

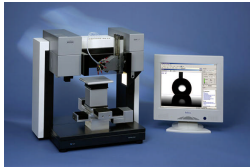
Effect of drop volume on static contact angles

Technical Note 310e

by

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Instruments



Drop Shape Analysis System DSA100

Abstract

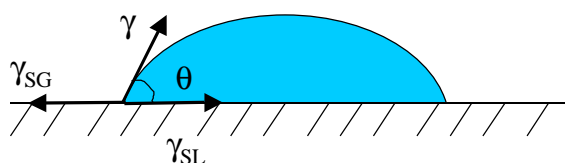
Measurement of contact angles of sessile drops deposited on surfaces is a powerful analysis tool that is widely used in several industry sectors, from cosmetics to semiconductors, coatings and food industry, wettability studies, surface treatments control, adhesion performance prediction, etc.

The purpose of this short note is to treat one recurrent question users have when measuring static contact angle : "how big a drop size should I use?". Indeed, the drop volume is important as we will see, in order to be sure that no size effect is influencing measured contact angles.

Surface and Contact Angle of Sessile Drops

When a drop is deposited onto a solid surface there are three interfaces involved : solid/air, solid/liquid and liquid/air. Once created, the drop will then instantly try to equilibrate the system by minimizing its energy at interfaces. This is mainly achieved by surface minimization between liquid and other phases. Practically, this state is reached when forces acting on the triple line solid/liquid/air are equilibrated. Young was the first in 1805 to propose a description of the phenomena, by projecting the forces at the three-phase contact line :

$$g \cos \theta = \gamma_{SG} - \gamma_{SL}$$



We can then say that the lower the contact angle θ is, the more is the liquid wetting the surface. Equilibrium geometry of the liquid

drop is reflecting the interactions between the surface and the liquid. Measured contact angles can then be used in conjunction with theories published in scientific literature to determine the surface free energy of solid, characterizing solid surfaces regarding wettability or adhesion properties.

The use of a goniometer allows precise determination of the contact angle value of a liquid on a surface along the triple-phase line, since the image analysis is done on a projection of the sessile drop.

Drop size study

Generally, when creating a drop at the tip of a needle, the volume used is of the order of a couple of microliters. Then, in practice the drop and the sample surface are brought in contact. Once the drop touches the surface, the needle and the surface are separated in order to leave the drop reach equilibrium on the surface. Depending on the affinity of a liquid on a particular surface, the drop will spread and wet the solid accordingly.

In case the drop volume is too large, gravity force is higher than the capillary force that

retains the liquid at the needle tip. Then the drop falls onto the surface, leading to an additional kinetic energy injected to the system. This energy will of course have an impact on the drop shape. It will lead to a larger contact surface between drop and solid, and thus stimulate an increased apparent wetting effect, not representing the true physical solid/liquid interactions of the system.

Let us now consider what happens when we change liquid volumes for sessile drops. Experimentally it is observed that the drop's shape changes from spherical shape to a more flat one. This is due to gravity effect.

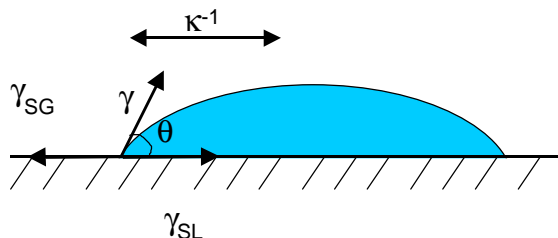
There is a length scale defined by the so-called "capillary length" κ^{-1} , above which gravity cannot be neglected anymore compared to capillary effects :

$$k^{-1} = \sqrt{\frac{g}{rg}} \quad [\text{Equation 1}]$$

This is based on equilibrating Laplace pressure γ/κ^{-1} and hydrostatic pressure $\rho g \kappa^{-1}$, at a depth κ^{-1} inside a liquid of ρ density. Calculating the κ^{-1} value for water gives a value 2.7 mm.

Below a drop radius of 2.7 mm for water the dominant forces are capillary terms and gravity effects can be neglected.

In the following table contact angle values measured using the Young-Laplace fitting method are displayed. Sessile drops of 1, 3, 5

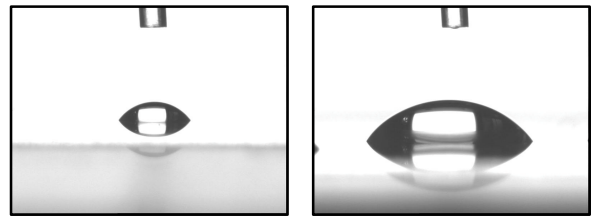


and 10 microliters of water deposited on a microscope glass plate were used. Mean values given in the table were obtained using at least three drops of each volume.

Volume (microliters)	Drop radius (mm)	Contact angle (°)
1	1.0	54.3
3	1.5	54.5
5	1.75	53.9
10	2.3	53.8

As can be seen the drop radius is always below the capillary length defined above, and same contact angles values are found whatever the drop size.

To illustrate these results, below are shown two pictures. The first represents a drop of 1 microliter and the second a drop of 10 microliters.



Summary

Contact angle measurements are becoming more and more widely used in several industrial fields, either for control purposes or R&D activity, like in coating applications, semiconductors, polymer development to biological research.

Many users wonder what maximum drop size they should use for static contact angle measurements. We recall a contact angle is the expression of resulting molecular interactions at interfaces between three phases (liquid, air and solid) and gravity effects must be avoided.

Based on the analysis above, we conclude that for water the use of a drop volume of 1 up to 10 microliters has no influence on static contact angle values.

For other liquids the optimum volume range varies with liquid density (see equation 1).