Advances in drop and bubble profile analysis tensiometry

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Abstract

Profile analysis tensiometry (PAT) with drops and bubbles is a successful methodology to characterize liquid−fluid interfaces. Questions about the most suitable size of drops and bubbles have been solved now on the basis of dimensionless numbers. The consideration of the standard deviation between measured and calculated liquid profiles as a sensitive measure for the applicability of PAT provides a tool for its correct use. For solutions of highly surface-active compounds, bulk depletion effects can cause systematic errors in the analysis of adsorption kinetics, equations of state, and the visco-elastic interfacial behavior of liquid adsorption layers. Great progress has been made in measurements of interfacial dilational rheology with large amplitude perturbations providing additional information about structure and dynamics of complex adsorption layers. Also, first attempts are successfully made to use artificial intelligence (AI) to enhance the efficiency of PAT applications. Thus, PAT has established a solid position in surface science.

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Introduction

Drop and bubble profile analysis tensiometry (PAT) is an old and at the same time novel methodology. Historically, the determination of the profile of a sessile and pendent drop or buoyant bubble was a rather time-consuming method due to the need of printing the photo taken from the drop or bubble and its analysis based on more or less accurate determination of geometric measures and subsequent complicated manual calculations with a pencil and a sheet of paper [1,2]. Hence, the surface tension γ of a liquid was available, but it had a rather low accuracy. Meanwhile, due to the availability of electronic cameras and powerful computers, this method evolved into the most frequently applied technique for systematic studies of liquid interfaces. The key progress was achieved by Neumann and his team in the eighties of the last century [3], who for the first time set up an instrument based on an electronic camera connected at that early time to a workstation [4]. The concept of this Axisymmetric Drop Shape Analysis (ADSA) represented the state of the art over many years until "normal" personal computers provided sufficient capacity to manage all required work like image acquisition, profile detection and fitting the Gauss-Laplace equation (GLE) to this profile, so that many different commercial instruments as well as single laboratory set-ups appeared. The first drop profile instrument based on a normal personal computer was the one by Benjamins et al. [5], allowing already to perform drop oscillations for measuring the dilational visco-elasticity of surface layers. Nowadays, even simple smartphones are able to manage the required job and provide data about the surface tension of liquid interfaces [6]. One of the great advantages of oscillating drops or bubbles is that one can generate almost ideal

expansions and compressions, avoiding any additional shear deformation. Such experiments are difficult to perform with other types of instruments and require special designs and protocols as proposed in Ref. [7].

A number of new findings were published during the last few years, dealing with the applicability, accuracy, and functionality of profile analysis tensiometry. One of the most frequently asked questions refers to the optimum size of drops or bubbles required for experiments with high accuracy [8,9]. Moreover, we know that the profile analysis has a limited range of applicability when used under highly dynamic conditions or when the drops/bubbles are covered, for example, by a crosslinked polymer membrane rather than an adsorbed layer. In both cases, an equilibrium balance of surface and bulk forces is required to measure physical quantities, and remarkable errors can be obtained when this balance is not in equilibrium. Mahmoudvand et al. [10] demonstrated that the standard deviation between experimental and theoretical drop/bubble profiles calculated via the GLE is a very powerful criterion to decide about the applicability of PAT. Some particular experiments have also been performed with the same surfactant solutions using the profile of a drop or bubble, respectively. Actually, no systematic differences should be expected, however, for solutions of very low surfactant bulk concentrations c, remarkably higher γ values are measured with solution drops as compared to bubbles, and the equilibrium values are established after significantly longer adsorption times, which can be explained by bulk depletion due to adsorption at the surface [11].

