Video Contact Angle Analyzer (VCA)

[Technical note 1]

This technical note explains the concepts of static and dynamic contact angle. The methods to measure the contact angle will be introduced.

Introduction

1. The concept of contact angle measurement

The contact angle, θ, is a well-established quantitative indicator for the level of wetting of a solid by a liquid. **Figure 1(a)** schematically illustrate the geometry of a droplet on a surface, where the contact angle is defined as the angle formed by the liquid droplet at the three-phase boundary where a liquid, gas and solid intersect.

The Young equation often used to describe the equilibrium at the three-phase contact precisely, as:

$$\gamma_{SV} = \gamma_{Sl} + \gamma_{lv} \cos(\theta_Y)$$

The interfacial tensions, γ_{SV} , γ_{Sl} and γ_{lv}, form the equilibrium contact angle of wetting, are usually referred as Young contact angle θ_Y.

Also illustrated in **Figure 1(b)** , a low contact angle indicates that the liquid spreads across the surface. On the other hand, high contact angle values show poor spreading.

In general, for contact angle that is less than 90 °, often referred as a hydrophilic surface. The extreme case of hydrophilic is the zero-contact angle, which indicates a complete wetting on the surface. In contrary to the hydrophilic surface, a contact angle that is greater than 90 °, the surface is referred to a non-wetting (hydrophobic) surface with the testing liquid.

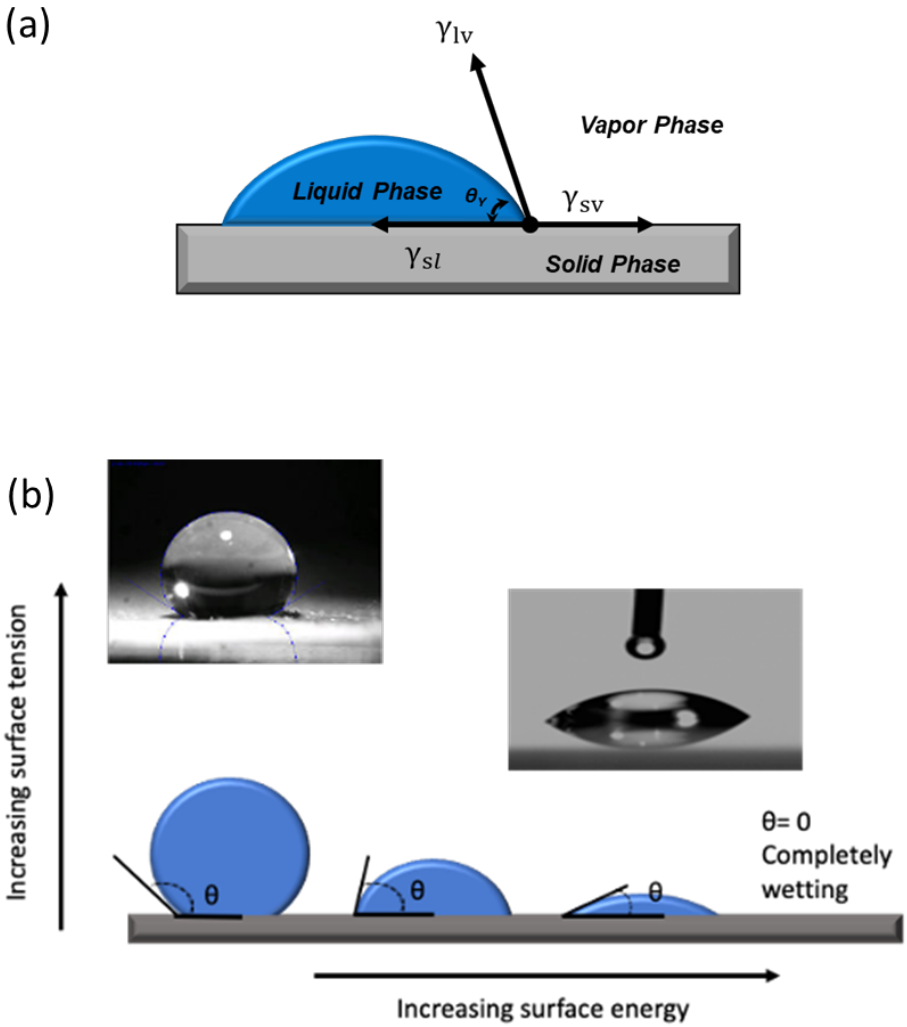

Figure 1: schematically illustrate the concept of contact angle. (a) the geometry of a droplet on a surface, where the contact angle is defined as the angle formed by the liquid droplet at the three-phase boundary. (b) The relationship between surface energy and contact angle. For contact angle < 90 °, the surface is referred as a hydrophilic. For contact angle > 90 °, it is referred as non-wetting (hydrophobic) surface.

