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A Wettability Evaluation on Super-hydrophobic and Hydrophobic Surface

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Abstract

The purpose of this paper is to evaluate wettability on solid surface. Wetting is the phenomenon that a liquid attaches to solid surface. In engineering, to control wettability is important for performance improvement of product. A conventional method has been a method to evaluate wettability by measuring the angle between a droplet and the contact surface. In practice, there are two theories to do this; namely Cassie expression and Wenzel expression. Generally, the former is used for things with high repellency, and the latter is used for things with not so high repellency. However, these expressions cannot explain what all the phenomena of the wetting. Because so, many studies are being done in order to solve this problem. Therefore a different method is necessary to evaluate surface (such as the super-hydrophobic surface) with super water repellency. This paper presents wettability evaluation by Laplace pressure. Thereby, we propose new evaluation method of wettability.

Keywords: wettability, Laplace pressure, contact angle, super-hydrophobic, hydrophobic

1 Introduction

Raindrops attach to and spread on the surface of glass. They also roll like a ball on a lotus leaf. These phenomena are called the wetting and important to engineering. For example, the contact state of solid and the liquid is very important in condensation and improvement of the boiling heat transfer characteristic in the field of the heat transfer[1]. Washing of electronic board is also important technology variously in electronic industry, and its value is often performed by evaluating wettability[2]. Like these, control of wettability is necessary for the various case. Recently, by femtosecond laser pulses, Guo et al. demonstrated a laser nano/microstructuring technique to create a combined black, superhydrophobic, and self-cleaning effect on a metal surface.[3] It's necessary to know wettability quantitatively to control, and wettability is being evaluated by the contact angle more than the old days. The contact angle is the angle at which the liquid–vapor interface meets the solid–liquid interface. That angle is given by Young's equation. This equation is derived from a perfectly flat surface. However, in many case, real surface is not so. Therefore, in practice, there are two theories to measure; namely Cassie-Baxter's equation and Wenzel's equation. Generally, the former is used for surface with high repellency, and the latter is used for surface with not so high repellency. It's often studied about wettability so far. Having gravity dependence of the contact angle by roughness of the surface is proposed by Sakai et al[4]. Usually, liquid on the solid surface exhibits either the Cassie-Baxter wetting state or the Wenzel wetting state. Because so, either Cassie-Baxter's equation or Wenzel's equation is used to evaluate wettability. However, a clear explanation about these use has not been given yet. In this paper, to evaluate wettability on super-hydrophobic surface, we propose method by Laplace pressure. In experiment, dropping differently volume of droplet on the solid surface, by photographing droplet with CCD camera, The shape of the contour is earned from image data. Laplace pressure of each volume of the water drop is calculated respectively by elliptic approximation. The present study was conducted using the surface which has super-water repellency. In measurement, a water drop is the macro size of 2-8 μL large.

2 Theoretical

In this chapter, we explain about theoretical wettability evaluation.

2.1 Young equation

The basis of contact angle measurements is determined by Young's equation. As shown **Fig .1**, when a droplet is placed on the solid surface, the characteristic contact angle is formed by

$$\gamma_{sv} = \gamma_{sL} + \gamma cos\theta \tag{1}$$

Where γ_{sv} , γ_{sL} and γ represents the different interfacial free energies (solid/vapor, solid/liquid and liquid/vapor) involved in the system. This equation can explain about wettability by the three interfacial free energies. When liquids spread on substrate, these free energies is $\gamma_{sv} - \gamma_{sL} \geq \gamma$ $(cos\theta \geq 1)$. Thus, θ is near zero. Contrarily to this, when liquids is a nearly spherical shape, these free energies is $\gamma_{sL} \geq \gamma_{sv}$ then $cos\theta$ is negative. The Young's equation assumes a perfectly flat surface referred to as an ideal surface.

2.2 Wenzel's equation and Cassie-Baxter's equation

Unlike ideal surface, real surface is not have perfectly flat. As shown in **Fig. 2**, Wenzel proposed models which explain the surface roughness on the wettability of a solid and is defined by the following equation.

$$\cos\theta_w = r\cos\theta \qquad (2)$$

Where r is the ratio of the true area of the solid surface to the apparent area, and θ is defined by Eq. (1).

In this model, droplet surface touches the bottom of surface which has the relatively low asperity. On the other hand, following model as shown in **Fig. 3** was proposed. This model is explained using the Cassie-Baxter equation

$$\cos\theta_{CB} = \Phi_s\cos\theta + \Phi_s - 1 \qquad (3)$$

Where, Φ_s is the fraction of solid/liquid interface in the entire surface beneath the droplet. Introducing the roughness ratio as r_f of the surface area beneath the droplet, the equation modifies to:

$$\cos\theta_{CB} = r_f\Phi_s\cos\theta + \Phi_s - 1 \qquad (4)$$

When f = 1 and $r_f = r$, the Cassie–Baxter equations becomes the Wenzel equation. Eq. (2) and Eq. (4) hold when the droplet is much larger than the roughness.

