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MASS-AREA METHOD TO MEASURE THE CONTACT ANGLE ON HYDROPHILIC SURFACES

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ABSTRACT

A mass-area method is proposed to overcome problems in the measurement of the equilibrium contact angles for rough and hydrophilic surfaces. A goniometer usually measures the contact angle at the top plane of a rough surface, not the contact line of the solid-liquid interface. The present method estimates the contact angle indirectly from the volume of the liquid and the size of the contact area, assuming a spherical cap and consistent with a minimization of the free energy. The present method shows a roughly linear relationship with measurements by a goniometer for smooth surfaces of various solid materials with various liquids, but the goniometer measurements are smaller. An example test and the error of the present measurement method are presented and discussed.

INTRODUCTION

The contact angle is defined at the contact line at which the solid, liquid, and gas phases meet. On rough surfaces, the contact line is not in one plane. The interface is distorted on the three-dimensional surface and the local contact angles vary along the contact line. The best definition for the apparent contact angle is the average of the contact angles along the contact line. One way to determine the apparent contact angle is to average many point measurements along the contact line. However, it is not easy to measure the local contact angle in either the Wenzel or Cassie-Baxter states.

For a hydrophilic surface, the top view allows better observation of the contact line and contact area. The contact area and volume of the liquid or mass can yield the average contact angle if we apply the minimization principle of the Helmholz free energy. Also the area and mass can usually be measured reliably. Surfaces are not generally homogeneous even when they are flat; therefore, local contact angles may not represent the whole surface. The present idea is also applicable to such fields.

The goniometer is one instrument used conventionally to measure the equilibrium contact angle of a liquid droplet on a solid surface. The contact angle is measured directly as the angle from the solid-liquid interface to the liquid-vapor interface, subtended through the liquid as the three-phase confluence is approached. Errors in measured contact angles are generally small for hydrophobic surfaces; however, that is not the case for hydrophilic surfaces, and the measurement becomes problematic for highly wet rough surfaces. An image of a water droplet on a rough surface is recorded by the goniometer, which usually measures the contact angle at the top plane of the rough surface, not the contact line of the solid-liquid interface. Therefore, uncertainty is higher for rough hydrophilic surfaces.

Good (1992) reviewed the various methods for measuring the contact angle. Good and Koo (1979) reported the effects of liquid volume on the contact angle. Their data showed that the limiting contact angles for large drops were in good to excellent agreement with the values obtained by the vertical plate. They observed the distortion of contact line and differences of local and apparent contact angles. Meiron et al. (2004) used 520 and 830 μL of ethylene glycol and water, assuming that the ratios between the drop base diameters and surface roughness parameters would be sufficiently large for the Wenzel equation to hold. They also used a global energy minimum (GEM) on real surfaces, vibrated the surfaces, and calculated the contact angles from the drop diameters and weights. However, the volume of the liquid needs to be limited to reduce the effect of gravity in the measurement of the contact angle. Onda et al. (1996), Yoshimitsu et al. (2002), McHale et al. (2004), Kurogi et al. (2008), Synytska et al. (2008, 2009) and Jung and Bhushan (2009) measured contact angles on various rough surfaces such as regular and irregular pillars, wire membranes, and fractal particles. They used the sessile drop method with 0.5 to 10 μL liquid droplets. Wong and Ho (2009) reported that the effect of line tension is important on the nano scale for rough surfaces.

A mass-area method for the measurement of the equilibrium contact angle for rough hydrophilic surfaces is

TABLE 1. DIMENSIONS OF SMOOTH AND ROUGH SURFACES TESTED IN THE PRESENT STUDY

ID	Material	Height (h_p)	Pitch (p_f)	Angle (θ_p)	Area ratio (f_{sl})	Shape
GS	Glass	-	-	-	1.0	Smooth
ES		-	-	-	1.02	EDM machined smooth
A45P300		362	300	45	1.15	
A90P300		150	300	90	1.11	
A150P300		40	300	150	1.02	
A45P500	Aluminum	604	500	45	1.51	EDM machined pyramid
A60P500		433	500	60	1.37	
A90P500		250	500	90	1.21	
A150P500		67	500	150	1.03	
A90P800		400	800	90	1.27	
A150P800		107	800	150	1.03	

Units of pyramid pitch and angle are μm and deg.

proposed in the present work. The contact angle is calculated from the volume of the liquid and the size of the area enclosed by the contact line. Effects of parameters such as roughness and volume on the accuracy of the measurement were investigated. The present method was tested on several kinds of liquid on a smooth surface. Also, contact angles on rough surfaces having different pyramid angles and pitches were measured and compared for the present mass-area and conventional goniometer methods.

