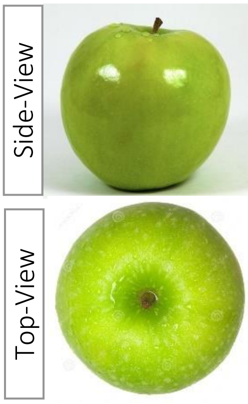
LAUDA scientific

Contact Angle Measurement from Top
MOB - *x* Series

Q: What are the main characters of MOB series?



A: It is

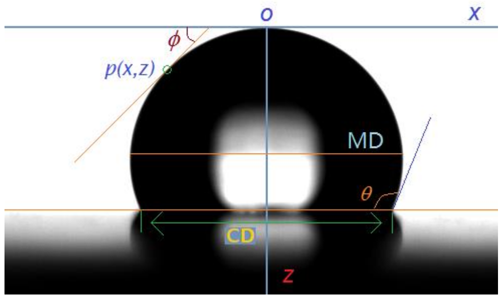
- based on the observation of a sessile drop from top, i.e. a Top-View method;
- applicable as long as a drop formed on a solid surface can be imaged/sighted from top, no matter the drop is resided on the bottom of a cavity, or is surrounded/hindered by nontransparent objects;
- best suitable for extremely low contact angles down to 0 degree;
- suitable for contact angles up to about 165 degrees;
- the perfect method for high-density surface mapping: drops can be deposited closely spaced and measured without any troubles.
- the optimal method for measurement on samples of (any) large size.

Q: What is the working principle of MOB?

$$2-\beta\left(\frac{z}{b}\right)=\frac{1}{R/b}+\frac{\sin\phi}{x/b}$$

$$\beta=\frac{b^2\cdot\Delta\rho\cdot g}{\gamma}=\frac{b^2}{\alpha^2},$$

$$\alpha=\sqrt{\frac{\gamma}{\Delta\rho\cdot g}}$$



A: The Top-View method is based on the same system equation as the conventional Side-View method, that is the Laplace-Young equation, which describes the surface/interfacial boundary of a sessile drop at hydrostatic equilibrium (see equations/picture on the right). The form of a drop is determined by the parameters a $\boldsymbol{\alpha}$ and $\boldsymbol{b}$, where $\boldsymbol{\alpha}$ is the capillary constant of the system and $\boldsymbol{b}$ is the radius of curvature at the drop apex *O*.

For a given liquid like water, $\boldsymbol{\alpha}$ is known, therefore, the volume V of a drop is a function of ***b*** and its height ***H***. Each pair of (***b***, ***H***) leads to a specific value of CD and MD, which are the drop's Contact Diameter and Maximum Diameter, respectively. If the contact angle is under 90 degrees, CD is visible from top and can be determined, while for drops with contact angle above 90 degrees, MD is visible and determined. With the knowledge of CD or MD, the pair of (***b***, ***H***), which leads to the exact same CD or MD as experimentally determined, can be calculated. Subsequently, with the values of ***b***, ***H*** and $\boldsymbol{\alpha}$, the contact angle at the 3-phase contact line (baseline) can be unambiguously computed. For a given $\boldsymbol{\alpha}$ and V, it is mathematically impossible to find a valid pair of (***b***, CD) as well as (***b***, MD), there can be only one of them. Consequently, the software can determine automatically, whether the drop diameter, which is determined by imaging the drop from top, is a CD or MD.

Therefrom, by knowing the volume of a drop and its capillary constant $\boldsymbol{\alpha}$, contact angle can be determined by measuring the drop diameter from top with the help of image analysis. The method is applicable for contact angle under as well as above 90 degrees.

Q: Which kinds of variations exist in the market?

A: There are mainly three variations that are used to determine contact angle by imaging a drop from top: a) Top-View method based on sphere model by measuring CD; b) Top-View method based on the measurement of drop curvature around the drop apex*;* and c) Top-View method based on the Laplace-Young model.

All three variations have one thing in common, that is the volume of a drop must be known.