In addition to improvements in the methodology of PAT, quite a number of new experimental protocols have been proposed during the last few years. This includes not only experiments based on large amplitude oscillations [12] but also classical PAT experiments with constant drop/bubble size or with small amplitude oscillations, such as those proposed by Dowlati et al. [13] or Ashoorian et al. [14]. These new approaches at a broader range of experimental conditions as well as how AI can help increase the efficiency and reduce the required experimental efforts for obtaining reliable experimental data nowadays even via deep learning methods [15,16], will be discussed here. Note, there are also other interfacial methods, such as the spinning drop tensiometry, which was further developed so that reliable interfacial layer oscillations can be performed even at very low values of the interfacial tension [17].

Improvements of the experimental performance

The question is: what is the optimum drop/bubble size for PAT to get the most accurate results was discussed in Refs. [8,9]. Berry et al. proposed to use the Bond number *Bo* or Worthington number *Wo* to estimate the optimum drop size for accurate measurements. Both numbers contain the surface/interfacial tension so that the optimum drop size depends on this unknown parameter:

$$\text{Bo} = \frac{\Delta\rho g}{\gamma} R_0^2, \tag{1}$$

$$\text{Wo} = \frac{\Delta\rho g}{\gamma} \frac{V}{\pi D} \tag{2}$$

with R_0 and V being the radius of curvature and volume of the drop, respectively, and D the diameter of the needle at which the drop is formed. The larger the values of Bo and Wo, the more accurate are the data obtained from PAT. However, the optimum values of Bo or Wo can hardly be determined prior to experiments. There are also situations in which the Bond number fails to determine the optimum drop size so that Yang et al. proposed a new dimensionless number instead, the Neumann number *Ne* [9]

$$\text{Ne} = \frac{\Delta\rho g}{\gamma} R_0 H \tag{3}$$

where H is the height of the drop. A perfect way to estimate the most suitable drop size for reaching the highest accuracy, however, does not exist anyway when surface-active compounds are present in the system as then γ is a function of time and decreases during the experiment, i.e. the corresponding values of all dimensionless numbers increase so that the drop with an initially optimum size would detach.

With respect to measurements of dynamic interfacial phenomena, the speed of the technique is essential. Thus, it is a new milestone to have this novel way of solving the Laplace equation via a deep learning procedure that enhances the speed of measurements and allows to correct insufficient experimental conditions [15].

It is worth mentioning that recently even the use of a smartphone [6] was proposed and demonstrated that surface tension measurements are doable even with simple and easily accessible parts. Although this achievement is impressive, the accuracy and functionality of such self-made instruments are far below the possibilities reached by commercial products of most of the leading companies. In particular, the various preprogrammed experimental protocols available with these instruments are of enormous value, the simplest of which is, for instance, the option to keep the size of a drop or bubble constant over a certain time interval.

As one can see from the definition of the dimensionless numbers by Eqs. (1)−(3), any inaccuracies in the parameter values for g and $\Delta\rho$ lead to direct errors in the measured values for γ. Thus, the value for g should be

the one valid for the place of measurements. Most critical is the value for $\Delta\rho$. For interfaces between two liquids with almost the same density, as it is the case for water/silicon oil system, small errors in the used density values could lead to enormous errors in the final determined interfacial tension.

The application of PAT to a number of systems for obtaining reliable experimental results is sometimes rather questionable. The use of the standard deviation (STD) of fitting an experimental profile by the GLE as a criterion for acceptable conditions can be an essential help. The authors in Ref. [10] show that during fast drop size changes, the STD value can increase significantly, well above the accuracy of profile fitting by the GLE, which is typically in the range between 0.1 and 1.0 μm for modern charge-coupled device (CCD) cameras. STD also increases strongly, by one or even two orders of magnitude, when the surface of a drop is covered not by a simple surfactant adsorption layer but by a compressed nanoparticle layer subject to collapse. Figure 1 shows the dynamic interfacial tension $\gamma(t)$ (IFT) for the interface between hexane and an aqueous 0.09 mM Cetyltrimethylammonium Bromide (CTAB) solution containing 1 wt% of silica nanoparticles (with a diameter of 9 nm). The experimental protocol consists of a first constant drop volume of $V = 20$ mm^3 followed by a large decrease and a subsequent increase back to the original drop size. Due to the compression, $\gamma(t)$ decreases strongly down to about 5 mN/m.