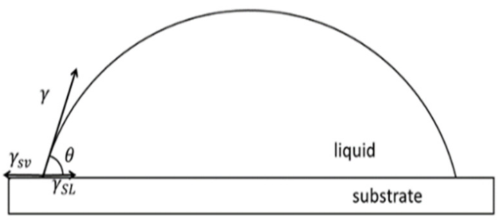

Fig. 1 Young's model

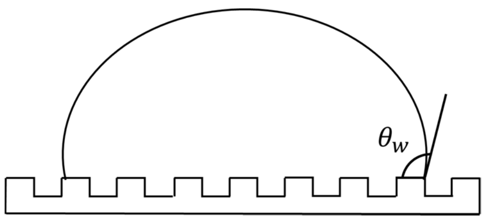

Fig. 2 Wenzel's model

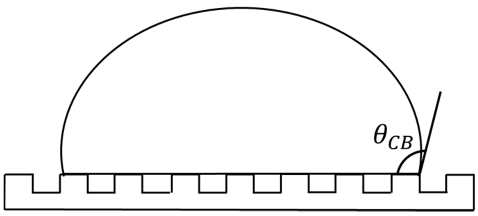

Fig. 3 Cassie-Baxter model

Fig. 4 shows the contact angles which calculated (using Eq. (2) and Eq. (3)) against the contact angles on a flat surface ($\cos\theta$). Point C is the critical point at which two theoretical lines intersect. The Wenzel state calculated by Eq. (2) is plotted in line in Fig. 4 for point C>90°. Similarly, The Cassie-Baxter state is plotted in line for 180°> point C. The point C is given by:

$$\theta_c' = \cos^{-1}\frac{1-\Phi_s}{r_f\Phi_s - r} \qquad (5)$$

Eq. (5) presents the theoretical point of wetting transition from the Cassie state to the Wenzel state. The wetting transition has been investigated. For example, Daiki et al. revealed that this transition occurred when the energy barrier was on the same order of magnitude as external forces, particularly the Laplace pressure in the present case[5]. And Yong et al. propose a criterion that the transition from the Cassie–Baxter regime to the Wenzel regime occurs when the droplet droop is greater than the depth of the cavity[6]. However, a clear mechanism of the transition has not been given yet. We propose an evaluation method of wettability on the solid surface by using Laplace pressure. In the experiment, we used a contact angle meter which is Drop Master-301 of the product of KYOWA.

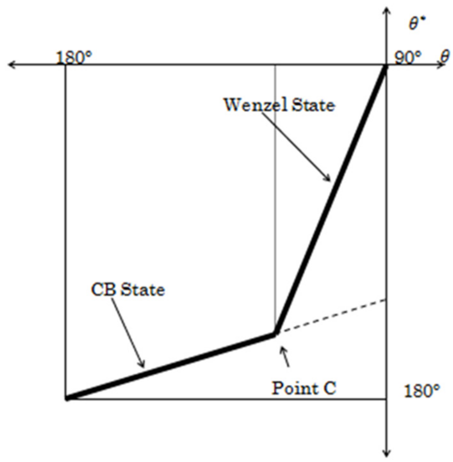

Fig. 4 Cassie-Baxter state to Wenzel state transition

3 Experimental

Using contact angle meter, a water drop ,to 2~8μL, is added dropwise onto the substrate from a needle provided above the stage. As shown **Fig. 5**, then we photograph an image of the shape of a water drop, and gather coordinates at each point of constituting pixels constituting a contour line of water drop of an image. Using gathered coordinates, long diameter and shot diameter is calculated by elliptic approximation. And using an ellipse approximated to the shape of water drop, the contact angle is determined. In the following, a more detailed explanation are given.