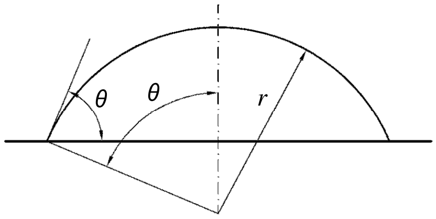
LIQUID DROPLET ON THE ROUGH SURFACE

Let us think that a liquid droplet is put on a smooth solid. Applying the minimization principle of free energy, the liquid droplet can be assumed as a spherical cap as shown in Figure 1 (a). The mass of the spherical cap and the solid-liquid interfacial area are:

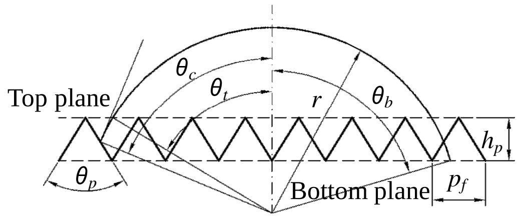
$$V_o = \frac{A_{sl,c}(1-\cos\theta)^2(2+\cos\theta)}{6} = \frac{\pi d_{sl}^3(1-\cos\theta)^2(2+\cos\theta)}{24} \quad (1)$$

The apparent contact angle can be obtained by the initial liquid volume V_o , and size of the contact area $A_{sl,c}$ or contact diameter d_{sl} .

The liquid droplet is on a surface of roughness height h_p, and their contact line is located in the fraction of f_v from the bottom plane, as shown in Figure 1 (b). The relationships of liquid volume, contact area in the average contact line plane, and contact angles at top, bottom and contact line planes are:



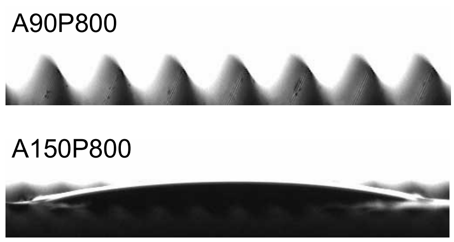
(a) Smooth surface



(b) Rough surface

FIGURE 1. EQUILIBRIUM CONTACT ANGLES ON THE SMOOTH AND ROUGH SURFACES

(a) Water droplet on the silicone surface



(b) Wetted rough surfaces

(c) Top view of water droplets on the pyramid surface of flat ES (left) and A150P300 (right)

FIGURE 2. WET SMOOTH AND ROUGH SURFACES

$$V_o = V_t + f_v(V_b - V_t) \tag{2}$$

$$V_b = \frac{\pi r^3}{3}(1-\cos\theta_b)^2(2+\cos\theta_b) \tag{3}$$

$$V_t = \frac{\pi r^3}{3}(1-\cos\theta_t)^2(2+\cos\theta_t) \tag{4}$$

$$A_{sl,c} = \pi r^2 \sin^2\theta_c = \pi d_{sl}^2/4 \tag{5}$$

$$\cos\theta_t = \cos\theta_c + f_v h_p/r = \cos\theta_b + h_p/r \tag{6}$$

where V_t and V_b are the volumes of spherical cap above the top and bottom planes of rough solid respectively. The parameters V_o, d_{sl}, h_p, f_v are measured values or obtained from geometry.

EXPERIMENT

Surface and liquid

Four kinds of surface-smooth glass, silicone wafer, and aluminum pyramids-were tested in the present work, as shown in Table 1. The smooth glass surface was a smooth, homogeneous reference surface. The rough glass surface was tested for the effects of a rough surface on the contact angle. The rough surface was aluminum (1100) that was electrical discharge machined with a 125-μm diameter wire. The final surface was composed of pyramids with 300 and 500 μm pitches, and 45, 90, and 150 degree angles, corresponding to area ratios from 1.15 to 1.6, as shown in Table 1.