When $\gamma(t)$ reaches values below 10 mN/m, an irregularity is observed, caused by the surface layer collapse. At the same moment, the standard deviation STD starts to increase from values around 1 μm up to 30 μm, pointing at the fact that the drop has no longer a Laplacian shape. When increasing the drop size again

back to its original value, the IFT increases again and returns back to values close to those measured before starting the compression, and also the STD decreases back to typical values of about 1 μm. We can conclude that only when the STD is sufficiently small, the PAT method is applicable and provides meaningful IFT data, while for STD values larger than about 5 μm, the resulting IFT data are only apparent values.

Similar effects were observed for aqueous dispersions of glass beads with diameters between 2 μm and 35 μm. Due to the sedimentation of the glass particles within the drop, its shape becomes deformed, and hence erroneous surface tensions are obtained from PAT [18]. The values of the measured surface tensions depend on the size and amount of added glass beads and are therefore only apparent values.

As generally accepted, the use of PAT is possible when interfaces are in a mechanical equilibrium and the adjacent bulk phases are essentially homogeneous. Otherwise, as shown above [10], the obtained results can be erroneous. In Ref. [19], PAT was applied to emulsion systems containing biosurfactants. It was observed that the surface tension decrease caused by the presence of biosurfactants disappeared step by step with increasing solution age, while parallel measurements with a Wilhelmy plate tensiometer (WPT) showed a stable, strong surface tension decrease of the biosurfactants. It turned out that the results of both methods were erroneous due to the presence of an oil component emulsified by the biosurfactants, leading in the case of PAT experiments to a "deactivation" and in the case of the WPT experiments to an overestimation of the biosurfactants' surface activity. A correct, careful handling of the studied liquid would have, however, allowed to reach correct results with both methods.

PAT is usually practiced with pendent drops or buoyant bubbles, as from experienced users we know that these modes are more accurate and easier to handle than experiments with sessile drops. Anyhow, a new data handling package has been developed by Tang and Cheng [20] that allows for reliable measurements of surface and interfacial tensions with sessile drops or bubbles. However, the handling of a number of experimental routines, such as drop oscillations, appears difficult to be realized, so some traditional geometries with pendent drops/buoyant bubbles remain superior.

As for many other technology fields, machine learning (ML) and AI approaches are opening interesting perspectives in the improvement of tensiometry techniques. For PAT, such an approach relies on the training of an artificial neuronal network using a large set of numerically-generated drop shapes via the GLE, and based on non-dimensional quantities like the above-defined dimensionless numbers *Bo*, *Wo*, or *Ne* in order to obtain shapes

Figure 1
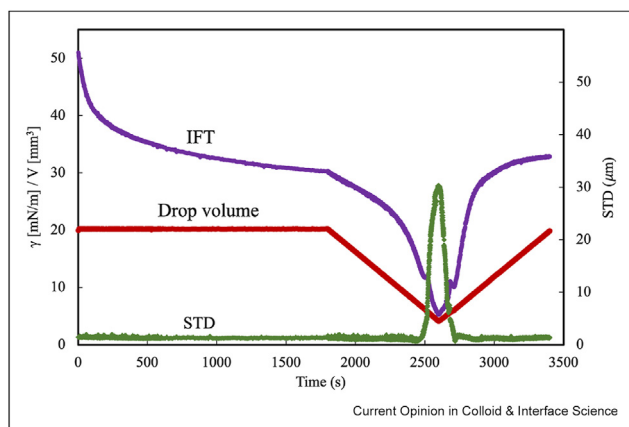
Change of interfacial tension $\gamma(t)$ and drop volume V(t) with time and the corresponding STD values for an aqueous nanofluid/hexane interface (details are given in the text); redrawn from Ref. [10].