Both case a and b are based on the sphere model, that means it is assumed that a drop is just a part of a sphere and its radius of curvature is a constant, independent of its location alone the drop profile. This is a very roughly approximation, similar to all sphere-model-based computation methods used in Side-View measurement. These methods deliver only reasonable results for small drops with low contact angles, and, in most cases, only if water is used as test liquid. The methodological error increase with increasing drop volume and contact angle value, and decreasing capillary constant α of test liquid used. Among all common test liquids, water has the largest value of α and is therefore closest to the sphere model assumption.

These variations should/can NOT be used for contact angles over 90 degrees, for the error would be too remarkable. Furthermore, the method given by case b is limited to a very narrow range under 90 degrees, and is very cumbersome in operation.

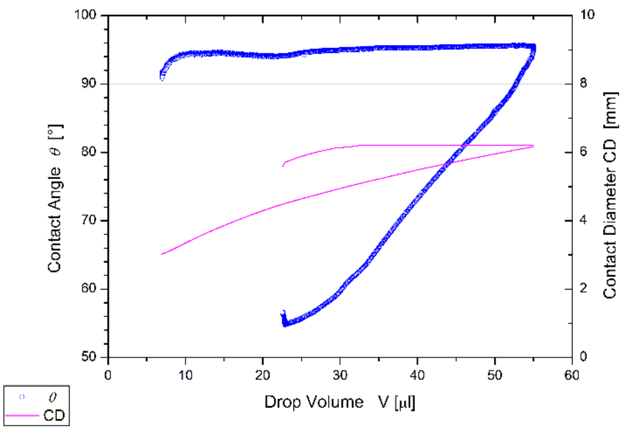
As mentioned above, MOB is based on the Laplace-Young model, which takes the gravitational effect and interfacial tension exactly into account. Therefore, there is no limitation for the method of MOB, concerning the kind of test liquids, the volume of drops and the value of contact angles.

Q: Which kinds of systems can be studied?

A: Systems consisting of solid/liquid/gas or solid/liquid/liquid. For a solid/liquid/gas system, conventional contact angle of a liquid or a gas bubble on a solid surface is measured; For a solid/liquid/liquid system, contact angle of a liquid on a solid surface, both of them embedded in another liquid, is studied.

Q: Can it be used to study dynamic contact angle?

A: Yes, dynamic contact angle (CA) like advancing/receding CA based on growing/reducing drop volume method can be also carried out with the Top-View method.



The figure on the right indicate such a measurement: the blue curve is the dependence of CA on dispensing volume (i.e. drop volume), and the pink curve reveals the corresponding change of contact diameter measured with drop volume. The advancing and receding CA can be determined clearly in association with the variation of CD.

Q: What are the most distinct differences compared to the Side-View method?

A: Knowledge of Volume of drop deposited and Magnification (MAG) factor of the optical system.

For the Side-View method, neither drop volume nor MAG-factor is decisive for the determination of contact angle. MAG-factor is only interesting if absolute values for geometrical variables other than contact angles, e.g.

drop width/height/contact diameter, need to be determined. The value of contact angle can be, in most cases, considered as drop volume – independent.

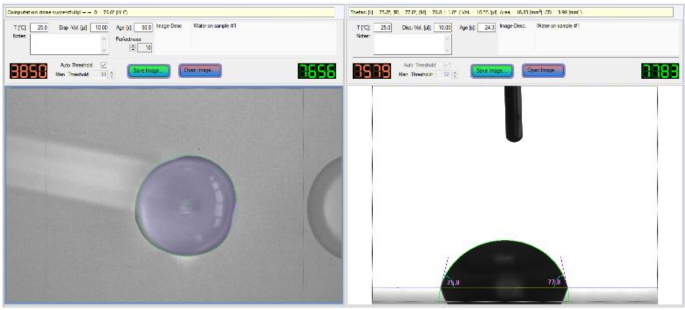
However, for the Top-View method, the volume of drop, as discussed above, is one of the most critical parameters involved in the computation. Another important parameter is the drop diameter, either measured as CD or MD, which must be measured as accurately as possible, therefor is the knowledge of MAG factor necessary. For most of MOB systems, they are equipped with a fixed-focus lens and its MAG factor has been determined in the factory before delivery. Only the value of drop volume must be read and entered correctly for the computation, if a manual dispensing unit is used.

