New approach to the determination of the contact angle in hydrophobic samples with simultaneous correction of the effect of the roughness.

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**Abstract**. This work presents the validation study of a method developed to measure contact angles with a confocal device in a set of hydrophobic samples. The use of this device allows the evaluation of the roughness of the surface and the determination of the contact angle in the same area of the sample. Furthermore, a theoretical evaluation of the impact of the roughness of a non-smooth surface in the calculation of the contact angle when it is not taken into account according to Wenzel’s model is also presented.

**Keywords**: contact angle, surface energy, confocal, roughness, hydrophobicity

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# Introduction

The study of surface energy is becoming increasingly relevant for the development of new materials. It plays a major role in friction, lubrication and wear phenomena in contact materials and specially, in flow-surface interactions with liquids. Within the past ten years, the coating community has witnessed a great increase in interest in nanostructured materials from a number of industrial applications, such as marine, aviation and wind blades1,2.

In order to evaluate the surface energy of a surface it is necessary to calculate it indirectly by means of the contact angle measurement of a liquid drop placed on it. Currently, the surface energy is usually obtained applying the calculation model based on Young’s equation (1).

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|  |  | (1) |

where is the surface energy of the solid, is the surface tension of the liquid, is the surface energy at the liquid-solid interface and θ is the value of the contact angle measured. However, said equation can only describe solid surfaces that are totally flat and smooth3 so using it on rough surfaces leads to an erroneous assessment of the surface energy. This means that the surface energy of a rough material should not be calculated directly from the contact angle measurements4 and the topography of the surface should be taken into account since the contact angle is related both to the surface energy and to the topography of the surface.

As a consequence, current techniques can only be applied to assess the global hydrophobicity of the surface, but cannot be used to determine the intrinsic surface energy5. The greater the roughness of the surface, the more erroneous it is to associate the measured contact angle only with the surface energy and the chemical properties of the surface. This is mainly due to the fact that, the greater the roughness, the greater the contact area between the liquid and the solid, and the greater the effect of any trapped air bubbles, factors which can only be suitably accounted for when the local microstructure is known6.

In order to solve this, some models have been proposed that describe this influence of the topography on the resulting contact angle7,8. In order to be able to use these calculation methods correctly in rough, real samples (as opposed to samples specifically prepared with a determined topography via etching or other such processes9,10), one must know with the utmost accuracy both the contact angle and the topography of the sample in the exact area of the sample where the drop has been placed.

Unfortunately, no commercial device is currently available to perform both topography and contact angle measurements. The use of two different devices leads to sample positioning uncertainty, implying that besides the time and resource consumption inherent to making two different measurements with two different devices, no assurance can be given that both measurements are performed on the same area on the sample and that the resulting calculated surface energy is correct.

In this paper, a measurement method is presented based on the patent EP16001763, to measure the contact angle with a confocal device which is designed for non-contact topography measurements. The reasons why we choose this specific device will be presented together with the advantages that it presents in this study. This method allows the measurement of both the topography of a solid surface and the contact angle of a drop placed on it, with a single device, in a top-view configuration. Thus, shifting in the sample position between the two measurements is avoided and the proper location of both measurements in the same area of the sample is ensured.

This work also reports a theoretical evaluation of the impact of not taking into account the roughness of a surface in the measured contact angle for non-smooth surfaces according to Wenzel’s model11. Furthermore, a validation study of the developed technique to obtain the contact angle by a confocal device is performed in a full range of hydrophobic samples.

# Roughness and contact angle

When measuring experimentally the contact angle of a solid surface, we must keep in mind that we will obtain a contact angle value which corresponds to a macroscopic measurement and does not reflect only the chemical properties of the material under study. It is important to note that the way of wetting of a liquid on a solid surface depends not only on the properties of the liquid and the chemical properties of the solid surface but also on its physical morphology. As we will see, the structure of a surface is of a key importance in the framework of wetting studies and the micro and nano structure of a surface is directly related with the modification of the wetting properties of the surface.