independent from the specific experimental magnifications and constraints. This approach was adopted by Kratz [15], who, in addition, discusses the performance of the method based on the use of the *Wo* number and the possibility of applications to the analysis of time-dependent series of images, such as those needed to measure the dilational surface rheology. The paper provides in addition an interesting introduction to the principles of capillarity for pendant drops, based on stability and bifurcation concepts. Soori et al. [21] have tested the performance of their ML approach for the analysis of pendant drop images to predict the surface tension of water-alcohol mixtures of unknown composition. A further important contribution in this area was made by Hyer et al. [16], who report the outstanding performance of their implemented convolutional neural network, able to analyze pendant drop images within 1.5 ms, obtaining surface tension values with absolute errors of the order of 0.15 mN/m. They have also tested the robustness of their algorithm, showing the possibility to keep the error below 0.3 mN/m in the inferred surface tensions from images of challengingly poor quality, caused, for example, by blurring, poor focus or vertical misalignment. With different degrees of performance, superior computational speed and robustness, as compared with the classical GLE best-fit analysis, are common crucial characteristics of ML approaches developed so far. In addition, these algorithms provide the possibility to infer the surface tension also in conditions where the mechanical equilibrium for axisymmetric drops is not fully respected. Thus, drop shape analysis based on ML carries an important potential in respect to studies of dynamic interfacial phenomena or for applications in industrial plants that could benefit from real-time measurements at a large number of points distributed along the production lines. Given the speed of developments in the area of ML, the described performances will likely improve even more in a short time, and the implementation of these algorithms in commercial instruments are likely going to occur soon. Besides the specific performances, the use of AI and ML thus represents a new milestone for drop profile analysis tensiometry, possibly comparable to the revolution associated with the introduction of computer-assisted profile analysis about 50 years ago [3].

New experimental protocols for profile analysis tensiometry

The methodology of PAT, including drops as well as bubbles, is suitable for a broad variety of experiments. Zuo with his team showed, for example, that via drop oscillations various types of waveforms can be generated [22,23] and used for interfacial studies. Due to its flexibility, PAT allows also the characterization of rather complicated surface-active systems, such as asphaltenes and their efficiency in stabilizing emulsions [14], for dispersions with solidifying surface layers [24], for the

characterization of ionic liquids [25], or for the quantification of interactions between surfactants and particles or proteins in liquid interfacial layers [13,26].

For practical applications in oil fields, measuring instruments have to fulfill particular conditions. A Python-based image processing technique was used in Ref. [27] to set up an automated analysis protocol to determine surface and interfacial tensions as well as contact angles, which is much faster than the classical fitting procedures of drop profiles via the GLE, however, with a much lower average accuracy. The use of artificial intelligence, as described in Ref. [16] for a time-saving use of PAT, and as demonstrated in other recent papers [28−30], will become more widespread and make existing methods and experimental protocols easier and more efficient, however, the accuracy described so far is still much lower than that reached by a conventional analysis.

Surface tension measurements at high atmospheric pressures and elevated ambient temperatures are still a great challenge. Most suitable for such measurements seems to be the PAT method. Barrabino et al. demonstrated that, for example, studies at the interface between liquid CO_2 and water are possible with PAT when a particular measuring cell is available [31]. Measurements, which are of importance for tertiary oil recovery based on the injection of CO_2 into the rocks, are feasible up to 1300 bar and 200 °C, and in addition to standard dynamic interfacial tension measurements, drop oscillation experiments for obtaining the dilational viscoelasticity of the respective liquid interfaces were possible [32]. This methodology is also essential for fundamental studies on the capture and storage of carbon in the underground [33].

PAT in a sessile drop mode has been used during the last 30 years to measure the surface tension of molten metals and alloys to design high-performance materials. The major drawback in these set-ups was the reactivity of the melt with the crucibles at the high temperatures. Thus, more recently, set-ups based on the utilization of pendent drops have appeared [34], which warrants measurements in nearly container-less conditions and allows therefore investigations of the interfacial properties of liquid metals even at very high temperatures [35].

