

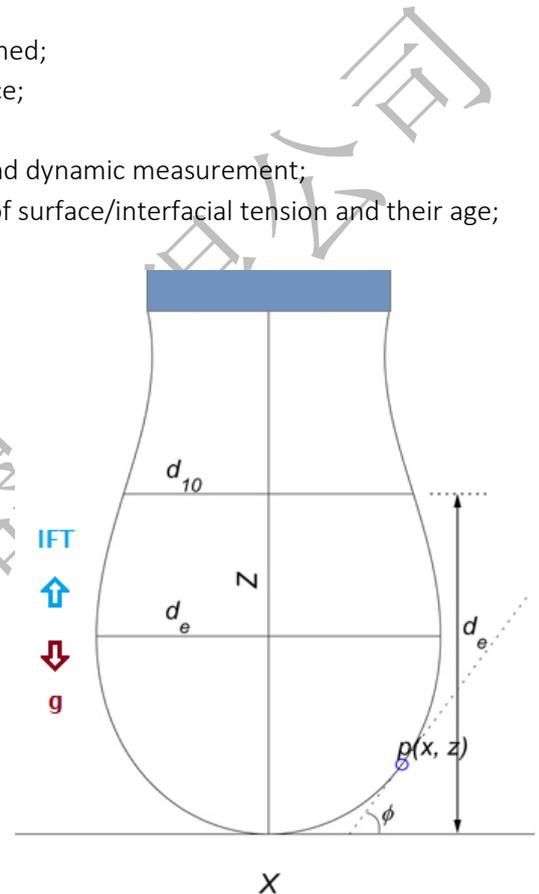
Q: What are the main characters of PDA?

A: It is

- an absolute method, only axis-symmetry of a drop is preconditioned;
- straightforward, easy and time-saving, as well as low-maintenance;
- for measurement of both surface and interfacial tension;
- one of the most accurate and reliable methods, both for static and dynamic measurement;
- with the widest measuring range, with regard to both the value of surface/interfacial tension and their age;
- minimum sample amount requirement;
- one of the most automated methods;
- the best method for viscous samples;
- the best method for studying interfacial tension of liquid/liquid-systems;
- the best suitable method for measurement under extreme conditions;
- ...

Q: What is the working principle of PDA?

A: PDA is based on the force balance between the surface/interfacial tension (SFE/IFT) and the gravitational force (g) at hydrostatic equilibrium, which is described by the Laplace-Young equation. From the density difference between the two phases across the drop interface, the gravitational force can be deduced. Therefore, the value of SFT/IFT can be determined by solving the system equation, which is unfortunately only possible under certain pre-conditions. One of them is the rotational invariance (axis-symmetry) of a drop, and, under this condition, the Laplace-Young equation can be reduced to the equation of Bashforth-Adams, which builds the base of PDA.



Q: Which kinds of variations exist in the market?

A: There are mainly two variations that are used to determine SFT/IFT from the profile of a pendant drop: a) the *selected-plane* method and b) *whole profile fitting* algorithm. In the former case computation is made based on only 5 coordinates from a drop profile; In the latter case, all coordinates (typically around one thousand) are used. Methods based on the *selected-plane* algorithm are strongly restrictive, and can be applied to only a limited kind of drops; Furthermore, the results obtained are usually associated with large uncertainties, typically above 2-3%.

PDA uses the *whole profile fitting algorithm*, which is applicable to any kind of drop forms and takes a number of unknown factors like camera tilting angle, drop apex coordinates, etc., into account at the same time, thus leads to much more reliable and accurate results, typically with a precision of 0.1%.

Q: Which kinds of systems can be studied?

A: Systems consisting of liquid/gas (surface tension SFT) or liquid/liquid (interfacial tension IFT). For SFT-measurements, there is no limitation on the color or transparency of the to be studied liquid phase; For IFT-measurement, one of the liquid phases must be at least partially transparency and the density difference between the two liquid phases shouldn't fall below 0.01g/ml.

Q: Can it be used to study dynamic surface/interfacial tension?

A: Absolutely, it is one of the best methods therefor. Using PDA, dependence of SFT/IFT over the time can be studied from a surface/interface age of about 25-50ms dependent of the system properties, up to hours or even days. PDA covers the largest time range among all available methods for studying the dynamic behavior of SFT/IFT. Though, as far as the shortest measurable surface age is considered, it lies a little bit behind the maximum bubble pressure method (MBPM), it does show its strength in reliability and repeatability as well as its robust against environmental noise like vibration.

Another unique feature of PDA is that the whole dependence curve of SFT/IFT vs. time (IFT(t)-Curve), from the very beginning to the end of measurement, can be obtained from one and the same (drop) surface/interface, whereas with MBPM, every point on a IFT(t)-Curve must be determined with a new created surface/interface. Therefore, much less time is required to obtain an IFT(t)-Curve with PDA, and the resulted curve is much smoother (such a curve may contain up to several thousand points) and more consistent with much fewer outlying points.

