

## Influence of surface roughness on contact angle and wettability

This technology note explains how the surface roughness influences on the contact angle and wettability of the substrate.

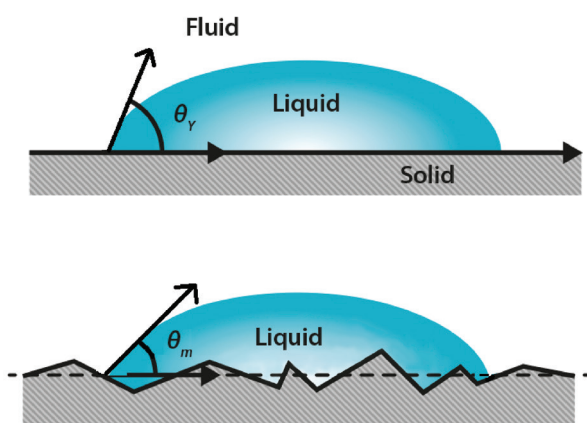
### Introduction

Both chemical and topographical properties of the surface are important parameters in many different applications and processes, where wetting and adhesion behavior needs to be optimized. Wettability can be studied by measuring the contact angle of the substrate with the given liquid. The well-known Young equation describes the balance at the three-phase contact of solid, liquid and vapor.

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

The interfacial tensions,  $\gamma_{sv}$ ,  $\gamma_{sl}$  and  $\gamma_{lv}$ , form the equilibrium contact angle of wetting, often referred to as the Young contact angle  $\theta_Y$ . The Young equation assumes that the surface is chemically homogenous and topographically smooth. This is however not true in the case of real surfaces, which instead of having one equilibrium contact angle value exhibit a range of contact angles between the advancing and receding ones.

In Figure 1, the droplet on ideal and real surfaces is presented. On an ideal surface the Young equation applies and the measured contact angle is equal to the Young contact angle (Figure 1(a)).



**Figure 1.** Definition of contact angles, (a) Contact angle on ideal surface is called Young contact angle, (b) Apparent or measured contact angle on rough (Wenzel) surface.



Attension Theta with 3D Topography Module

On a real surface the actual contact angle is the angle between the tangent to the liquid-vapor interface and the actual, local surface of the solid (Figure 1(b)). However, the measured (apparent) contact angle is the angle between the tangent to the liquid-vapor interface and the line that represents the apparent solid surface, as seen macroscopically. Actual and apparent contact angle values can deviate substantially from each other. To calculate real surface free energies of the solid the actual contact angles should be used.

The relationship between roughness and wettability was defined already in 1936 by Wenzel who stated that adding surface roughness will enhance the wettability caused by the chemistry of the surface [1]. For example, if the surface is chemically hydrophobic, it will become even more hydrophobic when surface roughness is added. Wenzel statement can be described with equation (2).

$$\cos \theta_m = r \cos \theta_Y \quad (2)$$

,where  $\theta_m$  is the measured contact angle,  $\theta_Y$  is the Young contact angle and  $r$  is the roughness ratio. 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 one) and can be calculated from a 3D roughness parameter  $S_{dr}$  as explained later.

It is important to notice that the Wenzel equation is based on the assumption that the liquid penetrates into the roughness grooves (as in Figure 1(b)). It has been stated that if the droplet is larger than the roughness scale by two to three orders of magnitude, the Wenzel equation applies [2]. Wenzel corrected contact angles have been utilized for example to study the wettability of paper sheets [3] and cell adhesion to biomaterial surfaces [4]. Both micro and nanoscale roughness have been shown to have influence on surface wettability. Additional information on applications can be found from application notes 16 and 17.

In cases where the liquid does not penetrate into the grooves, the Wenzel equation does not apply. In this case the Cassie equation is used instead. The Cassie equation was first developed to describe chemically heterogeneous surfaces, with two different chemistries [5].

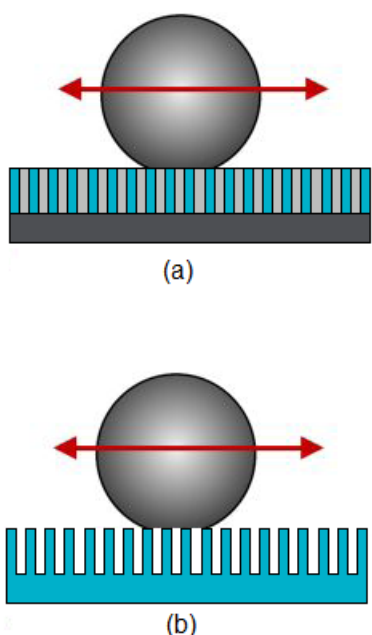
$$\cos\theta_m = x_1 \cos\theta_{y1} + x_2 \cos\theta_{y2} \quad (3)$$

In the equation (3),  $x$  is the area fraction characterized by the given chemistry and subscripts 1 and 2 indicate two different surface chemistries (Figure 2(a)). If, instead of having different chemistries on the surface, the second area is air like shown in Figure 2 (b), then equation (3) can be written as:

$$\cos\theta_m = x_1 (\cos\theta_y + 1) - 1 \quad (4)$$

since contact angle against liquid and air can be considered to be  $180^\circ$  ( $\cos\theta_{y2}$  is -1) and the area fraction  $x_2 = 1 - x_1$ . Equation (4) was developed by Cassie and Baxter [5] and is thus often called the Cassie-Baxter equation. It has been found that for the droplet to achieve the real Cassie-Baxter stage (no penetration of the liquid inside the grooves), the geometry of the roughness has to be carefully designed [6].

