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Attension [Technology Note] 1

Static and dynamic contact angles and their measurement techniques

This technology note explains the concepts of static and dynamic contact angle and goes through the measurement by using both optical and force tensiometers.

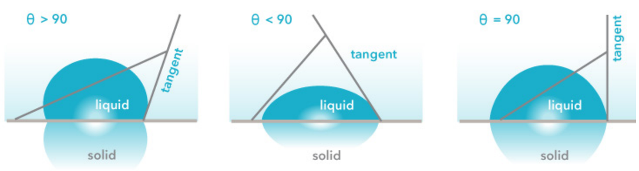
Introduction

Contact angle, θ, is a quantitative measure of wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. The well-known Young equation describes the balance at the three phase contact of solid-liquid and gas.

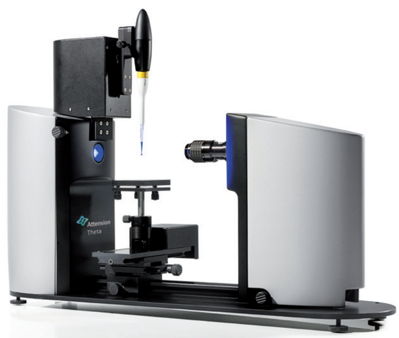
$$\gamma_{SV} = \gamma_{Sl} + \gamma_{lv} \cos\theta_Y \qquad (1)$$

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

From Figure 1, it can be seen that the low contact angle values indicate that the liquid spreads on the surface while high contact angle values show poor spreading. If the contact angle is less than 90 ° it is said that the liquid wets the surface, zero contact angle representing complete wetting. If contact angle is greater than 90 °, the surface is said to be non-wetting with that liquid. Contact angles can be divided into static and dynamic angles. Static contact angles are measured when droplet is standing on the surface and the three phase boundary is not moving. Static contact angles are utilized in quality control and in research and product development. Contact angle measurements are used in fields ranging from printing to oil recovery and coatings to implants. When the three phase boundary is moving, dynamic contact angles can be measured, and are referred as advancing and receding angles. Contact angle hysteresis is the difference between the advancing and receding contact angles. Contact angle hysteresis arises 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



[Figure 1]: Different contact angles on a surface



Attension Theta

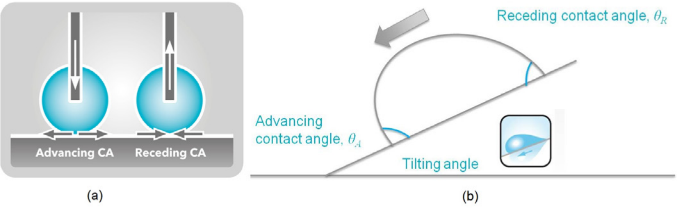
Attension Sigma

the maximum and minimum values the static contact angle can have on the surface. Difference between advancing and receding angles can be as high as 50 °. Dynamic contact angles and contact angle hysteresis has become a popular topic because of the recent interest in superhydrophobic and self-cleaning surfaces [3, 4]. This is important since small sliding angles (= angle the substrate has to be tilted to move the droplet) are needed for self-cleaning applications. Hysteresis is however also important in other situations such as intrusion of water into porous media, coating, and adsorption at liquid/solid interface.

Contact angle measurements by using optical tensiometer

Both static and dynamic contact angles can be measured by using Theta optical tensiometer. In practice, a droplet is placed on the solid surface and the image of the drop is recorded. Static contact angle is then defined by fitting Young-Laplace equation Figure 2. Schematic of dynamic contact angle measurement by using (a) volume changing method (b) tilting cradle. around the droplet, although other fitting methods such as circle and polynomial can also be used.

Dynamic contact angles can be measured by using two different approaches; changing the volume of the droplet or by using tilting cradle. Figure 2 (a) shows the principle of the volume changing method. In short, 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 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. In Figure 2 (b), 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.



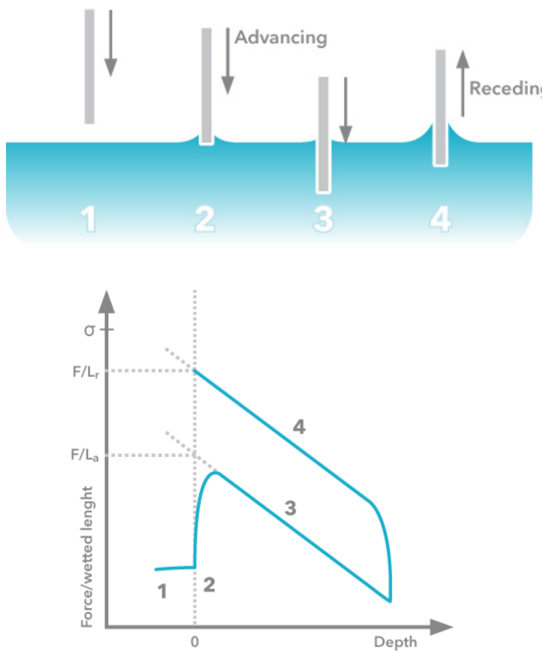
[Figure 2]: Schematic of dynamic contact angle measurement by using (a) volume changing method (b) tilting cradle.

Contact angle measurements by using force tensiometer

Dynamic contact angles can be measured by using Sigma force tensiometer. Force tensiometer measures the mass affecting to the balance when a sample of solid is brought in contact with a test liquid. The contact angle can then be calculated by using the equation (2) when surface tension of the liquid (γ_l) and the perimeter of the sample (P) are known.

$$\text{Wetting force} = \gamma_l\, P\cos\theta \qquad (2)$$

In Figure 3, a complete contact angle measurement cycle is presented. As can be seen, with force tensiometer the measured contact angle is always dynamic contact angle since the sample is moving against the liquid. When the sample is immerged to the liquid the advancing contact angle is recorded and when the sample is emerging the receding contact angle is measured.



[Figure 3]: Dynamic contact angle measurement by using Wilhelmy plate method.

Comparison of the contact angle measurement techniques

Optical tensiometer is the main measurement method for contact angle since measurement of both static and dynamic contact angles is 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 plate method since the calculated contact angle is the average over the whole immersed area. For the same reason, in Wilhelmy plate method the sample has to be homogenous on both sides [5].

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 fiber, samples that absorb the liquid and powders.

Fibers

Fibers and other thin objects can be measured by using optical tensiometer equipped with picoliter dispenser or with force tensiometer using Wilhelmy plate method. With optical tensiometer, the picoliter dispenser can produce droplets with the base diameter of about 30 to 50 µm. With special optics and 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. Force tensiometer on the other hand can be used by utilizing a special holder for the fiber. Due to extremely small forces exerted to the balance, anti-vibration table and cabinet are required for reliable measurements. Both of these methods are reviewed more in details in application note 1.

Absorbing substrates

Many times contact angles are measured on the substrates that absorb the measuring liquid. In this case contact angles are typically analyzed as a curves for further analyses. In case one values is needed, care must be taken that the contact angle is measured and reported repeatably. Most often the first contact angle value measured is then taken as the contact angle result. Since the absorption usually happens very quickly, high speed cameras are often utilized.

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. This and the Washburn method are explained in detail in theory note 5 and application note 7.

References:

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