International Journal of Heat and Mass Transfer 73 (2014) 810–818

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Experimental investigation on variations in geometric variables of a droplet on a low-surface-energy solid

Yukihiro Yonemoto [a,*], Tomoaki Kunugi [b]

[a] Priority Organization for Innovation and Excellence, Kumamoto University, 2-39-1, Kurokami, Chuo-ku, Kumamoto-shi, Kumamoto 860-8555, Japan
[b] Department of Nuclear Engineering, Kyoto University, C3-d2S06, Kyoto Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8540, Japan

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 21 February 2014
Accepted 21 February 2014
Available online 19 March 2014

Keywords:
Contact angle hysteresis
Microdroplet
Wetting phenomena

ABSTRACT

The changes in droplet geometry associated with volume change are experimentally investigated focusing on low surface energy solids. In particular, two experiments are performed to confirm the detailed droplet behavior such as the changes in height, radius, and contact angle, on a solid surface for a range of liquid surface energies. The first experiment involves the natural evaporation of droplets; droplet sizes from micrometer to millimeter are investigated. The second involves simply depositing droplets on a solid surface, then withdrawing liquid using a microsyringe. In this experiment, volume change is quantitatively evaluated. Our experimental results reveal details of the variations in droplet geometry among droplet radius, height, contact angle, and surface energy of the liquid.

1. Introduction

Wettability of liquids on solid surfaces relates to many industrial applications such as heat-transfer efficiency of heat exchangers and controlling a droplet size in atomizing devices [1,2]. In semiconductor manufacturing, wetting phenomena plays an important role in the development of microstructures using imprint technology [3,4]. As industrial and chemical devices become smaller to improve energy efficiency, spatial scales dominate the ordinary scales and surface effects in physical phenomena cannot be ignored. Therefore, an understanding and control of wetting phenomena is very important.

In numerical research of wetting phenomena, the boundary condition at the three-phase contact line on the solid surface is implemented using the contact angle. Dynamic wetting, via droplet impacts and spreading droplets on solid surfaces, is mainly studied [5–7]. Several dynamic contact angle models, which treat advancing and receding contact angles, are considered in such simulations [8]. In the simplest model, the dynamic contact angle is fixed as a static contact angle. The static contact angle is mainly evaluated by measuring a contact angle of a sessile droplet. However, even the contact angle of the sessile droplet actually exhibits various complex behavior such as size dependency of the contact angle and is studied experimentally and theoretically by many researchers by introducing the concept of line tension [9–11]. Currently, there is no consistent theoretical framework with respect to wetting phenomena characterized by the line tension [12,13]. Similar phenomenon is also observed in droplet evaporation. In particular, droplet evaporation exhibits complex contact line behaviors such as pinning and de-pinning, and stick–slip motion. These processes are thought to affect the potential barrier at the contact line [14]. An interpretation of the “equilibrium” contact angle and the contact line behavior are discussed in Ref. [15]. Ultimately, in numerical research, all that remains in treating the static contact angle is to rely on experimental values that are constant.

Droplet behaviors observed on solid surfaces have been widely studied. There has been however little consideration of the detailed relationships with respect to changes in droplet geometry among the radius, contact angle, height, and volume; this also includes a variety of surface energies of liquids. A comprehensive study would provide a breakthrough in topics on complex wettability such as size dependency of the contact angle and the contact line behavior. Thus, comprehensive and quantitative evaluations of the wetting phenomena for a droplet on a solid surface are very important for a basic understanding of wetting phenomena. Moreover, this can become basic benchmark data for future numerical simulations.

In the present study, changes in droplet geometry associated with volume change is experimentally investigated focusing on solids of low surface energy. Solids of high surface energy, mainly seen in metals [14], are not considered in the present study because metal surfaces have added complexity from crystal orientation and surface roughness [16] which leads to uncertainties in

---

* Corresponding author. Tel./fax: +81 963423690.
E-mail address: yonemoto@mech.kumamoto-u.ac.jp (Y. Yonemoto).

http://dx.doi.org/10.1016/j.ijheatmasstransfer.2014.02.059
0017-9310/

wetting phenomena. In this study, two experiments were performed to confirm details of the variations in geometrical variables such as contact angle, droplet height and radius on the solid surface. One experiment involved the natural evaporation of a droplet and its volume decrease. For the other liquid deposition and extraction from a solid surface were performed using a microsyringe; droplet behavior can be quantitatively evaluated. The present paper describes droplet features as its volume changes. In particular, our results show that the variations related to changes in droplet geometry for natural evaporation and microsyringe extraction are almost the same.