Starting from Young’s equation12, the surface energy of a solid can be obtained from the measured contact angle since the surface tension of the liquid is already known, provided that the surface under measurement is chemically homogenous and topographically smooth. The equation used for this is the following

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|  | (2) |

where corresponds to the intrinsic contact angle of this surface. Conversely, when we measure the contact angle on rough surfaces, this apparent measured contact angle is affected by the roughness of the surface. If we want to evaluate the surface energy of a rough surface by directly substituting this apparent contact angle value in Young’s equation, it will lead to an erroneous value since this equation has been developed for surfaces which are perfectly smooth.

Hence, if we want to perform the evaluation of its corresponding surface energy as reliably as possible from the measured apparent contact angle, which reflects both the effects of the chemical composition and the structural component of the surface, we must be able to correct the influence of the roughness of the surface on this apparent contact angle. From the bibliography, we know two main models to correct this contribution: Wenzel11 and Cassie-Baxter13. These two models can be distinguished broadly by the way the liquid wets the surface.

There is a particularly striking example in nature were both models can be observed. For example, a Wenzel scenario can be observed in a rose whose petals are hydrophobic but the water drops reaching the surface do not slip off and remain on the petal (Figure 1a). Due to the micro structure of the surface and the wetting conditions, the liquid drop remains stuck on the surface and do not slip.

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| Figure 1 (a) Image of a flower petal with a water drop stuck on its surface[[1]](#footnote-1) that represents a Wenzel scenario; (b) image of sliding water on a lotus leaf[[2]](#footnote-2) that represents a Cassie-Baxter’s scenario. |

On the other hand, the effect of water on a lotus leaf (Figure 1b), is easy to relate with Cassie Baxter model. The Lotus leaf has a particular micro structure on the surface allowing trapped air bubbles, which makes that the liquid cannot be stuck on the surface and in this case, the water slips on the surface. These leafs and their surface micro structure are of interest in superhydrophobic studies and self-cleaning surfaces development 14 due to their microstructure’s capability to drag the dirt particles as the water slips off on the surface.

In the present work, the samples studied are hydrophobic and all of them are in the framework of Wenzel’s regime since the deposited liquids drops remain stuck in the surface. In future work where superhydrophobic surfaces will be also studied, the correction of the effect of the surface roughness in the measured contact angle will be made by Cassie-Baxter’s model.

In the present work, the use of Wenzel’s model will allow to correct the effect of the roughness of a surface in the measured contact angle and we will then obtain its corresponding intrinsic contact angle which we will use in Young’s equation to further obtain the surface energy.

## Wenzel model

Earlier in the twentieth century, Wenzel11 started to evaluate the impact of the roughness, both the micro and nano structure of a surface, in the measurement of the contact angle on rough and chemically homogeneous surfaces.

Let us suppose a rough surface with a given micro structure. A liquid drop is placed on it and wets completely the contact surface, as Figure 2 shows. According to Wenzel, the total contact area between the solid and the liquid must be taken into account when calculating the surface energy so the surface is characterized by the roughness ratio factor (). This factor is defined as the ratio of the real solid-liquid area (), which takes into account the roughness of the surface, to its projection on a smooth surface () and is always greater than 1 since no surface is completely smooth at the molecular range.

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| Figure 2 Schematic diagram of Wenzel’s scenario where a liquid droplet wets completely a rough solid surface and the schematic representation of the real area (Arough) and the projected area (Aflat) of the droplet on a smooth surface to calculate the roughness ratio factor *r*. |

As the introduction of roughness not only influences the surface energy of the solid surface but also its interfacial energy, adding the roughness ratio factor in Young’s equation, where and , we finally obtain Wenzel’s equation (3).

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|  | (3) |

where corresponds to the apparent contact angle measured on the surface.