The liquids used for the contact angle measurements were distilled water, ethylene glycol, and hydraulic oil 32. The volume of the liquid droplet was varied from 1 to 20 μL.

Contact angle measurements

The reference contact angles were measured by the sessile drop method using a goniometer (KSV Instrument Ltd, CAM) with an accuracy of ±0.1 deg under the conditions of 20^{o}C and 40% relative humidity. A monochromatic LED was used to identify the liquid-gas interface, and an image was taken with a digital camera having a 550-mm focal length. The mean contact angle was calculated from the separate contact angles for both sides after fitting the curve of the liquid-gas interface to the Young-Laplace and circle equations. The goniometer system was calibrated to a 4-mm ball. The contact angles were measured at four different points for each sample, and average values were calculated. For each experiment, the surface was cleaned in an ultrasonic bath of acetone (5 min), isopropyl alcohol (10 min), rinsed with de-ionized water, and blown with nitrogen gas to eliminate static electricity on the surface before measurement.

The present mass-area method was modified in the present study from that of Meiron et al., using small liquid droplets to minimize the effect of gravity. The volume of liquid was measured by a 5 μL micro-syringe with 0.05 μL accuracy and a 25 μL micro-syringe with 0.25 μL accuracy. The sessile liquid mass was confirmed with an electric balance (Mettler, AE240) having 0.1 mg accuracy. The error in the mass is less than 1.0% for a 10 μL liquid droplet. The cleaned solid surface was located under the digital microscope (AmScope MT130). A liquid droplet was placed by the micro-syringe on the solid surface carefully just above the surface. The image of the top surface was taken with a digital camera (1.3 M pixels) attached microscope from 200-300 mm after about 30 seconds for equilibrium. The contact line was identified by edge enhancement, and the inside area calculated by an image processor after tracing the edge. The error in the area measurement was about ±4% for a contact liquid diameter of 5 mm.