2. Experiment

In this study, water–ethanol binary mixtures were used for considering wettability on a solid surface [17–20]. Six mixtures of different surface energy densities were used; we employed the labeling scheme a: 0.0719 J/m^2, b: 0.0570 J/m^2, c: 0.0384 J/m^2, d: 0.0312 J/m^2, e: 0.0274 J/m^2, f: 0.0211 J/m^2. Surface energies were measured using a DM300 (Kyowa Interface Science Co., Ltd., Saitama, Japan). The two experiments performed are illustrated in Fig. 1. The geometric variables of a droplet (Case 1) were measured during its natural evaporation to confirm the wettability of droplets from micrometer to millimeter sizes. The volumes were 0.013, 0.038, 0.44, and 10 μl. Two liquids of differing energy densities (σ_{lg} = 0.0719 and 0.0570 J/m^2) were mainly used. With respect to microdroplets, the droplets were composed of purified water. In syringe-drawn reduction (Case 2), a droplet of a certain size was set on a solid surface and liquid was extracted from the droplet. The setting and extraction of liquids were performed using microsyringes (outer diameters are 80 and 200 μm). Liquid extraction was performed at small and large intervals. In the case of the small interval extraction, the liquid of small volume was extracted from the droplet until the droplet becomes small. The initial droplet volumes are 10, 20, and 40 μl. In the case of the large interval extraction, each droplet was reduced to half its size, i.e., 5, 10, and 20 μl. In this process, three kinds of liquids (σ_{lg} = 0.0719, 0.0570 and 0.0384 J/m^2) were mainly used. For both experiments, the droplet radius, height, and contact angle were measured.

Before each experiment, the solid material made of silicon rubber, was rinsed using ethanol and purified water and then dried. In this experiment, temperature and humidity were in the ranges of 20.0–25.0 °C and 47.0–55.0%, respectively. An image of the droplet is captured using a CCD camera (Yashima Optical Co., Ltd., Tokyo, Japan). The maximum error in size measurement was ±14.5 μm/pixel. The microdroplet is measured using a microscope (Leica Microsystems, Wetzlar, Germany). In this case, the maximum error in size measurements is ±10.9 μm/pixel. The contact angles were measured using commercial software (FAMAS; Kyowa Interface Science Co., Ltd., Japan) for which the measurement accuracy is within ±1°.

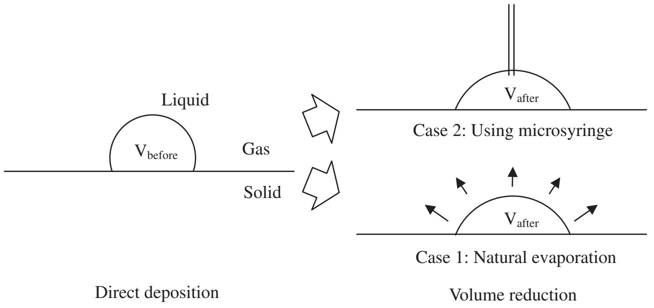

Fig. 1. Schematic of the evaporation and extraction experiments.

3. Results and discussion

3.1. Droplet behavior due to natural evaporation

Fig. 2 shows the natural evaporation evolution for micrometer and millimeter-sized droplets with respect to the relationship between radius (R) and contact angle ($\cos\theta$). When the droplets are initially deposited on the solid surface, the static contact angle for all cases is the same. From this figure, the contact angle gradually recedes from the static contact angle but radius remains constant for all four sizes. At a certain contact angle, the droplet radius then decreases (receding of the contact line) while the contact angle remains constant. These two kinds of the constant contact angles are observed in other literature [14]. Finally, at a certain value of the radius, the droplet radius and the contact angle reverse roles. The interesting point is that as the contact line recedes the constant contact angle region is smaller as the initial droplet volume becomes small whereas the constant droplet radius regions have the same width in all cases.

The relationship between the droplet height (h) and the radius (R) during this process is shown in Fig. 3. The droplet radius decreases as the droplet height decreases. The difference in the droplet height in the constant droplet radius region decreases as the droplet size reduces, although the difference in the contact angle range over the same interval was the same for all cases shown in Fig. 2. Fig. 4 shows the relationship between h and R for purified water and binary mixtures. The droplet volumes are 10 μl in both cases. The initial droplet radius for the binary mixtures is larger than that for water because the surface energy is smaller for binary liquids than for purified water. Of course, the initial droplet height for the binary liquid is smaller than that for water because the volumes are the same (volume conservation). Thus, the experimental data shifts towards low values. However, the trend between the two liquids is qualitatively the same. With respect to the relationship between R and $\cos\theta$, the trend is also the same, as shown in Fig. 5.

3.2. Droplet behavior under microsyringe extraction

In this section, the results of the droplet behavior on the solid surface using microsyringe extraction are discussed. Fig. 6 shows the relationship between R and $\cos\theta$ for purified water. The black triangles are the results where liquid is extracted a number of times starting from droplet volumes 10, 20, and 40 μl at various small intervals. The white circles represent results where the

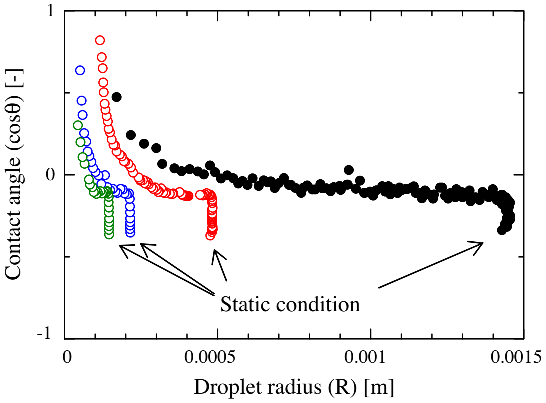

Fig. 2. Radius vs contact angle in the evaporation process of micrometer and millimeter size droplets: red circle 0.44 μl, blue circle 0.038 μl, green circle 0.013 μl and 10 μl. The liquid is purified water.