3.1 Laplace pressure

There is the pressure difference between the inside and the outside of a curved surface that forms the boundary between a gas region and a liquid region. It is called Laplace pressure. As seen in **Fig. 6**, when soaking water drop in the oil, the pressure difference is caused by the surface tension of the interface between liquid and oil. Then, displacing the surface between liquid and oil implies a change in surface energy δW equal to:

$$\delta W = -p_o dV_o - p_w dV_w + \gamma_{ow} dA \tag{6}$$

Where p_o is pressure of oil, and p_w is pressure of water. $dV_o = 4\pi R^2 dR = -dV_w$ is a displacing volume of water drop, and $dA = 8\pi R dR$ is a displacing surface area. The equilibrium is given by δW=0, we get Laplace pressure:

$$\Delta p = p_o - p_w = \gamma_{ow} \frac{2}{R} \tag{7}$$

It is represented generally by:

$$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{8}$$

Where γ is a surface tension, and r_1, r_2 is radius of curvature. In this study, assuming that the sphere which as the same volume of water drop, we compare Laplace pressure of water drop with Laplace pressure of the sphere. In the solid of same volume, shape which has minimum surface area is the sphere. For this reason to compare Laplace pressure of water drop with Laplace pressure of spherical drop can show wettability. If water drop of Laplace pressure was nearer the sphere of Laplace pressure, substrate shows the high repellency.
In the experiment, to evaluate wettability by Laplace pressure, an aluminum which treated with teflon and hydrochloric acid was employed as the substrate material. It shows an angle of 157 degrees by Tangent Method. The contact angles of water were measured with a contact angle meter.

3.2 Elliptic approximation

The computation for the determination of the radii was carried out in Scilab's program. Using CCD camera, we get an image of water drop on the substrate. By using coordinates, the shape of water drop is determined from this image. Scilab's program calculates radii r_1, r_2 and Central coordinate (a, b) of the water drop by elliptic approximation. The calculation method is shown below.
An ellipse is defined by

$$\frac{(x-a)^2}{{r_1}^2} + \frac{(y-b)^2}{{r_2}^2} = 1 \tag{9}$$

When multiply Eq. (9) by ${r_2}^2$, Eq. (9) is modified to:

$$y^2 = -\frac{{r_2}^2}{{r_1}^2}x^2 + 2\frac{{r_2}^2}{{r_1}^2}ax + 2by + {r_2}^2 - \frac{{r_2}^2}{{r_1}^2}a^2 - b^2$$

$$y^2 = \begin{bmatrix} -x^2 & 2x & 2y & 1 \end{bmatrix} \begin{bmatrix} \frac{r_2^2}{r_1^2} \\ \frac{r_2^2}{r_1^2}a \\ b \\ r_2^2 - \frac{r_2^2}{r_1^2}a^2 - b^2 \end{bmatrix} \tag{10}$$

Substituting coordinates, Eq. (10) is written by

$$\begin{bmatrix} {y_0}^2 \\ {y_1}^2 \\ {y_2}^2 \\ \vdots \\ {y_n}^2 \end{bmatrix} = \begin{bmatrix} -{x_0}^2 & 2x_0 & 2y_0 & 1 \\ -{x_1}^2 & 2x_1 & 2y_1 & 1 \\ -{x_2}^2 & 2x_2 & 2y_2 & 1 \\ \vdots & \vdots & \vdots & \vdots \\ -{x_n}^2 & 2x_n & 2y_n & 1 \end{bmatrix} \begin{bmatrix} \frac{{r_2}^2}{{r_1}^2} \\ \frac{{r_2}^2}{{r_1}^2}a \\ b \\ {r_2}^2 - \frac{{r_2}^2}{{r_1}^2}a^2 - b^2 \end{bmatrix} \tag{11}$$

When assume it *Y=AX*, from a pseudo – inverse $(A^T A)^{-1} A^T$

$$X = (A^T A)^{-1} A^T Y \tag{12}$$

By calculating matrix *X*, r_1, r_2 is obtained. In addition to this, we calculate a contact angle from approximated ellipse.
In order to calculate contact angle at (x_0, y_0), as seen in **Fig.7**, Eq. (9) is modified.

$$y - b = r_2\sqrt{1 - \frac{(x-a)^2}{r_1^2}} \tag{13}$$

$$\frac{dy}{dx} = \frac{r_2}{r_1^2}\frac{x-a}{\sqrt{1 - \frac{(x-a)^2}{r_1^2}}} \tag{14}$$