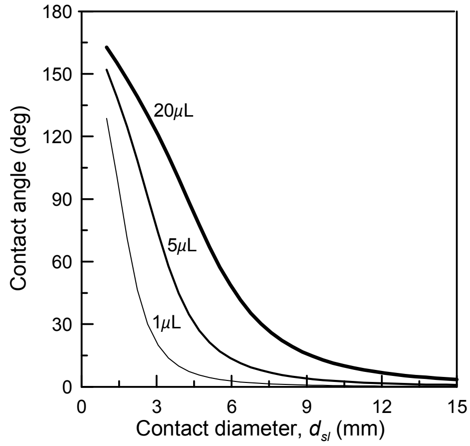


FIGURE 3. RELATION BETWEEN CONTACT ANGLE, CONTACT DIAMETER, AND LIQUID VOLUME IN THE PRESENT MASS-AREA METHOD

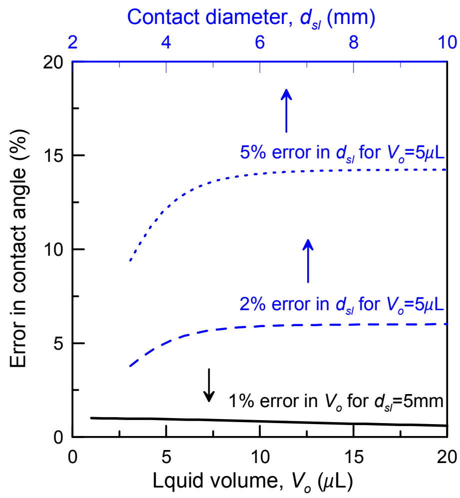


FIGURE 4. MEASUREMENT ERROR OF CONTACT ANGLE BY VOLUME AND CONTACT DIAMETER ERRORS IN THE PRESENT MASS-AREA METHOD

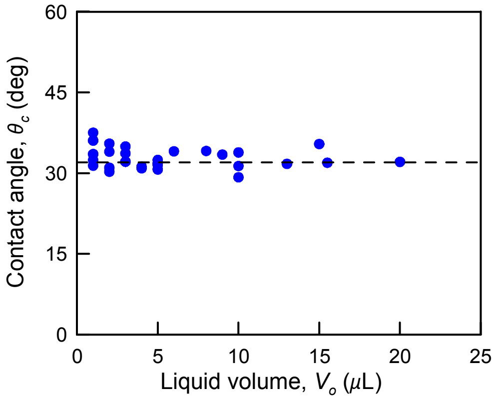


FIGURE 5. CONTACT ANGLES OF WATER FOR INCREASING WATER VOLUME ON GLASS BY THE PRESENT MASS-AREA METHOD

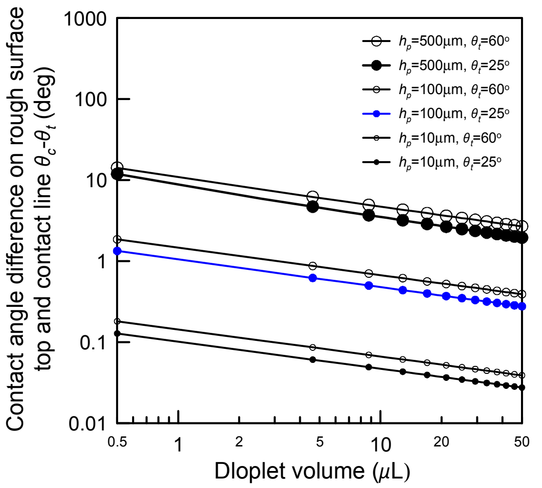


FIGURE 6. CONTACT-ANGLE DIFFERENCE BETWEEN TOP AND CONTACT LINE ON ROUGH SURFACE. RATIO OF LIQUID VOLUME BELOW ROUGHNESS TOP TO THE VOLUME $f = 2/3$.

RESULTS AND DISCUSSION

Figure 2 (c) shows images of water droplets taken from above an aluminum surface ES and an A150P300 machined by EDM. Not all of the droplets were spherical caps, because of the non-homogeneity of the solid. The contact lines were irregular on the pyramid surface.

Figure 3 shows the relationships between the contact angle, contact diameter, and liquid volume in the present mass-area method. The method is sensitive at small angles, for example 25 degrees for 20 μL liquid. The sensitive angle range becomes lower as the volume decreases. The relationship between droplet diameter and contact angle is almost linear at contact angles greater than 45 degrees for the 1-20 μL liquid.

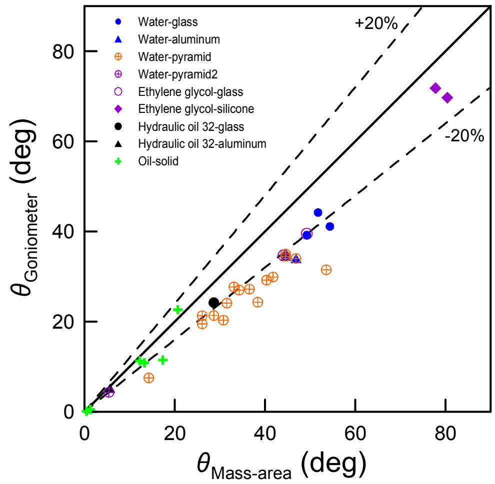


FIGURE 7. COMPARISON OF APPARENT CONTACT ANGLES ON SMOOTH AND PRYRAMID SURFACES BY THE PRESENT MASS-AREA METHOD AND GONIOMETER

The sources of error in the present method are volume of the liquid and solid-liquid contact area or diameter. Figure 4 shows the effects of errors in liquid volume (bottom horizontal axis) and solid-liquid contact diameter (top horizontal axis) on the contact angle measurement. The bigger source of error is the solid-liquid contact area or diameter measurement–resulting in approximately a three-fold error in the contact angle. However, an error in the volume measurement has only a small effect. A precise area or diameter measurement is thus required to increase the accuracy of the contact angle measurement. The present experimental error for the contact angle is about 18% for the conditions of 10 μL and 30 degrees of contact angle. Figure 5 shows the change of contact angle for increasing water volumes on the glass by the present method. Deviation of the contact angles is large for small volumes, decreasing as the volume of liquid is increased. This is the reason that the experimental error for small diameters is large, as shown in Figures 3 and 4.

