White Paper

AUTHOR:
SUSANNA LAURÉN, PHD
BIOLIN SCIENTIFIC

Contact angle – What is it and how do you measure it?

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Contact angle – What is it and how do you measure it?

Contact angle, θ (theta), is a quantitative measure of wetting of a solid by a liquid. The behavior of single drop on a surface tells you a lot about the properties of your solid.

The most obvious example is the application of different types of coatings and surface treatments. For example, if contact angle between the paint and the surface to be painted is high, that will lead to poor spreading and non-uniform coating. Contact angles can also be used to check if a surface treatment has been successful. Plasma treatment is often utilized to improve the adhesion between the substrate and the coating to be applied. The low contact angle between water and treated substrate indicate the success of the surface treatment.

In practice, a drop of liquid is placed on a surface and the contact angle is measured as shown in **Fig. 1**. Low contact angle values, i.e. below 90°, are related to good wetting whereas high contact angle values, above 90 °, indicate poor wetting. When the contact angle is 0°, the surface is said to wet completely. If the liquid applied on the surface is water, terms hydrophilic and hydrophobic are used, respectively.

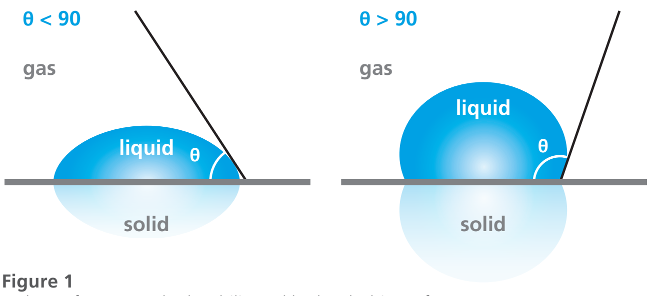

Figure 1
A drop of water on hydrophilic and hydrophobic surfaces

Contact angle basics

The contact angle is geometrically defined as the angle formed by a liquid at the three-phase boundary where a liquid, gas, and solid intersect. There are three different forces acting on this three-phase contact point between solid, fluid and fluid as shown in **Fig. 2**.

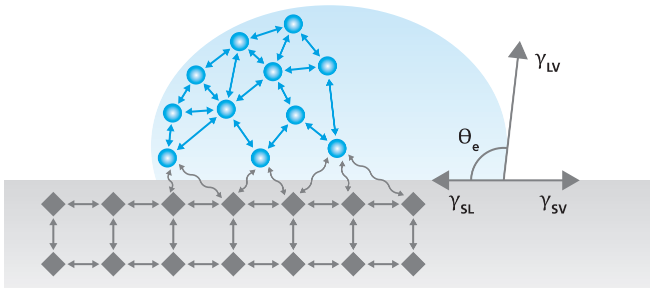

Figure 2
Three-phase contact point where solid, fluid and fluid meet

This white paper gives a very practical tutorial for contact angle theory and measurement techniques. Concepts like static, dynamic, and roughness corrected contact angle are explained and linked to the real-life application. Different measurement methods are reviewed and compared to help you to choose the best method for your surface. At the end of the white paper, contact angle measurements on more advanced substrates, like fibers and powders are discussed.

The γ_{lv} is the surface tension of a liquid, γ_{sl} is the interfacial tension between the solid and liquid and γ_{sv} is the surface tension of the solid i.e. surface free energy.

The well-known Young´s equation describes the balance at the three-phase contact.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} cos\theta_Y \qquad (1)$$

The interfacial tensions, γ_{sv}, γ_{sl}, and γ_{lv}, form the equilibrium contact angle of wetting, many times referred to Young´s contact angle θ_Y.

Young's equation assumes that the surface is ideal. This means that it is flat, rigid, perfectly smooth, and chemically homogenous. Furthermore, it assumes that the system is stable i.e. there is no interaction between the liquid and the substrate. As neither of the above-mentioned criteria is fulfilled in real life, advancing and receding (i.e. dynamic) contact angle measurements are often performed. Surface roughness can also be corrected by measuring roughness corrected contact angle. Contact angles are thus divided into three categories; static, dynamic and roughness corrected.