By substituting Eq. (13) to (14), from which we get

$$\frac{dy}{dx} = \frac{r_2^2}{r_1^2}\frac{x-a}{y-b} \tag{15}$$

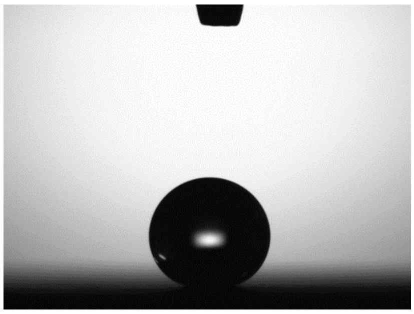

Fig. 5 water drop on the substrate

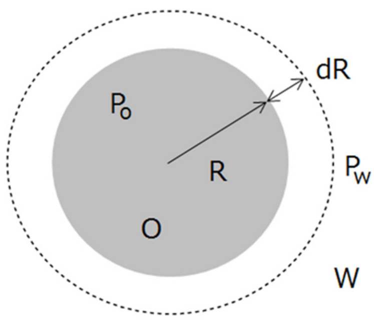

Fig. 6 soaking water drop in the oil

Thus we can get angle at an optional position by Eq. (15) and substituting (x_0, y_0) , contact angle is determined by:

$$\theta = 180 - \frac{\left|tan^{-1}\frac{r_2^2 x_0 - a}{r_1^2 y_0 - b}\right|}{\pi} 180 \qquad (16)$$

4 Results and Discussion

The results of the experiment are shown in **Fig. 8**. This figure shows the Laplace pressure for each volume of water drop. Circles dos represent the Laplace pressure when the water drop is a sphere. Also square dots represent measured Laplace pressure. Approximate line is calculated by least squares method. As previously stated, employed as the substrate material shows an angle of 157 degrees. **Fig.9** shows the contact angle for each volume of water drop. Here it can be seen that this the substrate material has high repellency. Hence, shape of water drop may be considered to be nearly sphere. As can be seen from **Fig.8**, spherical drop and water drop show nearly same shapes. From this figure, we can observe that this substrate has high repellency. This result is generally consistent with the expectation. However as seen in **Fig 8**, Laplace pressure of water drop which size of 5-8 μL large, has variation. Consequently several Laplace pressure of water drop is over than Laplace pressure of sphere. It is inferred from this result that weight of water drop affects Laplace pressure.

5 Conclusions

As a results of experiments of evaluating wettability by Laplace pressure, the following conclusions are drawn.

(1) As expected, this substrate shows a low wettability by our evaluation method. Hereafter, by experimenting various substrates, it is possible to evaluate wettability with this method.
(2) As seen in **Fig 9**, by elliptic approximation, obtained data has variation. To obtain more accurate data, this method is open to further discussion.
(3) Using various substrate, by examining relationship between Contact angle and Laplace pressure, it is necessary to confirm the reliability as the evaluating method.

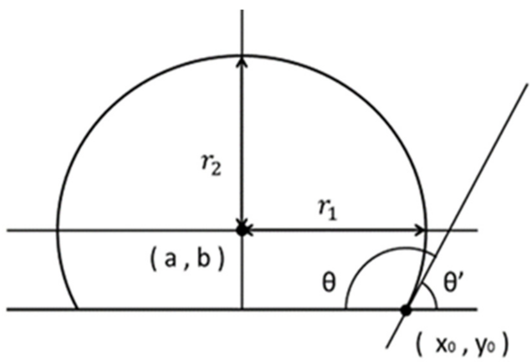

Fig. 7 Tangent of the ellipse

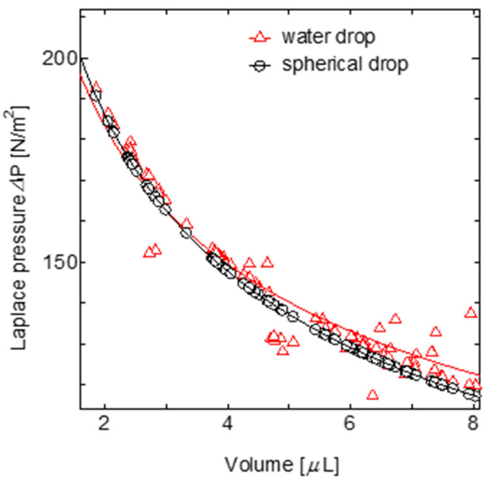

Fig.8 V- ΔP graph

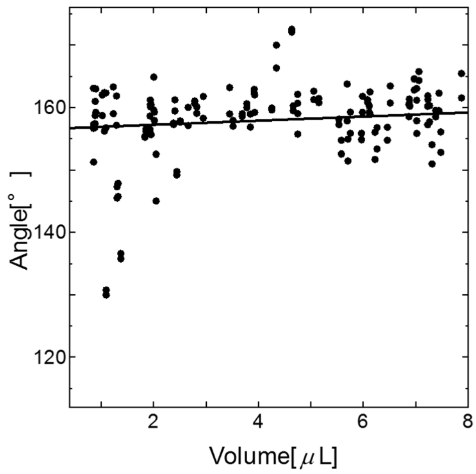

Fig. 9 Graph of Volumes for contact angles

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Received on December 27, 2016
Accepted on March 15, 2017