTOFAB). Each experiment was repeated three times. The standard deviation of the contact angle, the radius of the contact line and the total time for droplet evaporation was respectively 3°, 8.69 μm and 60 s. Because the size of the symbol in the figures is larger than the size of the deviation, the error bars of the parameters weren't marked in the figures.

To estimate the wetting state of the droplets on the test section, the micro-pillars at the edge of the droplet were visualized using the 6D beam-line of the Pohang Light Source-II synchrotron X-ray facility (in this study, the spatial resolution is 1.74 μm). First, the micro-pillars on the surface were aligned in X-ray injection. Only structure images, labeled "dry images", were obtained. After dosing 6.3 μl of deionized water droplets on the micro-pillared surfaces, the images were subsequently obtained again in the same position. These were labeled "wet images" and contain both the silicon structure and the water droplet.