2. Static and dynamic contact angle

Contact angles measurement can be divided into static and dynamic contact angles. Static contact angles are measured when the liquid droplet is steadily standing on the surface and the three-phase boundary remain static. The static contact angle measurement is often practically utilized in quality control, research, and product development [1]. The application in industry ranging from inkjet printing, advanced textile, biomedical sensing to gene delivery.

Contrary to the static contact angle measurement, the dynamic contact angle measures the contact angle when three phase boundaries are moving. The detailed method for dynamic contact angle measurement will be describe in the following sections. The dynamic contact angle can be categorised into advancing and receding angles. The difference between the advancing and receding contact angles is referring to dynamic contact angle hysteresis, which could possibly arises due to the following factors: (1) chemical and topographical heterogeneity of the surface, (2) solution impurities absorbing on the surface, or (3) swelling, rearrangement or alteration of the surface by the solvent [1]–[3].

Advancing and receding contact angles give the maximum and minimum static contact angle can have on the surface. The difference between advancing and receding angles can be as high as 50 °. Due to the availability of application, the dynamic contact angles and hysteresis has become a popular topic. For example, to develop a superhydrophobic or self-cleaning surfaces, it is important to know the sliding angles (i.e. the smallest angle that the substrate need to be tilted to move the droplet), and a rigorous dynamic angle measurement can provide valuable information. On the other hand, hysteresis is also particularly important in various field. The intrusion For example, when water diffuses into porous media, the coating, and adsorption at liquid/solid interface interaction phenomena can all monitored by the hysteresis measurement [1][4] .

Dynamic contact angle measurements using droplet shape analysis

Both static and dynamic contact angles can be obtained via video contact angle analyser (VCA). In practice, a droplet is placed on the solid surface. With the state-of-art optical path design and a sensitive digital camera. Digital images of the test drop can be recorded. Static contact angle is then calculated by fitting the droplet shape image to the Young-Laplace equation.

Similarly, the dynamic contact angle measurement can be obtained. There are two well-established dynamic contact angle measurement methods, which are: (a) volume changing method, and the (b) tilting substrate method. They are schematically shown in **Figure 2** and **figure 3**, which will be discussed in the following paragraphs. Similar to the static contact angle measurement, the outline of the testing droplet is detected

and quantified via its digital image, which can generally be fitted by the Young-Laplace equation. While other quantitative methods such as fitting with circle or polynomial curve can was also reported and can be employed [1]–[3], [5], [6].

1. The volume changing method

The volume changing method is realized via the following steps: (1) formation of a a small droplet is on the tip of the syringe, (2) syringe tip is then brought close to the surface. (3) gradually increase the volume of the droplet by injecting target liquid to the syringe tip, until the droplet contacts the target surface. As schematically shown in figure (a), with the gradually increasing volume of droplet, the advancing contact angle is formed between the droplet and the surface. The detailed image series can be recorded, and analysis in-situ with the camera of the VCA system [1], [5], [7].

Similarly, the receding angle can be measured via the volume changing method., the volume of the droplet is gradually decreased. In **Figure 2**, the principle of the tilting cradle method is shown. The droplet is placed on the substrate which is then gradually tilted. The advancing angle is measured at the front of the droplet just before the droplet starts to move. The receding contact angle is measured at the back of the droplet, at same time point.