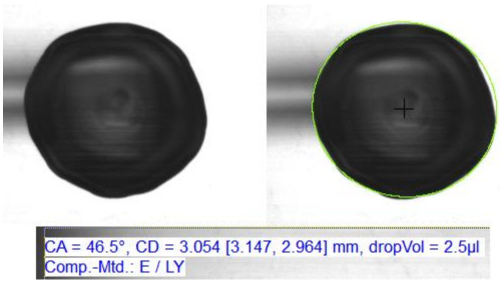
Another notable difference between these two methods is the tendential dependence of measurement accuracy on the value range of contact angles. With the Side-View method, measurement of flat sessile drops with contact angles below about 15° becomes a growing challenge as the contact angle decreases further, since it becomes increasingly difficult to acquire accurate coordinate points along the edge (profile) of a side-viewed drop image. On the other hand, the Top-View method sights the contact area (or boundary) of a drop on a substrate surface from top, and is not affected at al by its shrinking height as the contact angle decreases. So, the Top-View method outplays its Side-View counterparty in feasibility, accuracy and reliability as the contact angle value diminishes.

However, in the range of contact angle > 90 degrees, the Top-View method can only view MD (drop's maximum diameter) instead of CD (drop's contact diameter). The dependence of MD on CA (contact angle) is much weaker than CD on CA, so that the sensitivity of the method decreases as the CA increases, which affects the resolution of the computed CA-results. Consequently, the accuracy of Top-View method drops as the CA grows. In the range of (90 - ca. 160), the Side-View method is thus superior to its counterparty Top-View, and from a value of ca. 165 degrees, only the Side-View method should/can be applied.

Q: Can the method be checked by a conventional method?

A: Definitely, namely by measuring the same drop at the same time from top (Top-View) and side (Side-View), as shown in the picture on the right: 76.6° from Top-View and 76.8° from Side-View. The agreement is in general excellent and that's not magic, for they are based on the same mathematical model.

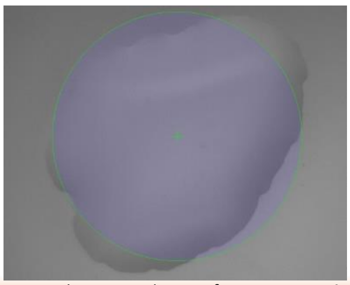




Q: Can the method be used for drops that reveal irregular boundaries?

A: Definitely, and it can be even advantageous to work with the Top-View method in such cases.

An ideal liquid drop on a perfect solid surface should have a circular 3-phase contact boundary, independent of contact angle value. However, in the praxis, due to (chemically/geometrically/physically conditioned) inhomogeneity of real substrate surface, a drop adopts most likely an irregular boundary shape, especially when the contact angle is low. An irregular 3-phase contact boundary means that the value of contact angle along the boundary is not a constant, it is actually location-dependent. Therefore, if the conventional Side-View method is used, we will get two different contact angle values from the left and right side. Moreover, if we change the azimuthal angle of the Side-View



Water drop on a glass surface: CA = 32.5°

observation, we will find that we may get another two different values for the left and right side of the same drop. That is, the values we get with the Side-View method are actually dependent of the azimuthal angle of view. If the latter is kept unchanged during the measurement, the values we will get are by pure chance and may NOT be representative for the whole boundary.

In this case it is advantageous to analyze the drop from above: by determining the average or effective diameter of a drop's contact area, contact angle can be then calculated and represents an averaged or effective value over irregularities in the three-phase contact line, which is more significant for characterizing wetting property than just a pair values from an arbitrary azimuthal angle with the Side-View method.