The group of Lin performed a number of very interesting experiments with a bubble profile analysis tensiometer using randomly appearing fluctuations in the closed system of the buoyant bubble caused by the temperature control loop [36]. The temperature fluctuations caused a volume change of the bubble and hence a change in the surface area A, leading consequently to surface tension changes. An accurate analysis

of the observed minute area perturbations and the corresponding surface tension changes as a result allowed to determine the dilational visco-elasticity in the respective moment of the experiment, leading finally to a time dependence of the visco-elasticity. In Ref. [37], the authors used this protocol, actually consisting of a buoyant bubble under temperature control, to determine the establishment of the equilibrium adsorption layer of proteins, using the observed changes in the dilational surface visco-elasticity. This type of experiments allowed to accurately determine the time required by a protein adsorption layer to reach the equilibrium state. The equilibrium state characterized by constant dilational surface viscosity data is reached much later than it is typically concluded from the constant dynamic interfacial tensions [38].

The analysis of surface tension changes caused by temperature fluctuations, used to determine the dilational visco-elasticity of fluid interfaces is a new approach and represents a complementation of experiments with formed harmonic oscillations of pendent drops/buoyant bubbles. It is worth mentioning here that this type of experiment has limits in the applied frequency, i.e. too high frequencies lead to wrong experimental results. In Ref. [39], it was for example shown that oscillations at a frequency of 1 Hz, which is almost one order of magnitude higher than the allowed maximum frequency, the surface layer of a pure water drop becomes visco-elastic, which is physically nonsense. A similar problem arises when the profiles of drops or bubbles are captured under dynamic conditions, for example, immediately after drop/bubble formation or during a growth process. Also under these conditions, the resulting values of surface or interfacial tension are erroneous, as shown in Ref. [40].

Although the majority of measurements of the dilational surface and interfacial rheology are performed presently by PAT with oscillating drops and bubbles, Zamora et al. [17] and Marquez et al. [41] proposed to use also the spinning drop method. This is of particular importance for studies of oil/water microemulsions where the measured tensions are extremely low and the classical PAT technique fails. The application of the oscillating spinning drop methods is particularly important for the tertiary oil recovery, although the analysis of the relaxation mechanisms in a spinning tube is very difficult due to the complex structure of the liquid flow which is in dynamic rotation and not in a quiescent equilibrium state as it is the case in PAT measurements.

The experimental investigations of the mechanical behavior of fluid interfaces are often complicated by the need to accurately separate the impact of the interface from that of the adjacent bulk phases. Moreover, while interfacial shear rheology can be studied via more or less ideal shear deformation experiments, in dilational interfacial rheology it is much more difficult to produce ideal expansions and compressions without a remarkable shear contribution. Moreover, in many cases, the interfacial layers are not perfectly homogeneous and sometimes even show particular structures, so that specific assumptions are to be made for a correct analysis of experimental data. In Ref. [42], an overview of the computational interfacial rheology is given that allows to analyze systems, in particular of liquid–fluid interfaces, covered by polymers, particles or any other molecular or supramolecular surface-active materials. The presence of complex structured interfacial layers complicates the correct data analysis via the GLE due to the presence of additional stresses of different nature, considered in detail by Sagis et al. [43]. This is particularly essential when in drop/bubble oscillation experiments the interfaces are covered by crosslinked membranes with a respective macroscopic thickness rather than by a monomolecular layer [44]. As mentioned above, reliable feedback can be obtained for the applicability of PAT in such situations by analyzing the standard deviation between the calculated and experimental drop/bubble profiles [10].