If we depict the behavior of this equation (Figure 3) we can easily differentiate between a hydrophilic and a hydrophobic region. In the first one, i.e. , for any measured the corresponding will be always larger, , so this means that the introduction of roughness in the surface increases the hydrophilicity of the surface and the liquid will tend to wet further. For the hydrophobic region, i.e. , we get the opposite situation. For any measured, it will have associated a smaller value of which means that the liquid will tend to wet less, so the surface becomes more hydrophobic.

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| Figure 3 Representation of the measured Wenzel’s apparent contact angle *θW* as a function of the Young’s contact angle *θY*for *r* = 1.2 as an exemplary value. |

Therefore, Wenzel’s equation predicts that the introduction of roughness on a surface enhances its wetting properties since it makes a hydrophilic surface even more hydrophilic and a hydrophobic surface even more hydrophobic. As a consequence, it is clear that if the aim is to evaluate the surface energy in a solid with a rough surface we first must decouple the effect of the enhancement of the wetting properties due to the roughness of the surface.

After this introduction, we are going to present the developed mathematical method to calculate the contact angle from the measurement of different parameters of a liquid drop placed on the surface under study.

# Mathematical method

The measured parameters with the confocal device are the height () and the apparent diameter () of the liquid drop placed on the surface under study. In our measurement conditions, the drop volume is already known and small enough to discard gravity effects, so the shape of the drop can be approximated by a truncated sphere15.

The calculation of the contact angle is performed based on the geometric shape of the drop so two possible situations must be taken into account depending on the surface wettability properties as shown in Figure 4a and b.

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| Figure 4 Schematic representation of a drop placed on a (a) high wettability surface; (b) low wettability surface. |

In a high wettability surface, shown in Figure 4a, the mathematical expression which relates the contact angle with and corresponds to equation (4). Conversely, in a low wettability surface shown in Figure 4b, the mathematical expression corresponds to equation (5).

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|  |  | (4) |

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|  |  | (5) |

# Experimental setup

As we introduced previously, there is currently no available commercial device which allows performing both topographic and contact angle measurements. However, in this section we present a powerful methodology to address this issue.

This section introduces the confocal device used to measure the set of parameters of the drop that are used to calculate the contact angle by means of the developed measurement method described above. We will also expose why we choose a confocal device and the principal advantages that it presents when compared to other available techniques to perform the concerned study. Furthermore, we will explain how we can obtain the roughness factor introduced by Wenzel to correct the measured contact angles by the effect of the roughness of the surface and the accuracy that this device can achieve in the performed measurements.

## Confocal device

A confocal device is a device that uses the confocal microscopy technique to perform topographic measurements with high accuracy and reliability. As we will see, it capabilities can be extended to contact angle measurements without any loss in accuracy and adapting the measurement method to the conditions of the study.

The device used is the S-Neox, from Sensofar Metrology Company who develops, manufactures and commercializes high-end 3D surface metrology tools. The S-Neox is a very accurate and reliable non-contact 3D surface profiler that provides confocal, interferometry and focus variation techniques to perform the measurements.

The device is equipped with a set of microscopic objectives from 2.5 to 150X magnification with numerical apertures up to 0.95 all of them located in a manually controlled revolver objective holder, to measure smooth surfaces with certain steep local slopes limitation. In our particular case of study, the deposited drops on hydrophobic samples will have rounded shapes so the slope on the upper part of the drop gets very steep as shown in Figure 5.

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| Figure 5 Schematic representation of a deposited drop on a solid sample under measurement showing the maximum slope αmax feasible to be measured by the confocal device. |

Due to this fact, the methodology applied to measure the height of the drop is adapted to this measurement condition, with the proper microscope objective, as protected in the patent EP16001763.

S-Neox is also equipped with a three-axis mechanical stage used as a sample holder controlled by software and its resolution is up to 2 nm with linear stage and 0.75 nm with piezo stage. With these capabilities, the apparent diameter of the drop can also be easily measured even when the drop is larger than the field of view of the used microscope objective to perform this measurement.