For low contact angles, where the contact areas often have an irregular form than a circle, the value of real contact (or spreading) area per unit volume liquid can provide a more meaningful index for characterizing wettability and spreading behavior than a pair values of contact angle at two arbitrary locations along the three-phase contact line.

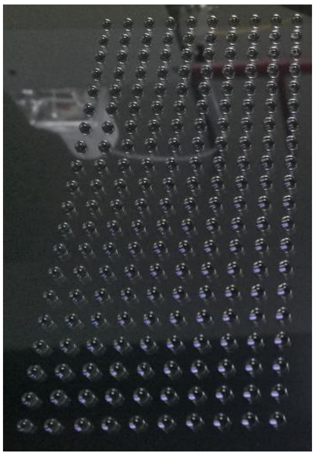
In addition to it, *a drop image from top-view holds an immediate picture in front of your eyes about the homogeneity* of a surface at this location.

Q: How large drops are used for measurement?

A: It depends on the range of contact angle and on the available sample surface area to be measured.

Typically, a volume of 1-10µl is used for measurement: the larger the contact angle, the bigger the drop size should be. For contact angles under about 60 degrees, 1-3µl is a good choice, whereas for contact angles over 90 degrees 5-10µl is preferred. For contact angles larger than 130 degrees, 10-20µl can be used.

Q: How closely the drops can be placed for high-density surface mapping?



A: As closely as possible, so long they don't touch each other (s. picture on the right).

Q: Can it be used for curved surface?

A: Yes, it can be used for concave as well as for convex surfaces. The correction of contact angle for the curvature is done by the software automatically.

Q: Why do I get totally wrong or invalid values?

A: If you get completely wrong CA-values, or it is impossible to perform computation, please consider the following points at first:

a) Does the fitted drop contour coincide with the contact area of the drop?
For drops with reasonably regular boundaries, the computed contour should match the drop image nearly perfect. For drops with irregular boundary contours, the real contact area of the drop should be in accordance with the area enclosed by the computed contour.
If this is not the case, check the image processing parameters and image ROI (ref. user manual for details).

b) Is the Magnification (MAG) factor (image scale) correct?
MAG factor is a deciding value for the computation and must be determined and set correctly. For most of MOB systems, they are equipped with a fixed-focus lens and their MAG factors have been determined in the factory before delivery and stored in the accompanying files. You may recall this pre-determined value by clicking on the "Default" button on the "Computation Parameters"-tab in the Settings-Dialog.

c) Have you entered the correct value for the Drop Volume?
Drop Volume is another decisive value for the computation and must be entered correctly.

If an automatic dispensing unit is used for forming a drop, its dispensed volume value will be automatically taken over for the computation. However, the volume value will be only correct when also the correct size (in ml) and the correct Piston Stroke Length (in mm) for the installed syringe have been entered into the Settings-tab of “Syringe Pumps”, which applies also for a manual dispensing unit.
In addition: For a manual dispensing unit, don’t forget to reset the value before starting dispensing, and the value displayed in mm (piston movement) needs to be entered into the software, which will convert the distance number into dispensing volume by using the parameters (size and piston stroke length of the used syringe) set before.

d) If the device has been paused for a long time, or the syringe has been newly refilled (attention: removement of any air bubbles), the first drop should be discarded, for its volume can be wrong because of evaporation with the capillary and/or tubing.
e) Check further if you have entered the correct property values like density and surface tension for the liquid used.

Q: How about its precision and reliability?

A: As mentioned above, the precision of Top-View method is dependent of contact angle range.

Resolution/Precision: ca. 0.1-0.2° （$0° < \theta < 90°$); ca. 0.3-1° （$90° < \theta < 160°$)

Q: What kinds of configurations are available?