Large amplitude oscillatory dilations

First of all, large amplitude deformations of interfaces happen quite often in practice. In addition, this type of experiment is particularly suitable to visualize most relaxation mechanisms within the interfacial layer. Sagis and Fischer [45] recently summarized the use of experiments with oscillating drops or bubbles at large amplitude oscillatory dilations (LAOD) as a very efficient way to determine the interfacial dilation rheology of complex liquid interfacial layers in the non-linear visco-elastic (NLVE) regime. The standard output from PAT tensiometers yield the dilational modulus E_{FT} as evaluated from a first-harmonic Fourier transform analysis of the surface tension response. However, more detailed information about the rheological behavior of highly nonlinear visco-elastic interfacial systems remains encoded in higher harmonics [45,46]. To deal with this, a graphical method based on the analysis of Lissajous plots Π ($\Delta A/A_0$) was proposed in Ref. [45] (Π is surface pressure, and $\Delta A/A_0$ is the dimensionless amplitude of area deformation for a fixed initial surface area A_0). The nonlinear asymmetric surface stress response $\bar{E}$ to LAOD of an interfacial layer can be decomposed into four contributions: two pairs of large-strain ($\bar{E}_{LE}$ and $\bar{E}_{LC}$) and minimum-strain ($\bar{E}_{ME}$ and $\bar{E}_{MC}$) moduli for the regimes of expansion ($\bar{E}_{LE}$ and $\bar{E}_{ME}$) and compression ($\bar{E}_{LC}$ and $\bar{E}_{MC}$), which in turn, allow for the evaluation of a strain stiffening factor S as: 1) S = 0 for linear visco-elasticity behavior; 2) S > 0 for strain-hardening; and 3) S < 0 for strain-softening [45]. The thus defined stiffening factor S is a measure of the degree of elastic intracycle non-linearity and can be evaluated for both regimes of dilation, namely expansion

(S_E) and compression (S_C). Groot et al. [12] refined this approach by analyzing separately odd and even harmonics, as previously suggested by Bykov et al. [46]. The authors tested the improved methodology on complex water/air interfaces stabilized by proteins or lecithin, and provided a physical interpretation of each $\bar{E}$-contribution [12]. Their approach was presented in a quite general form and then applied to drop/bubble profile experiments for systems containing peptides [47], native proteins [48−50] or protein aggregates [51]. For example, in Ref. [50], LAOD was applied to β-lactoglobulin adsorption layers of H_2O/D_2O aqueous solutions in order to identify possible isotopic effects on the protein adsorption and rheological behavior, which is of high relevance to neutron reflectometry studies, where the usage of mixed H_2O/D_2O media is a necessary prerequisite. The experimental results did not only provide interesting interfacial rheology data but also showed that combined LAOD/dynamic surface pressure $\Pi(t)$ measurements can be a suitable test prior to designing optimal time windows in experimental protocols for neutron reflectometry experiments. For illustration, in Figure 2 some results of LAOD experiments are shown as examples.

It is worth mentioning that the calculated values for the S-factors are quite low in magnitude (of the order of 0.1), which was found also for β-Lactoglobulin (BLG) at the W/O interface [52] and for other proteins at the W/A interface [12]. This means that the degree of elastic nonlinearity remains comparatively low with the increase in the relative amplitude $\Delta A/A_0$ even of up to about 20 % [12,50].

The approach by Mielke et al. [53] is also worth mentioning as a powerful analysis of nonlinearities in the dilation rheological behavior of fluorocarbon/hydrocarbon tetrablock amphiphiles at the water/air interface, which yields unique visco-elasticity characteristics of these interfacial layers: nonlinearities emerged even under 'mild' conditions, such as surface pressures of $\Pi \approx 5$ mN/m and oscillation amplitude of only $\Delta A/A_0 = 1$ %. Just for comparison, typical values of the amplitudes of transition to a NLVE regime for protein layers at the water/air interface are ca. $\Delta A/A_0 = 3−5\%$ [48,50] or even up to $\approx 10\%$ [45,47].