Unlike interferometric techniques, we do not have any limitation of the field of view that directly translates in a loss of information, loss in accuracy in the measurement of the height of the drop and unfeasibility of the measurement of the apparent diameter of the drop, as we concluded from previous developed work16.

The accuracy provided by S-Neox allows us to perform our measurement with the precision shown in Table 1, adapted to the measurement conditions of our study.

Table 1 Introduced errors by the confocal device in the measurement of and of the liquid drop.

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| Errors | |
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| 1 | 10 | |

The evaluation of the roughness of the sample under study is performed by means of the topographic measurement performed by the confocal device. From the topography we can obtain the Developed Interfacial Area Ratio (Sdr)17 which is defined as the additional surface area contributed by the texture as compared to a flat plane on the same measurement region size and is expressed in percentage. With this parameter, we can calculate the roughness ratio factor by applying equation (6).

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|  |  | (6) |

Once calculated, we can correct the calculated contact angle with the effect of the roughness of the surface. All using only one device and without shifting the sample between different devices.

To validate the methodology, the contact angle calculated by the measurements performed with the S-Neox will be compared with the ones obtained from a commercial contact angle meter used as a reference values.

The commercial contact angle meter used in this work is the DSA-100, from KRUSS Company, located at the TWI facilities in Cambridge. This company produces first-class measuring instruments for surface and interfacial chemistry. This device is specialized in coatings’ characterization and its technology allows the user to measure the contact angle of a liquid drop and the evaluation of the surface energy of the solid surface under measurement.

We performed contact angle measurements on the same samples which were also measured with the S-Neox to have a reliable and accurate values of these contact angles to be compared with the ones obtained with the S-Neox.

The DSA-100 works from side view and calculates the contact angle by fitting the contour of the image of a drop with different available models. This device also allows the calculation of the surface energy, differentiating from the disperse and the polar component when the proper liquid is used.

## Coating sample preparation

Six hydrophobic coatings solutions where prepared and deposited onto glass microscope slides by TWI. The coating solutions are based on a commercially available polysilazane matrix (TutopromTM: DurXtreme GmbH, Ulm, Germany) loaded with silica nanoparticles (TWI. Ltd. Cambridge, UK). Two sizes of silica nanoparticles where used, 45nm and 120nm. The composition of the coatings prepared where as Table 2 shows.

**Table 2** Summary of coating solutions formulations developed by TWI.

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| Samples | Tutoprom matrix (%wt.) | 45nm hydrophobic silica (%wt.) | 120nm Hydrophobic silica (%wt.) |
| M1 | 25 | 67.5 | 7.5 |
| M2 | 10 | 89 | 1 |
| M3 | 5 | 94.5 | 0.5 |
| M4 | 25 | 0 | 75 |
| M5 | 10 | 0 | 90 |
| M6 | 5 | 0 | 95 |

Coatings where deposited by simple dipping method. The glass slides were introduced in the coating solution and withdrawn at 100 mm/min speed. They were then dried in an oven at 150⁰C for one hour.

# Results and discussion

This section presents the results obtained from the contact angle measurements performed by both the DSA-100 and the S-Neox on a full set of samples (Figure 6) described in section 4.2. The hydrophobic behavior increases as the loading of additives increases. All the samples have been measured with water and Diiodomethane as measurement liquids.

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| Figure 6 Pictures of full set of samples used in this study yielded by TWI. The samples are of a glass substrate with different hydrophobic coatings. |

At first sight, the different nature of the sample can be seen in Figure 7 where the topography of the coatings of samples M2, M4 and M6 measured by the confocal device is shown.

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| C:\Users\Usuario\Documents\PhD Noemí\Paper Optical Engineering\Revision Paper OE\Documentos enviados\Figuras\Figure 7.png |
| Figure 7 Topographic measurements of samples M2, M4 and M6 performed by the confocal device. |

In Table 3 and Table 4 the contact angle measured by DSA-100 and S-Neox are shown for water (WCA) and Diiodomethane (DCA) respectively as measurement liquids for each measured sample. The measured by S-Neox and its corresponding calculated factor is also included together with the calculated according to Wenzel method.