A: MOB is very versatile, flexible and can be adapted for variable applications individually.

a) As a hand-held mobile device: **MOB - M**;
b) Suspended onto a bench frame to build a benchtop contact angle meter, which is particularly useful for small-sized samples: **MOB - D**;
The measurement can be fully automated.
c) Combined with the conventional Side-View method to build up a Dual-View contact angle measuring device, which allows for studying of contact angle and dynamic wetting processes simultaneously from side and from top: **MOB - C**;
d) Mounted onto a robotic positioning system with integrated automatic dispensing unit(s) for performing full-area surface-mapping measurement of contact angle/surface free energy (SFE), fully automatically by floating the measuring module over the sample surface: **MOB - L**.
e) Integrated into an in-process control system: as a part of quality assurance or monitoring system: **MOB – P**

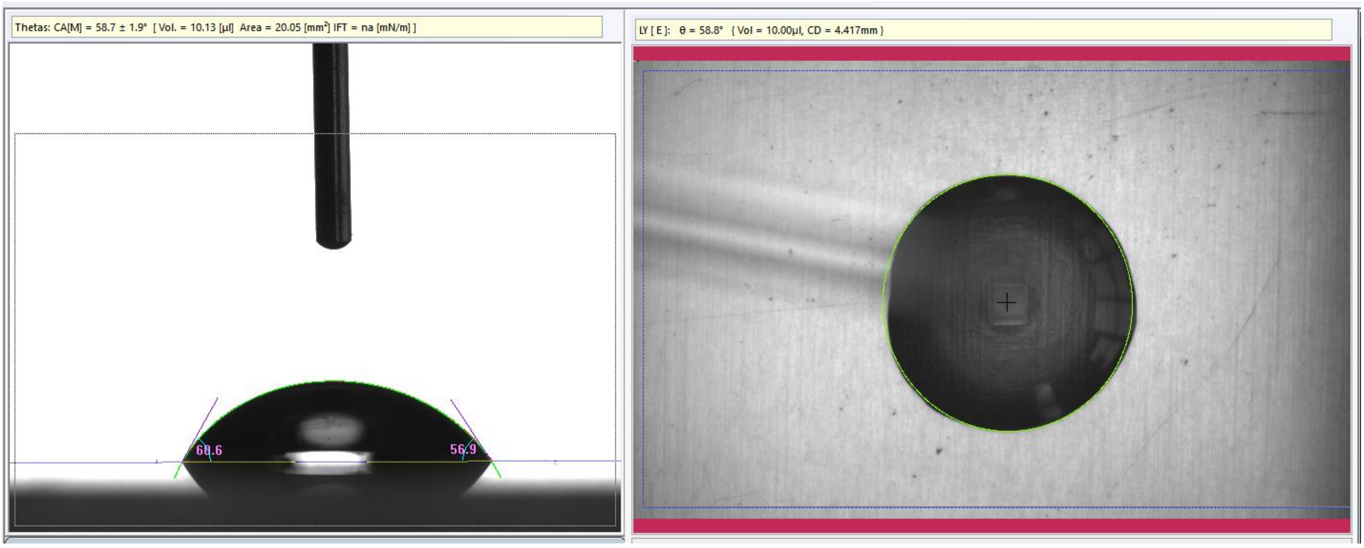
** All modules can be equipped with more than one dispensing unit so that SFE value can be computed just after one test.*

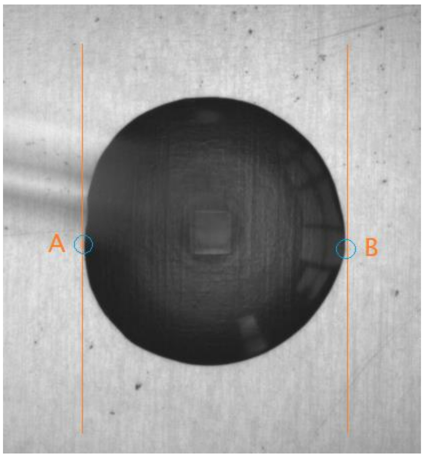
Q: For which application fields is a combination with a MOB-C meaningful?

A: A standard LSA-device, when combined with a MOB-C extension module, is an extremely versatile measuring system, which not only unifies all the advantages of both Side-View and Top-View measuring methods, but also provides a unique option to study a drop at the same time from different perspectives. Such a system can be employed in a number of different variations.