Q: Can viscous samples be measured?

A: High viscosity can be a serious problem for all IFT-methods. However, PDA is the method, which allows even samples of relatively high viscosity to be measured. Moreover, it is the best and last method to be considered for high viscous samples: if a sample can't be measured by PDA due to its high viscosity, it is hardly possible to find any other better suitable method.

Samples with a viscosity up to about several teens of **Pa·s** (1Pa·s = 1000cps) may be measured by PDA. For high viscous samples if measurement can't be performed at room temperature, it is always worth considering to carry out measurement at elevated temperature, because viscosity of liquids decreases usually quickly with increasing temperature. Based on the temperature dependence of SFT/IFT, values around room temperatures can be then derived reliably via extrapolation.

Q: How much sample is required for a measurement?

A: Using PDA, very small sample quantity is required. For an SFT measurement, as low as several teens of microliters (µl) may be enough. For an IFT measurement, about several milliliters (ml) of environmental phase and several hundred microliters (µl) of drop phase are sufficient.

Q: Is the value of SFT/IFT dependent of drop size?

A: Yes and no.

Strictly speaking, the value of SFT/IFT obtained from a drop image can be dependent of drop size. The extent of this dependence is however again strongly related to the drop size and to system properties: this dependency decreases rapidly to vanishing small as the size grows over a certain limit, which is easy to be reached in the praxis. Under this limit, the obtained value may deviate from its correct result to an extent of up to several percentages in the worst cases.

The SurfaceMeter software of LAUDA Scientific builds a "Drop Quality Index" to give user an intuitive feedback of how reliable the resulted value is, and it can even create fully-automatically drops of suitable size for SFT/IFT

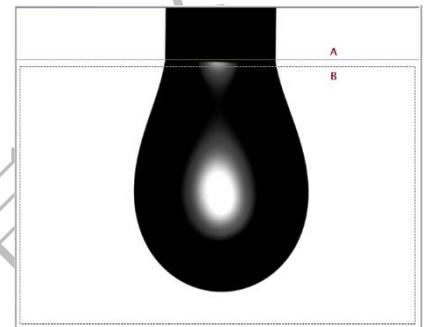
measurement and match its size automatically in dependence of the variation of SFT/IFT values (dynamic SFT/IFT !) during the whole measurement procedure in such a way that the drop is kept large enough for producing reliable result values but small enough for preventing it from dripping off.

This dependence is caused by the experimental errors or limited accuracy in determining the coordinates of drop contours and, consequentially, mathematically conditioned. Just imagine: the value SFT is calculated by the oversimplified formula $SFT = X / Y$, and X and Y are two values determined experimentally with errors δX and δY , respectively, whose magnitudes remain nearly constant, independent of the absolute magnitude of $|X|$ and $|Y|$. So, it is obvious that the relative error in the resulted SFT value will decrease with increasing of $|X|$ - and $|Y|$ -magnitude.

Q: How to get quickly started?

A: As an example of a sample SFT-measurement of a liquid in air:

- Choose a (disposable or glass) syringe and a needle of proper size, fill the sample liquid into the syringe and remove air bubble if any;
- Load the filled syringe (with needle installed) onto the device;
- Adjust the position of needle so that it appears in the image view, focus the needle;
- Form a test drop by slowly dispensing, the drop should be large enough so that its form deviates remarkably from a sphere; Adjust the zoom so that the drop fills 1/2-2/3 height of image view;
- Readjust the needle position and re-focus the needle/drop, about a height of 1/2D (D = needle's width) of the needle should be appeared at the top of image and the needle should be positioned in the horizontal middle of the view (s. picture top-right);
- Adjust the image illumination (or exposure time of camera) so that the background of the image just turns from completely white (grey value = 255) to a little bit grey (e.g. grey value = 200 - 240);
- Freeze the image and determine the MAG-factor (magnification) value (ref. to user manual for details);
- Set the interface type to "Pendant Drop (V)" (see picture on the right);
- Open the "Drop Properties..." - dialog and enter the density values;
- Place the guide lines and ROI as shown in the picture above: line "A" defines the 3-phase contact line of liquid/air/needle and is usually the bottom line of nozzle; line "B" must be set under "A" and limit the highest position, to which the drop profile will be taken for computation;
- click on the "Drop Profile Detection" - icon  on the main toolbar and a red line should appear over the drop image, which indicates the collection of coordinate points of the drop contour;
- click on the "Computation" - icon  on the main toolbar and a green line should appear over the red line. The green line is the fitted theoretical drop profile: the closer the green line coincides with the red line, the better the computation;
- Switch to live image, create a new drop, and repeat the measurement (steps k and l). Measurement can be done with live or frozen image, clicking on the "Drop Profile Detection" – icon may be skipped.