The liquid fills the grooves of the rough solid. The contact angle differs according to the plane, as shown in Figure 1 and Figure 2. Goniometers normally measure the contact angle near the top plane, while the mass-area method does so in the plane of the contact line. Figure 6 shows the contact angle difference between the top and contact line planes. The difference decreases as the liquid volume increases, and as the contact angle decreases. Increasing the roughness height makes the difference greater. As an example, a contact angle difference is about 0.7 degrees in the case of 5 μL liquid, 100 μm roughness and 25 degrees of surface.

Figure 7 shows a comparison of contact angles on a smooth glass surface as measured by the mass-area method with those taken by the goniometer, sessile drop method. The contact angles were measured at four locations in the goniometer method, and pictures taken of the tops of the wetted areas. The mass-area method showed roughly linear relationships. The present method's measurements were 20% larger than the goniometer ones. The differences between the measurements were not small, and may be due to distortion at the liquid-gas interface. The contact angle of the pyramid rough surface is compared with that of the smooth surface. The results of the present method for the rough surface-pyramid surface are roughly linear to those of the goniometer. However, the degree of variation was greater with the goniometer than the mass-area method. The reason seems to be the irregular contact line on the solid, as shown in Figure 2 (b).

The present apparent contact angles on the pyramid surfaces compared with Wenzel model. The baseline contact angle on the EDM flat surface was about 32 degrees. The contact angles measured by both methods decreased as the roughness ratio increased. It is the similar trend as the Wenzel model. However it was not easy to compare quantitatively, because the contact angles of the present pyramid shape were almost zero. The more detail studies are needed to get reliable contact angle data.

CONCLUSIONS

The present study proposes a mass-area method to measure the equilibrium contact angle on hydrophilic surfaces. From preliminary tests we draw the following conclusions:

(1) The present method showed a roughly linear relationship with measurements by a goniometer on the smooth surface for the range of $0^o < \theta < 80^o$ for various liquids and solids. The goniometer measurements were smaller than those of the present mass-area method. These differences were not small and could not be ignored.

(2) The parameter study reveals that the present mass-area method is sensitive for contact angles less than 20 degrees, and has merit in the small contact-angle range. The big source of error in the method is from measurements of the solid-liquid contact area or diameter: the error in the diameter of the solid-liquid contact region gives about 3 times the error in the contact angle.

(3) The errors in the measurements of the contact angles on rough surfaces varied with roughness height, shape of surface and total liquid volume. The roughness height was a major parameter difference from the smooth surface. However, errors due to the roughness height were several degrees under experimental conditions such as 5 μL liquid on a 500 μm rough pyramid surface.

(4) The mass-area method also has problems to overcome to measure the contact angle accurately, such as contact line identification, its contact area, and measurement procedure. The present method could give supplementary information regarding the equilibrium contact angle, rather than replace the goniometer method.

The direct angle measurement by the traditional goniometer is based on the local force balance of three phases at the contact line. The present mass-area method is conceptually based on the total mass and surface energy balances. The both method would compensate each other to understand the surface wettability even though there are some difference in the measurement.

NOMENCLATURE

$A_{sl,c}$	projected area of solid-liquid side interface on the average contact line plane, m^2
d_{sl}	average diameter of solid-liquid side interface contour on the contact line plane, m
f_v	ratio of liquid volume below roughness top to the volume between roughness top and bottom
f_{sl}	ratio of solid-liquid contact area to solid-liquid interfacial projected area on the solid plane
h_p	roughness height, m
p_f	pitch of pyramid, μm
r	radius of liquid spherical cap, m
V_o	liquid volume, m^3
V_t	volume of spherical cap above top plane of rough surface, m^3
V_b	volume of spherical cap above bottom plane of rough surface, m^3

Greek symbols

θ	contact angle on the smooth surface, rad
θ_b	contact angle on the roughness bottom plane, rad
θ_c	average contact angle on the contact line plane, rad
θ_p	angle of pyramid, deg
θ_t	contact angle on the roughness top plane, rad
σ	surface tension, N m^{-1}

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