Table 3 Summary of the measured contact angle by DSA-100 and S-Neox for water (WCA) as a measurement liquid. The measured *Sdr* parameter by the S-Neox and its corresponding calculated *r* factor is also shown and the calculated *θY* taking into account the roughness of the surface under study.

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| --- | --- | --- | --- | --- | --- |
| Sample | DSA-100 | S-Neox | | | |
| WCA (°) | WCA (°) |  |  | Calculated |
| M1 | 108.49 | 107.92 | 0.79 % | 1.0079 | 107.07 |
| M2 | 119.27 | 110.35 | 1.01 % | 1.0101 | 109.25 |
| M3 | 126.24 | 126.74 | 0.49 % | 1.0049 | 126.14 |
| M4 | 100.7 | 98.83 | 0.04 % | 1.0004 | 98.79 |
| M5 | 111.29 | 106.52 | 0.42 % | 1.0042 | 106.07 |
| M6 | 120.55 | 120.57 | 0.16 % | 1.0016 | 120.38 |

Table 4 Summary of the measured contact angle by DSA-100 and S-Neox for Diiodomethane (DCA) as a measurement liquid. The measured *Sdr* parameter by the S-Neox and its corresponding calculated *r* factor is also shown and the calculated *θY* taking into account the roughness of the surface under study.

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| --- | --- | --- | --- | --- | --- |
| Sample | DSA-100 | S-Neox | | | |
| DCA (°) | DCA (°) |  |  | Calculated |
| M1 | 82.82 | 82.23 | 0.79 % | 1.0079 | 81.59 |
| M2 | 88.84 | 84.56 | 1.01 % | 1.0101 | 83.81 |
| M3 | 99.04 | 98.34 | 0.49 % | 1.0049 | 97.86 |
| M4 | 75.09 | 73.06 | 0.04 % | 1.0004 | 73.03 |
| M5 | 80.51 | 79.28 | 0.42 % | 1.0042 | 78.94 |

As can be seen, the contact angles calculated by means of the developed method are pretty similar to those measured by the DSA-100 when water it the measurement liquid, even though the methods of measurement are completely different. On the other hand, when Diiodomethane is the measurement liquid, the values obtained by the developed method are not as accurate as the ones obtained by the DSA-100. This is because the values of the contact angles are smaller than or similar to 90° and this introduces an uncertainty in the developed method that will be dealt with in future work.

As the values of the are relatively low, the measured samples are not rough enough to see the difference between the corrected and the non-corrected contact angle. Further studies will be made on rougher samples to address this point.

Nevertheless, we have demonstrated that we can calculate the contact angle and evaluate the roughness of a surface exactly in the same area of the surface to be measured, and correct the influence of this roughness in the contact angle according to Wenzel’s model by using a unique, accurate device designed for topographic measurements.

# Conclusions

This work presents the validation study in hydrophobic samples of a new method developed to measure contact angles with a device designed for non-contact profilometry, in this case, a confocal device. The use of a confocal device is proved to enable the sequential evaluation of the roughness of the surface and the determination of the contact angle in the same area of the sample, allowing to relate both measurements with great accuracy. Furthermore, this work also presents a theoretical evaluation of the impact of the roughness in contact angle measurements and the error committed when this is not taken into account, according to Wenzel’s model.

# Acknowledgements

This work is supported by the AGAUR (Agència de Gestió d’Ajuts Universitaris i de Recerca) project 2014 DI 047. The author acknowledges the The Welding Institute (TWI) and all its workers in the coatings department for helping, teaching and supporting in the training with the DSA-100. The author is thankful to Carlos Bermudez for his inestimable help in the S-Neox device training and in data analysis.

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**Bibliographies**

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