Q: How to achieve the best performance?

A: To reduce the error of measurement and to achieve the results with best possible accuracy, following points need to be considered:

- a) Needle Size: Choose a needle/capillary of suitable size: usually thin needles with a diameter under 1mm should be avoided for SFT/IFT-measurement, except for extremely low IFT-measurement. For SFT above 20mN/N, needles with a diameter of 1.5-4mm are preferred (ref. to user manual for details).
- b) Illumination: For SFT/IFT determination, it is preferred to apply a low image illumination and contrast settings, to reduce possible blooming or overexposure effects on the drop contour, which will affect the results.
- c) MAG: Image Magnification (MAG) factor must be determined with great care. If a precision needle is used for forming drops and its outer diameter has been determined exactly (with a precision of 0.001mm or better), it is superior to use the same needle as a reference object for calculating the MAG-factor as well. Reference objects used for MAG-determination should have a reasonable dimension, preferentially in a range of 1.5 - 4mm. Needles under 1mm are not appropriate for this purpose. After MAG-factor has been determined, you shouldn't change a) image illumination/contrast and b) zoom adjustment any more. As long as the focusing position remains the same, the MAG-value doesn't change. The Focus-Assistant tool  can be thereby very useful.
- d) Drop Size: Form a large enough drop: as mentioned above, for small drop sizes, its effect on SFT/IFT-values may not be ignored. By performing computation, the software displays not only the results like values of SFT/IFT, drop volume and surface area, but also the value of Drop Quality Index, which is displayed within parentheses directly after the value of SFT/IFT (s. below). So long this index value is above 60, the result value is confident.

IFT = 73.75 [69] (Vol. = 27.77 [μl] Area = 38.33 [mm²])

- e) Vibration: It is always preferable to place your LSA-device on a workbench, which stands separated/decoupled from your work table, on which PC/monitor/keyboard/mouse and, most likely, your arms are to be situated/resided. A pendant liquid drop in air can suffer much from any direct vibrations, which are unavoidable if you are for example striking, while the drop is being analyzed, on the keyboard that resides on the same table as the device. This disturbance can be effectively reduced with the help of a small decoupling between these two places.
Such kind of disturbance becomes indistinctive when bubbles in liquid, liquid/liquid interfaces, and more viscous liquids than water are studied.

Q: Why do I get totally wrong values?

A: If you get completely wrong SFT-values, it is usually quite easy to fix it, follow the following points:

- a) Is the **Magnification** (MAG) Factor (image scale) correct?
The value of SFT/IFT is inversely proportional to the quadrate of MAG, therefore a small deviation in this value causes already a big impact on the final result values. Check the value and, in case of doubt, determine it again with great care.
- b) Have you entered the correct value for the **density difference**?
The value of SFT/IFT is directly proportional to the density difference of two phases. For most aqueous liquids in the air, this value should close to 1 (or 0.997) g/ml. For measurement of interfacial tension between two liquid phases, this value is usually much lower than 1. Check its correctness again.
- c) If the value obtained is much lower than expected (for example you get a value under 65mN/m for pure water), and you've ruled out the possible factors listed above, contamination can be another matter worth of consideration. Contamination leads in most cases to the reduction of SFT value due to the nature that surface-active molecules prefer to be gathered in the surface layer, which causes a drop of SFT value. All parts like syringe (for filling sample liquid), capillary or needle (for forming drops) and connections/adapters, which are in direct contact with the sample liquid that is being measured, must be cleaned thoroughly.

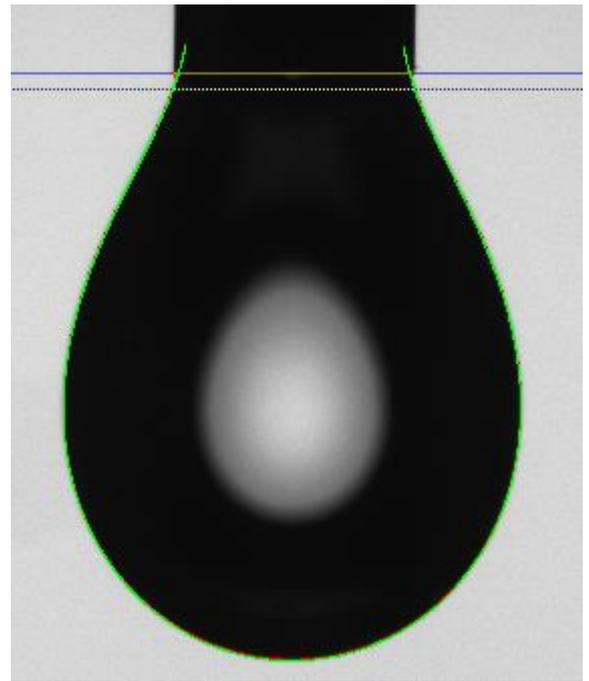
On the other hand, if the value obtained seems to be unexpectedly high, the primary reason for such kind of discrepancies can usually not be found in the contamination.