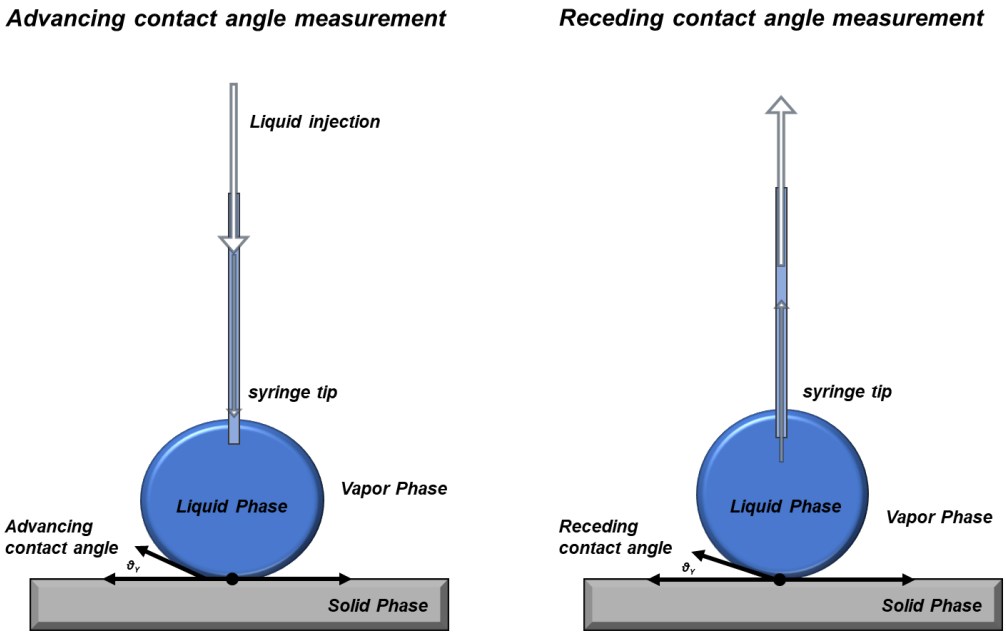

Figure 2: Schematically shows measument of dynamic contact angle via volume changing method. (Left) : Advancing contact angle measurment. (Right) Receding contact angle measurment.

2. Tilting substrate method

The principle of tilting substrate method is shown in **Figure 3.** The droplet is placed on a substrate tilting platform, in which the substrate is gradually tilted. The advancing angle is measured at the front of the droplet just before the droplet just before the droplet start to move. The receding contact angle is measured at the back of the droplet. Based on this method, the roll-off angle (i.e. the tilting angle at which the droplets start to move) can be obtained. A low roll-off angle is related to low contact angle hysteresis.

Dynamic contact angle analysis plays an important role in modern surface technology. The information provided by dynamic contact angle measurement con be used to study the heterogeneity of the surface and is the most powerful tools in developing superhydrophobic self-cleaning surface, quick mirroring identifying surface roughness or impurities. This can be extremely helpful in pioneer material development.

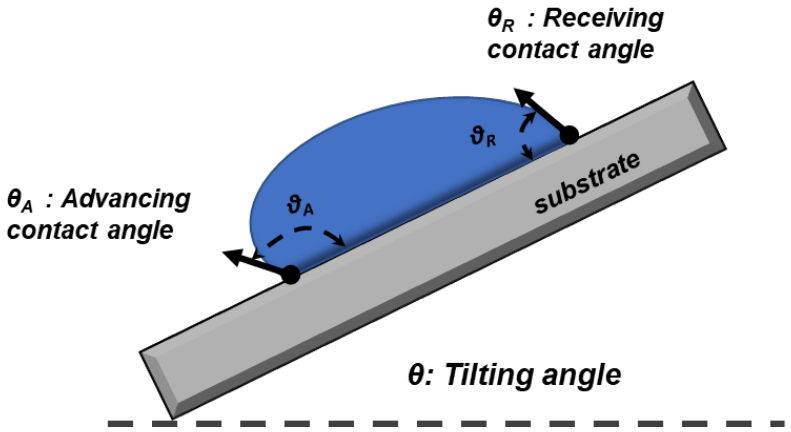

Figure 3 : Schematically shows measurment of dynamic contact angle via tilting substrate method.

Reference:

[1] K. L. Mittal, Ed., *Advances in Contact Angle, Wettability and Adhesion*. Hoboken, NJ, USA: John Wiley & Sons, Inc., 2013.

[2] L. Feng *et al.*, "Super-hydrophobic surfaces: From natural to artificial," *Adv. Mater.*, vol. 14, no. 24, pp. 1857–1860, Dec. 2002.

[3] L. Gao and T. J. McCarthy, “Contact angle hysteresis explained,” *Langmuir*, vol. 22, no. 14. American Chemical Society , pp. 6234–6237, 04-Jul-2006.

[4] Z. Chen, L. Dong, D. Yang, and H. Lu, “Superhydrophobic graphene-based materials: Surface construction and functional applications,” *Adv. Mater.*, vol. 25, no. 37, pp. 5352–5359, 2013.

[5] B. E. Rapp, Microfluidics: Modeling, mechanics and mathematics. Elsevier Inc., 2016.

[6] Droplet Wetting and Evaporation. Elsevier, 2015.

[7] “Video Contact Angle System - VCA Optima.” [Online]. Available: https://www.astp.com/contact-angle-vca-optima. [Accessed: 16-Dec-2020].