Static contact angles – quick and easy

Static contact angles are measured when the droplet is sitting on the surface and the three-phase boundary is not moving. Static contact angles are by far the most measured wettability values. It is most suitable for relatively smooth and homogenous surfaces. Static contact angles are also used to define the surface free energy (i.e. surface tension of solid) of the substrate. Static contact angle offers a quick, easy and quantitative measurement of wettability. They are thus utilized in quality control and in various research and product development, ranging from printing to oil recovery and coatings to implants. Static contact angle measurement is based on Young's equation which assumes that interfacial forces are in thermodynamically stable. In practice, however, there exist many metastable states of a droplet on a solid, and the observed contact angles are not equal to Young contact angle. Because phenomenon of wetting is not just a static state, other contact angles i.e. dynamic and roughness corrected are measured.

Dynamic contact angles and contact angle hysteresis for more information

When the three-phase boundary is moving, dynamic contact angles can be measured, and are referred to as advancing and receding angles. As the terms imply, advancing contact angle is measured when the droplet front is advancing and receding when the droplet front is receding. On an ideal surface, these two values are close to each other. However, most often, the measured contact angle depends on the direction on which the contact line is moving. Contact angle hysteresis is the difference between the advancing and receding contact angles. Contact angle hysteresis arises mostly from the chemical and topographical heterogeneity of the surface, solution impurities absorbing on the surface, or swelling, rearrangement or alteration of the surface by the solvent [1, 2]. Advancing and receding contact angles give the maximum and minimum values the static contact angle can have locally on the surface. The difference between advancing and receding angles can be as high as 50°.

Dynamic contact angles and contact angle hysteresis are utilized to study the heterogeneity of the surface. It has become a popular topic because of the recent interest in superhydrophobic and self-cleaning surfaces [3, 4]. Criteria for the surface to be super-hydrophobic is that the static contact angle is above 150° and that the contact angle hysteresis is less than 10 degrees.
In the applications where superhydrophobicity is utilized, such as self-cleaning, the contact angle hysteresis plays an important role, as the droplet should easily roll-off the surface. Hysteresis is however also important in other situations such as intrusion of water into porous media, coating, and adsorption at liquid/solid interface.

Roughness corrected contact angles to separate the effect of roughness from surface chemistry

Contact angles are affected by roughness. Surfaces with the same chemical composition but different roughness will have different contact angles. Two wetting states can be distinguished; Wenzel and Cassie-Baxter. Cassie-Baxter refers to a situation where droplet sits on a rough surface so that air pockets are formed in between the drop and the substrate (**see Fig. 3 a**). When, the whole surface area is wetted, and no air pockets are formed (**see Fig. 3 b**), surface roughness can be related to the contact angle by Wenzel equation [5].

$$\cos \theta_m = r \cos \theta_Y \tag{2}$$

, where θ_m is the measured contact angle, r is the roughness ratio and θ_Y is the Young contact angle.

The roughness ratio is defined as the ratio between the actual and projected solid surface area (r = 1 for a smooth surface and > 1 for a rough surface). It is important to note that the Wenzel equation is based on the assumption that the liquid completely penetrates into the roughness grooves (**as in Fig. 3b**). If you are more interested in the theories behind the roughness measurements and contact angle correction, please download the white paper **"The Attension Theta optical tensiometer with 3D topography module for roughness corrected contact angles"**.Roughness corrected contact angles are especially useful when different types of surface treatments are done. Surface treatments such as plasma treatment affect both the chemistry and the roughness of the surface. By correcting the contact angles measured, it is possible to separate the effect of roughness on the contact angle. Roughness corrected contact angles can also be utilized to measure roughness corrected surface free energies. Surface free energy is the chemical property of the solid. As static contact angles do not take the roughness into account, the surface free energies calculated are affected by the surface roughness. Thus, chemically the same material with different roughness levels will lead to different surface free energies if contact angles are not corrected for roughness. This can lead to misinterpretation of the results.