- d) Does the fitted theoretical drop profile (the green line) coincide with the experimental drop contour (the red line) well? Usually for low viscos liquids, this match should be nearly perfect (s. Figure).

If it shouldn't be the case: Freeze the image if it is live, click



on the "Drop Profile Detection" Icon on the main toolbar, and check if the drop contour (red line) can be extracted successfully, and, in most cases, completely. If it is not the case, check the image illumination, focusing and image processing parameters for edge detection. If you are not able to fix the problem, save the image to a file and attach it when you ask for technical support.



Q: Is PDA suitable for measurement under extreme conditions?

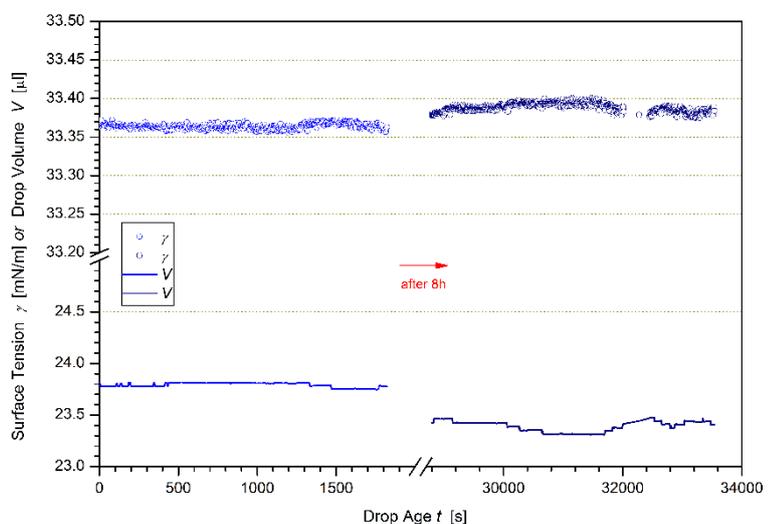
A: Definitely, PDA is the method of choice for working under extremely temperature and pressure conditions, because PDA is an optical contactless measuring method, there is no mechanical or material coupling between its sensor and sample that is studied, the measuring technique can thus be placed completely outside of the measuring environment, where extreme conditions may prevail. Measurements under conditions of up to several thousand degrees and up to several hundred bars have been carried out with the help of PDA.

Q: How about its accuracy and reliability?

A: Amongst all methods, PDA is one of the most accurate measuring methods and is unique concerning both its sensitivity (precision) and stability.

PDA is peculiar in that its high **relative** precision remains nearly constantly high at around 0.005%, independent of the absolute value of SFT/IFT that is being measured. That means, for water samples with a SFT value of about 72.5mN/m, the absolute precision will be around $(0.005\% \cdot 72.5 =) 0.004\text{mN/m}$, whereas for a liquid/liquid-system with an IFT value of around 10mN/m, the absolute precision will be as high as ca. 0.0005mN/m. Therefore, PDA is most suitable for determining SFT/IFT in any range, which is of exceptional interest for extremely low IFT measurement.

The figure on the right side shows the results of a long-time measurement of a rapeseed oil drop in air under room temperature. Under the assumption of the relative stability of the sample oil within a time period of 30 minutes, all value points are located within about $\pm 0.05\%$ of the median value.



Q: What kinds of properties can be additionally studied?

A: In addition to SFT/IFT value, PDA determines all geometrical properties of a drop incl. volume, surface area, height/width, etc., and with the help of suitable hardware, it can modulate the change of these parameters with time and determine the resultant response of SFT/IFT on the changes, simultaneously. Therefore, PDA is a perfect alternative to a Langmuir Film Balance (Langmuir Through), and a powerful tool for studying surface/interfacial rheology and relaxation behavior of surfactants incl. diffusion coefficients.

Based on the measurement of dependence of SFT/IFT on the concentration of surfactants and/or additives, PDA can be used to determine the CMC (critical micelle concentration) and to optimize or screen detergent compositions.

Moreover, PDA can be run fully-automatically, and is thus suitable for in-process monitoring of surface activity.

Q: Which other SFT/IFT-methods are available from Lauda Scientific?

A: In addition to PDA, there are following methods available for measuring SFT/IFT:

- Drop Volume method (DVT);
- Liquid Bridge/Meniscus method (LBM);
- Sessile drop analysis method (SDA);
- Maximum bubble pressure method (MBPM);
- Force balance method (Du Nouy, Wilhelmy Plate).

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