## Depletion effects in single drop experiments

When measuring the dynamic and equilibrium surface tension of a solution drop of a strongly surface-active surfactant at low c the values differ significantly from those measured with an air bubble formed in the same solution. This effect was found much earlier and used as a tool to estimate the amount Γ of adsorbed proteins at the drop/bubble surface [54]. The difference is called depletion effect, as it is caused by the adsorption of surfactant at the drop surface and leads to a certain loss of concentration inside the single drop. As only emphasized recently [11], the depletion can cause large differences in the obtained adsorption layer characteristics in a quantitative analysis of experimental data. Depletion becomes significant when $\Gamma \times A \gg c \times V$. The volume of single drops in PAT is typically of the order of 15 mm^3, which corresponds to a drop diameter of about $2r = 3$ mm. When taking spherical geometry as a rough approximation for a drop, we get $V/A = r/3$, so that we obtain $V/A \approx 0.0005$ cm. Thus, for surfactants adsorbing significantly at $c = 10^{-6}$ mol/l, we obtain the condition for depletion of $\Gamma \gg 5 \times 10^{-11}$ mol/cm^2, which is the case for almost all proteins and also for many long chain

Figure 2
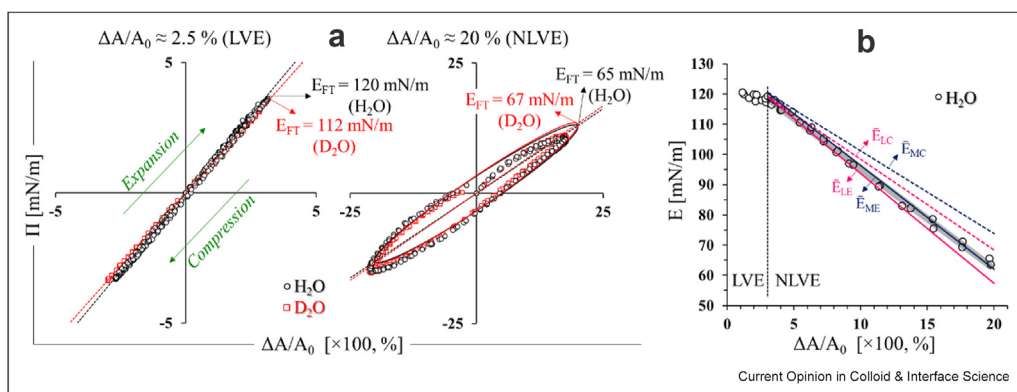
LAOD experiments at f = 0.1 Hz applied to β-lactoglobulin adsorption layers at the water/air interface (pH 7, 10 mM phosphate buffer). **(a)** Lissajous plots Π vs. ($\Delta A/A_0$) at a steady state ($\Pi \approx 20$ mN/m) for solutions in H_2O or D_2O for two amplitudes in the linear (LVE) and nonlinear (NLVE) visco-elasticity regime. The straight lines through the origin (0,0) are the long axes of the elliptic contours obtained from first-harmonic Fourier transform analysis (examples are shown on the right-handside panel); the evaluated values for E_{FT} are depicted in the graphs. **(b)** Evaluated dilational modulus E vs. $\Delta A/A_0$ for H_2O; symbols are experimental E_{FT} and the gray-shaded ribbon is a linear regression through the data in the NLVE regime; lines are linear regressions for the moduli $\bar{E}_{LE}$, $\bar{E}_{ME}$, $\bar{E}_{LC}$, and $\bar{E}_{MC}$. Adapted with permission from Gochev et al. [50]. Copyright 2024 American Chemical Society.