- As a conventional contact angle meter based on Side-View method;
- As a novel contact angle meter based on Top-View method;
- As a unique measurement instrument, which analyzes a (sessile) drop from the Side-View and from the Top-View simultaneously.

This versatility empowers it to handle nearly every situation in the praxis. The strengths and weaknesses of measurement methods based on Side-View and Top-View have been referred above. We want to give here an example of employing both methods simultaneously.





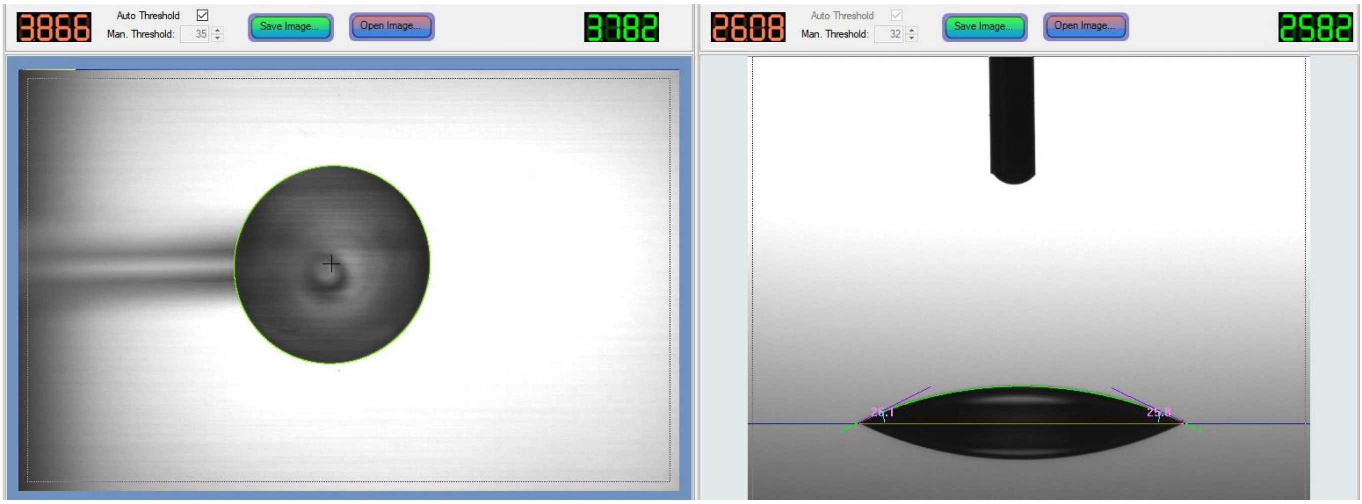
The picture above shows two images from a same water drop (on a glass surface) at the same time from side and from top, respectively. The contact angle results obtained from the Side-View image are 60.6° (left) and 56.9° (right), a difference of about 4° ! However, with this image alone, it is not easy to understand (the cause of) this difference. From the image obtained from the Top-View it can nevertheless be clearly seen that the drop has a three-phase contact perimeter which deviates remarkably from a circle form (see picture on the left). The left (60.6°) and right (56.9°) contact angles obtained from the Side-View image correspond to point A and B, respectively. And it can be also obviously realized why the contact angle has a higher value at point A than at point B: the run up at A is steeper but shorter than at B. Furthermore, it is apparently to see that the value of contact angle varies alone the perimeter boundary.

By observing and analyzing a drop from side and top simultaneously, more detailed information can be obtained regarding the dynamic behavior of a wetting/spreading/ imbibition process.

Q: Which other methods are available for contact angle measurement from Lauda Scientific?

A: In addition to the Top-View method, there are following methods available for measuring contact angle/wettability:

- Side-View method based on sessile drop (SD);
- Liquid Bridge/Meniscus method for fibers, rods and plates (LBM);
- Drop-on-Filament method for single fibers (DoF);
- Washburn method for powder/porous samples (POM);
- Force balance method (modified Wilhelmy Plate).



when a surface is homogeneous, the 3-phase contact perimeter boundary is close to a circular form even for low contact angles.