Figure 3
Droplet on (a) Cassie-Baxter (b) Wenzel state

Measurement methods

Contact angles are typically measured by using either optical or force tensiometers. With the optical method static, dynamic and roughness corrected contact angles can be obtained whereas force tensiometry can only be used for the dynamic measurements. Optical methods include the sessile drop (static), needle method, tilting (dynamic) and meniscus methods. The force-based measurement is called Wilhelmy method. In this section, a short description of each method is given.

Sessile drop

A sessile drop is the most used contact angle measurement method. In practice, a droplet is placed on the solid surface and an image of the drop is recorded. The static contact angle is then defined by fitting Young-Laplace equation around the droplet, although other fitting methods such as circle and polynomial can also be used. Sessile drop method is also used to calculate roughness corrected contact angles.

Needle method

In the needle method, a small droplet is first formed and placed on the surface. The needle is then brought close to the surface and the volume of the droplet is gradually increased while recording the contact angle at the same time. This will give the advancing contact angle. The receding angle is measured the same way but this time, the volume of the droplet is gradually decreased. The principle is shown in **Fig. 4**. The method is also described in a standard [6].

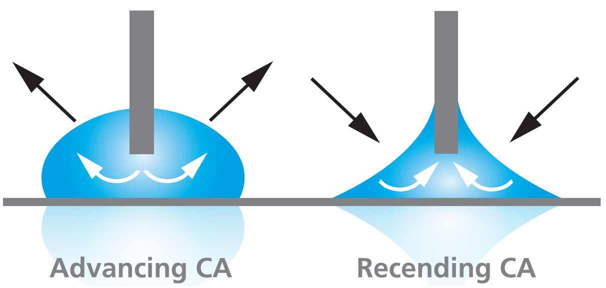

Figure 4
Advancing and receding angles by needle method

Tilting method

In **Fig. 5**, the principle of the tilting 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 as the droplet starts to move. The receding contact angle is measured at the back of the droplet, at the same time point. With this method, the roll-off or sliding angle can also be determined. The roll-off angle refers to a tilting angle at which the droplet starts to move. A low roll of angle is related to low contact angle hysteresis.

The tilting can be done either by tilting the sample stage or by tilting the whole instrument. When the whole instrument is tilted, the camera is tilted along with the sample, so the software sees the substrate being horizontal throughout the experiment. This makes the placement of the droplet less critical as the optical path is not changing. The method is described in a standard [7].

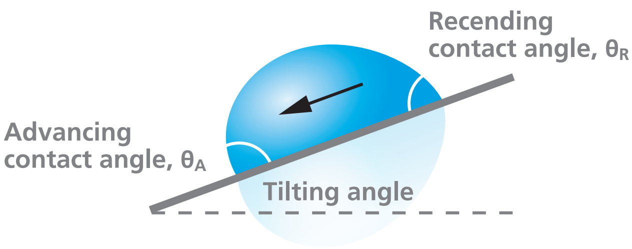

Figure 5
Measuring advancing and receding angles with the tilting method

Meniscus method

It is also possible to measure contact angles by a meniscus method. This method is especially useful when measuring thin objects like rods and fibers down to 7 um. In this method, the sample is immersed into liquid as shown in **Fig 6**. When the sample is pulled from the liquid a meniscus is formed and the contact angle is optically measured. The contact angles measured with the meniscus method cannot be directly compared to static nor dynamic ones as the wetting conditions are different. Also, angles above 90° can not be measured.

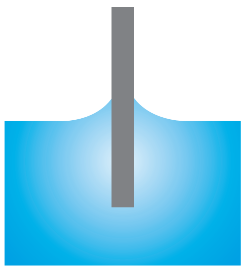

Figure 6
Meniscus measurement principle (redraw with contact angle fitting and proper container)

Wilhelmy method

Dynamic contact angles can be measured by using force tensiometry and the Wilhelmy method. Force tensiometer measures the mass affecting to the balance when a solid sample is brought in contact with a test liquid. The contact angle can then be calculated by using the equation (3) when the surface tension of the liquid (γ_l) and the perimeter of the sample (P) are known.

$$Wetting\ force = \gamma_l\, P cos\theta \quad (3)$$

In **Fig. 7**, a complete contact angle measurement cycle is presented. As can be seen, with the force tensiometry the measured contact angle is always dynamic since the sample is moving against the liquid.