Figure 3
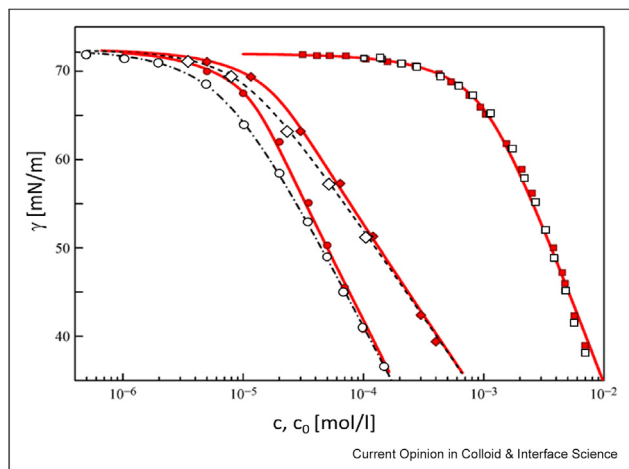
Surface tension isotherms for solutions of SDS in pure water (■ □), in water with addition of 0.5 mol/l NaCl (◆ ◇), and for $C_{10}OH$ in pure water (● ○); open symbols measured with bubbles formed in the solution and closed symbols measured with solution drops; further details are given in the text, according to Ref. [11]. SDS, sodium dodecyl sulfate.

surfactants. In Ref. [11], data for a number of surfactants were analyzed and one example is shown in Figure 3. As one can see, the surface tension isotherms for a surfactant like sodium dodecyl sulfate measured with single solution drops and in addition with a bubble in the surfactant solution (no depletion because the ratio V/A is typically 3 orders of magnitude larger than for a single drop) are identical. The same surfactant in 0.5 mol/l NaCl shows already measurable differences (at low c) between the "drop" and "bubble" data, and for decanol, the differences are already enormous.

Depletion due to adsorption effects at the surface of single solution drops has not only a strong impact on dynamic and equilibrium surface/interfacial tensions but also on the visco-elasticities of interfacial adsorption layers when measured with single oscillating drops [55]. The impact of depletion effects on the dilational interfacial visco-elasticity was shown, for example, in studies of Akanno et al. [56] on mixed adsorption layers of polymers and surfactants. In Ref. [57] it is shown how this complicates the data analysis so that it is recommended to use bubbles instead of drops in PAT experiments, as long as drops cannot be avoided, like in studies at liquid/liquid interfaces.

Conclusions

Simple set-ups for drop profile analysis tensiometry can suffer from a lower accuracy, but via the combination with artificial intelligence, for example the approach proposed recently in Ref. [15], this experimental tool can provide a manifold of data with a sufficiently high precision. Still, high-end instruments will keep their

leading role in the characterization of fluid interfaces due to their great number of available complex experimental protocols and additional features like temperature and drop/bubble size control.

New experimental protocols allow for accurate measurements not only of interfacial tension but also of the dilational visco-elasticity at high pressure and high temperature. It was also shown that for particular systems, the use of PAT can lead to erroneous results, for example when the drop bulk contains sedimenting particles or the surface is covered by a kind of membrane rather than a monomolecular adsorption layer. In such cases, the analysis of the standard deviation (STD) as a measure for the deviation of the experimental from the calculated profile, helps to decide whether PAT is applicable or leads to systematic errors. Recently, PAT-STD analysis has also been developed as a novel methodology for recognition of complex layer formation, and transformation of regular adsorbed layers to membrane-like film formation.

For the future use of PAT as a routine tensiometry method, it is recommended to find the most suitable size of the drop/bubble, and to check if the important conditions for the method — homogeneous bulk and isotropic surface layer are fulfilled. In any case, we can expect that the fields of application of PAT will further grow and provide a large amount of data that give us insights into molecular processes inside the bulk of surfactant/protein solutions as well as those happening at the interface.

Declaration of competing interest

During the preparation of this work the authors did not use any type of artificial intelligence.

The authors of this manuscript declare to have no conflicts of interest. The Ms has been submitted only to this journal and all supporting institutions are mentioned.

Data availability

No data was used for the research described in the article.

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   * of special interest
  ** of outstanding interest

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