

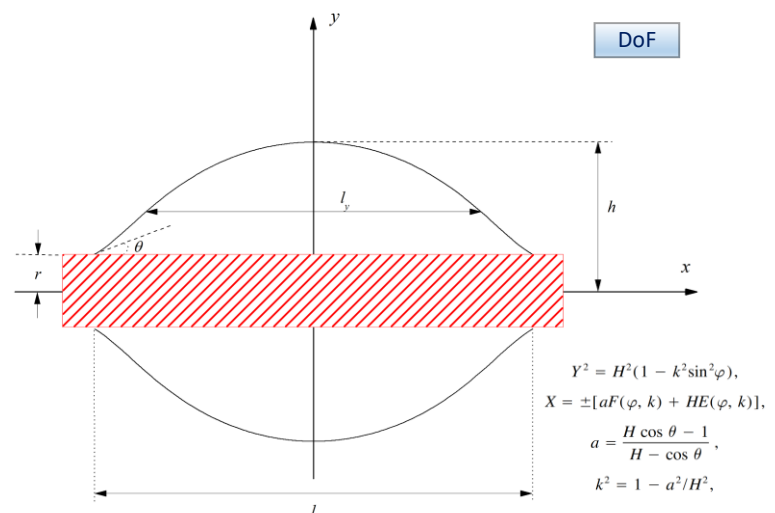
Determination of wettability of cylinder-shaped samples (monofilaments) is of general scientific and technological interest. The wetting behavior of fibers in liquid matrices (e.g. dyeing mixtures or polymer melts) plays an important role in the textile industry and in the fabrication of advanced fiber-reinforced composite materials. Those samples may have dimension down to ca. 5µm (OD throughout the text) as in the case of microfibers, or up to several millimeters like wires and rods/cannulas. However, direct measurement of contact angles is here usually much more difficult than on planar surfaces. Due to the cylindrical shape and small diameters, drop surface changes steeply or even reveals inflexion point as it approaches the three-phase contact points (note: the profile of a sessile drop on a planar surface never shows an inflexion point). Common computation methods used for contact angle measurement based on sessile drops, incl. the Laplace-Young method, are no more applicable for this kind of samples.

There are very few measuring methods available therefor. One common method is based on the Wilhelmy plate principle and computes the contact angle indirectly from the force measured. For microfibers, a number of fibers, instead of a single one, must be employed due to the limited resolution of load sensor, and it is always a challenge to hold and keep these fibers orthogonal to the liquid surface during the measurement. Moreover, the resulted values lack often reproducibility.

Another method for measuring the contact angle is, similar to the conventional sessile drop method used for planar surfaces, based on the direct microscopic observation of single droplets on a single filament (i.e. monofilament), however, by employing quite different computation algorithms to determine contact angle from the drop profile.

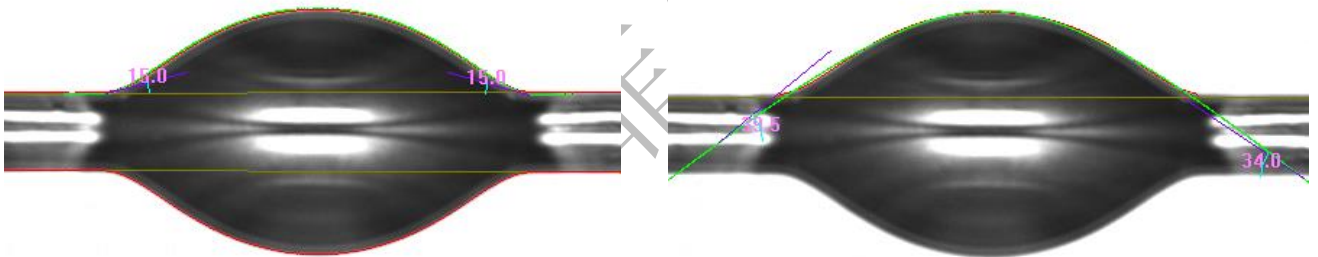
The mathematical model used for describing and computing the contact angle for a droplet on a filament (DoF) system, is based on the same general Laplace-Young equation (see formulas on the right) as used for a conventional sessile drop.

Nevertheless, the boundary conditions employed are quite different, which result to completely different drop contours (s. picture). If the length  $l$  and height  $h$  of the droplet can be measured precisely, then the contact angle can be computed from the system equation, which is called the *maximum drop length-height method* (MLH). In the praxis, however, it is quite difficult to determine precisely the maximum drop length  $l$ , in particular for microfibers with diameters under about 15µm, because it is hardly feasible to recognize unambiguously the three phase contact points on the fiber surface, neither visually nor mathematically. The value of contact angle is, however, quite sensitive even to small errors made in the value of drop length  $l$ .



To overcome this difficulty, SurfaceMeter software implements several computation methods to compute contact angles from drop profiles of DoF-systems. In addition to the maximum drop length-height method, it provides the generalized drop length-height method (GLH) as well. The GLH method determines the value of contact angle not alone from the  $(l, h)$ -value pair, but also from a lot of other profile coordinate pairs. Therefore, the whole droplet profile is employed for the computation, not only just two as in the case of MLH, which makes the method much more robust and accurate.