When the sample is immersed in the liquid the advancing contact angle is recorded and when the sample is emerging the receding contact angle is measured.

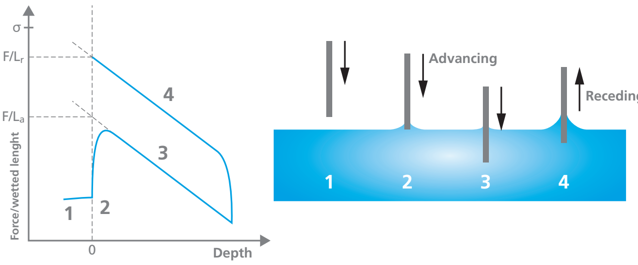

Figure 7
Wilhelmy method

Comparison of the contact angle measurement techniques

The optical tensiometer is the main measurement method for contact angle since measurement of both static and dynamic contact angles are possible. It is also possible to study the homogeneity of the sample by measuring contact angle on several different places on the same sample. This is not possible with the Wilhelmy method since the calculated contact angle is the average over the whole immersed area. For the same reason, in Wilhelmy method, the sample must be homogenous on both sides. [8]

Contact angle measurements of special samples

Although contact angle measurement is many times quite straightforward, there are some special cases that require more careful planning for the measurement set-up. These include fibers and powders.

Fibers

Fibers and other thin objects can be measured by using optical tensiometry equipped with picoliter dispenser, with meniscus method or with force tensiometry using Wilhelmy method. With the optical tensiometer, the picoliter dispenser can produce droplets with the diameter of about 30 µm in air. With special optics and a high-speed camera, it is possible to take an image of this small droplet and the contact angle can be determined in a similar fashion than by using microliter size droplets. Meniscus measurement can also be used for fibers. If the fiber is thin (below 200 µm) a special optics is required.

Force tensiometer, on the other hand, can be used by utilizing a special holder for the fiber. Down to 7 µm, fibers can be measured. It should be noted that the measurement with picoliter droplets leads to static contact angles whereas Wilhelmy method is a dynamic method, giving both advancing and receding angle. The contact angle measured with the meniscus method is somewhere in between and cannot be directly compared with contact angles measured with other two methods.

Powders

Contact angles on powders can be measured by using sessile drop measurement on the compressed powder tablet or by using the force tensiometer with the Washburn method. When compressed tablets are measured, it can behave like the absorbing substrate if the powder is hydrophilic or the droplet can stay on the surface if the powder is hydrophobic. The main issue with the tablet compression is that the surface properties of the tablets can vary a lot, which can lead to misinterpretation of the results. Roughness on the tablet surface could be taken into account by measuring the roughness corrected contact angle.

To study loose powders, the Washburn method must be utilized.

In this method, the powder is packed in a cylinder with holes at the bottom (**Fig. 8**). The holder is slightly immersed into measurement liquid and the liquid uptake as a function of time is recorded. The time it takes for the liquid to penetrate is related to contact angle through Washburn equation. As the method is based on the capillary action, it is limited to below 90° contact angles.

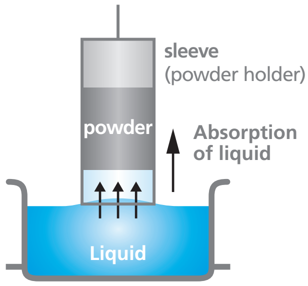

Figure 8
Washburn method

Conclusions

Contact angle measurements offer a quick and versatile method to study wettability of the surface. As wettability of the surface can be related to phenomena such as adhesion and spreading, it offers a very useful tool to the variety of industries. Although static contact angle measurements are by far the most used, measuring advancing, receding and roughness corrected contact angles are also widely utilized. These methods can offer additional information on the properties of the solid surface. With several different measurement methods available, the method has to be chosen based on the sample and application at hand.

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