The most stable contact angle is the one associated with the absolute minimum of the Gibbs energy curve which can be connected to the Young contact angle. The contact angles calculated from the Wenzel and Cassie-Baxter equations have been found to be good approximations of the most stable contact angles [7].



[Figure 2] (a) Droplet on a chemically heterogeneous surface (Cassie) (b) Droplet standing on a pillar surface (Cassie-Baxter).

## Roughness parameters

Surface roughness cannot be accurately characterized by using a single roughness parameter. Instead a set of surface roughness parameters are defined. Parameters that characterize surface profiles are called 2D parameters and are marked with the letter "R". These parameters are widely utilized in different applications but are not really able to provide the full information on the three-dimensional surfaces. Parameters to characterize surface topography are called 3D parameters and are marked with the letter "S". Some of the 3D parameters have their 2D counterparts; others are specifically developed for 3D surfaces [8]. A summary of these parameters as stated by the ISO 25178 (and their 2D counterparts) is presented in Table 1 [9, ISO25178].  $S_a$  is an arithmetic mean height of the surface.  $S_q$  and its 2D counterpart are the most widely used roughness parameters that give the standard deviation of height.  $R_p$  and  $R_v$  give the maximum height of the summit and maximum depth of the valleys, respectively.  $R_z$  gives the peak to peak value and  $R_{10z}$  is calculated as a mean height value of five local maxima and local minima.  $R_z$  is more sensitive to noise than  $R_{z10}$ . The ratio between the interfacial and projected area  $S_{dr}$  gives the additional surface area contributed by the texture. This parameter is especially useful in wettability studies since it can be used to calculate the roughness ratio  $r$ , according to equation (5).

$$r = 1 + S_{dr}/100 \quad (5)$$

| Symbol             | Name                             | Equations   | Description   |
|--------------------|----------------------------------|---|---|
| $R_a, S_a$         | Arithmetic average               | $S_a = \frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M  h(x_i, y_j) $  | Average of  z   |
| $R_q, S_q$         | Root mean square (RMS) roughness | $S_q = \sqrt{\frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M h^2(x_i, y_j)}$   | Standard deviation of z   |
| $R_p, S_p$         | Maximum height of peaks          | $S_p = MAX(h_p)$  | Max z   |
| $R_v, S_v$         | Maximum depth of valleys         | $S_v = MIN(h_v)$  | Min z   |
| $R_z, S_z$         | Maximum height of the surface    | $S_z = ( S_p  +  S_v )$   | Max z - Min z   |
| $R_{10z}, S_{10z}$ | Ten point height                 | $S_z = \frac{\sum_{i=1}^5  h_{pi}  + \sum_{i=1}^5  h_{vi} }{5}$   | Average of five highest local maxima and five deepest local minima. |
| $S_{dr}$           | Area factor                      | $S_{dr} = \frac{(Textured\ surface\ area) - (Cross\ sectional\ area)}{Cross\ sectional\ area}$<br>$= \frac{\sum_{j=1}^{N-1} \sum_{i=1}^{M-1} A_{ij} - (M-1)(N-1)\Delta x\Delta y}{(M-1)(N-1)\Delta x\Delta y}$<br>$+ 100\%$ | Ratio between the interfacial and projected areas                   |

[Table 1] Some typical 2D and 3D roughness parameters.

## Roughness measurement

Surface roughness can be measured by using several different methods and different sampling areas. Atomic force microscopy (AFM) is often utilized for surface roughness studies. It should be noted that the measurement area of the AFM is usually limited to few square micrometers, which also limits the roughness scale that can be seen. AFM is able to measure only the nanoscale roughness whereas larger surface structures are not seen. Stylus profilometers provide a similar type of measurement but the stylus is usually a few micrometers in diameter which makes it impossible to penetrate into smaller structures. Both AFM and stylus type profilometers are usually relatively slow especially if 3D roughness parameters are defined. There is also the additional disadvantage of having the needle in contact with the substrate which can lead to sample damage. Optical methods are therefore preferable although they set some requirements for the optical properties of the materials. Overall, care should be taken when comparing surface roughness data between different instruments and even between different instrument operators since measurement parameters can have a significant effect on the results [10].

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