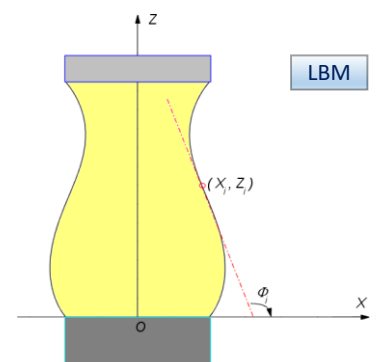
The pictures on the top right show the results of two different computation methods used for a droplet on a glass fiber with a diameter of about  $40\mu\text{m}$ : by applying the GLH and TrueDrop method, respectively. TrueDrop method is a robust method for computing contact angles for conventional sessile drops, it delivers in general very good results for nearly all kind of drop forms, both for symmetrical or asymmetrical. However, as can be seen from the pictures, it failed to fit the drop profile of a DoF system and the resulted values deviate severely from which obtained by using the GLH method. In contrast to the TrueDrop method, the fitted theoretical drop profile (green line) of GLH method coincides with the drop image almost perfectly, down to the region of three-phase contact points.



The pictures above show another results of computation for a water droplet on a  $10\mu\text{m}$  fiber. The inflexion point can be distinctly recognized here, and lies between the top (apex) and the three-phase contact points. By using the GLH method, we get a contact angle of 15 degrees, whereas 39.5 and 34.0 degrees are obtained if the conic method is applied. The value of contact angle is therefore decisively related to the computation method used. Common methods developed for conventional sessile drops are NOT suitable for DoF-systems and will deliver quite often irrelevant values.

Droplets on microfibers with diameters  $< 15\mu\text{m}$  have volumes usually under 100pl (pl = picoliter). Therefore, special Picoliter Dispensing Unit is required to perform such kind of measurements. In addition, high magnification optical system and special sample table for microfibers are necessary.

In addition to DoF method, LAUDA Scientific provides another optical method for study wetting behavior of monofilaments, for diameters from several micrometers to several millimeters. This is the so-called Liquid-Bridge Meniscus (LBM) method. The following three pictures display a measurement with a ca. 0.2mm monofilament in water. Besides the static contact angle, by moving the

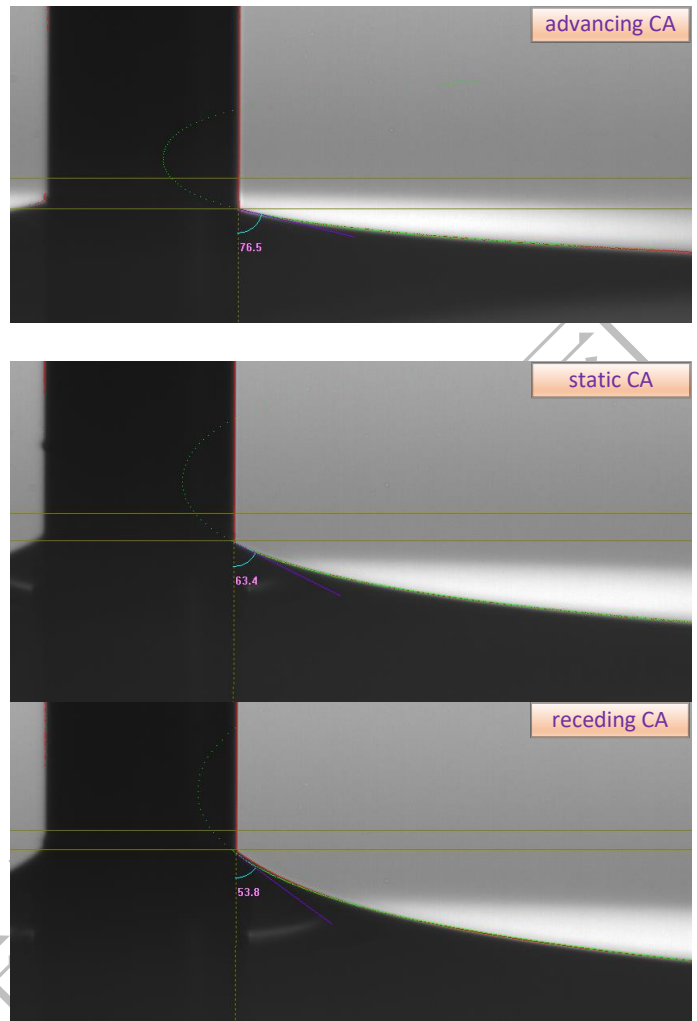


sample slowly into or out of the liquid phase, dynamic (advancing and receding, respectively) contact angles can be determined.

In contrast to DoF, even contact angle larger than 90 degrees can be measured with LBM. The gravitational effect has been taken also into account in LBM, so it can be applied to filaments of arbitrary dimensions. Moreover, there is enough liquid phase available, so evaporation of liquid is not a problem at all for LBM, but a serious for DoF.

The picture on the bottom indicates a metal cannula with an outer diameter of ca. 2.4mm in cooking oil. By fitting the liquid meniscus into the governing Laplace-Young system equation, not only the contact angle (7.6 degree) can be determined precisely, but also the surface tension (33.51 mN/m) of the environmental cooking oil.

With DoF and LBM, we provide our customer the best measuring methods currently available in the market for studying wettability of individual monofilaments, from micrometer fine microfibers to millimeter thick rods. With our module for powder and porous samples (POM), microfibers can be also studied as fiber bunch.



#### References:

1. Yamaki, J., and Katayama, Y., *J. Appl. Polym. Sci.* **19**, 2897 (1975).
2. Carroll, B. J., *J. Colloid Interface Sci.* **57**, 488 (1976).
3. Wagner, H. D., *J. Appl. Phys.* **67**, 1352 (1990).
4. Song, B., Bismarck, A., Tahhan, R., Springer, J., *J. Colloid Interface Sci.* **197**, 68 (1998).
5. Zhang, L., Wang, J., Fuentes, C.A., Zhang, D., Van Vuure, A.W., Seo, J.W., Seveno, D., *Carbon*, 122, 128 (2017)

