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From drop-shape analysis to stress-fitting elastometry

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ABSTRACT

Drop-shape analysis using pendant or sessile drops is a well-established experimental technique for measuring the interfacial or surface tension, and changes thereof. The method relies on deforming a drop by either gravity or buoyancy and fitting the Young–Laplace equation to the drop shape. Alternatively one can prescribe the shape and measure the pressure inside the drop or bubble using pressure tensiometry. However, when an interface with a complex microstructure is present, extra and anisotropic interfacial stresses may develop due to lateral interactions between the surface-active moieties, leading to deviations of the drop shape or even a wrinkling of the interface. To extract surface-material properties of these complex interfaces using drop-shape analysis or pressure tensiometry, the Young–Laplace law needs to be generalized in order to account for the extra and anisotropic stresses at the interface. In the present work, we review the different approaches that have been proposed to date to extract the surface tension as the thermodynamic state variable, as well as other rheological material properties such as the compression and the shear modulus. To evaluate the intrinsic performance of the methods, computer generated drops are subjected to step-area changes and then subjected to analysis using the different methods. Shape-fitting methods, now combined with an adequate constitutive method, do however perform rather poorly in determining the elastic stresses, especially at small area strains. An additional measurement o f the pressure or capillary-pressure tensiometry is required to improve the sensitivity. However, pressure-based methods still require the knowledge of the undeformed reference state, which may be difficult to achieve in practice. Moreover, it is not straightforward to judge from what point onwards one needs to go beyond the Young–Laplace equation. To overcome these limitations, a method based on stress fitting, which uses a local force balance method, is introduced here. One aspect of this new method is the use of the Chebyshev transform to numerically describe the contour shape of the drop interface. For all methods we present a detailed error analysis to evaluate if, and with what precision, surface material parameters can be extracted. Depending on the desired information, different ideal experimental conditions and most suitable methods are discussed, in addition to having a criterion to investigate if extra and anisotropic stresses matter.

1. Introduction

1.1. Pendant drop tensiometry: success and pitfalls

The analysis of the shape of pendant or sessile drops or bubbles, has developed into an important and standard technique in the interfacial science of fluid–fluid interfaces. Such investigations are concerned with the measurement of surface tension of a liquid–air interface, interfacial tension between two liquids and with the mechanical and physicochemical behavior of adsorbed substances at such interfaces.

The interfacial properties are derived from the shape of drops or bubbles, an idea first presented by Worthington, as early as 1881 [1]. He projected the silhouette of a pendant drop on a paper screen, sketched its contour and evaluated the curvature using a graphical method. Worthington recognized that there is a balance between the hydrostatic pressure, which changes with height and the Laplace pressure caused by the presence of a curved interface.

The Young–Laplace equation expresses this balance:

$$(\kappa_1 + \kappa_2)\sigma_{\alpha\beta} = p - \rho g z. \tag{1}$$

Herein, κ_1 and κ_2 are the two principal curvatures, $\sigma_{\alpha\beta}$ the surface or interfacial tension[1], p the pressure difference over the interface at the vertical position $z = 0$, ρ the density difference and g the gravitational acceleration.

Due to the non-linear dependency of the curvatures on the drop radius and height, the application of the Young–Laplace equation in a

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[1] The subscript $\alpha\beta$ is not an index but rather clarifies that the stress σ is due to the presence of two adjoints α and β.

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parameter fitting process is complicated. It was cast into its modern form by Rotenberg et al. in 1983 [2], who developed an algorithm that compared numerically sampled drop shapes to computationally obtained profiles. Computer assisted iterative fitting allowed to use many points on the interface and improved the precision compared to fitting of only few characteristic points to tabulated data as done in the pre-computer age [3,4].

Since then, numerical fitting has been subject to constant improvements in terms of robustness, efficiency and precision. Provided that robust numerical schemes are used, Axisymmetric Drop Shape Analysis (ADSA or DSA) developed in the group of Neumann [5] is an accurate method for the determination of the surface tension of pure surface-tension interfaces by fitting the drop shape to a solution of the Laplace equation of undetermined surface tension [6]. A key aspect for the method to work is that the drop needs to be deformed enough by gravity [7,8]. Without a hydrostatic pressure contribution the drop is spherical and the curvature does not vary. As a consequence only the ratio between surface tension and pressure is fixed, but not their absolute values.

A variation of the DSA method is the capillary-pressure tensiometer (CPT) introduced by Sudgen in 1922 [9] and the pulsating-bubble surfactometer (PBS) [10]. Both methods couple a shape analysis with a pressure measurement, using generally smaller capillaries to increase the pressure signal. The shape analysis simplifies considerably when the capillary pressure is provided, as only the curvature has to be determined. So for the CPT method having a near spherical or hemispherical shape is an advantage as the curvature is then easily determined. Recently Peters et al. [11] presented a new approach based on a force balance, which is expected to be more robust, because it requires only the tangent angle (derivative) of the interface and not the curvature (double derivative). Applying a derivative to experimental data is known to amplify noise.

DSA was originally developed for the determination of the surface tension, but it has been used for interfacial tensions between immiscible liquids [12] even for very small values [13] or transient conditions [14,15]. DSA has also been applied to a film balance for insoluble substances [16,17]. However, when going to interfaces which become “complex”, due to the presence of an interfacial structure with lateral interactions between the interfacial moieties, there will be a corresponding mechanical response particular to the interface. A scalar value of the surface tension will no longer suffice to describe the properties of that interface and the shape of pendant drops deviates from a Laplacian one. A striking example of this was, for example, seen in interfacial layers from the protein HFBII hydrophobin, where an increase in the error of the fit of the pendant-drop profile by means of the Laplace equation was observed as the layers were expected to undergo a transition from fluid to elastic solid films [18], with interfaces even being observed to crumple. In the case of evaporating drops with asphaltene particles at the interface buckling has also been observed, where an inverted curvature indicates a build-up of compressive stresses [19]. Also, these observations indicate that an analysis is required which goes beyond the mere usage of surface tension. Botto et al. [20] used simulations of particle-laden drops and showed how the microstructure–surface stress relationship influences the drop shape. In particular, they showed how the isotropic and anisotropic surface stress stem from the interparticle forces and the organization at the interface for the case of repulsive spheres.

In the following, we present a review of the different approaches which have been developed to tackle the problem of static drops or bubbles in presence of an elastic, structured interfaces, in particular subjected to step area changes. We extend the analysis and provide robust algorithms to obtain the material parameters, with some guidelines for the best experimental conditions. The analysis is also relevant for oscillatory pendant drop experiments, when the interface is viscoelastic. The static case for elastic interfaces represents the limit of a high Deborah number. In that case, hydrodynamics and mass transfer kinetics may obviously lead to additional complexity, see for example Alvarez et al. [21] and Balemans et al. [22] for recent accounts on mass transfer and momentum transfer effects, respectively.

1.2. Pendant drop elastometry

Carvajal et al. [23] were the first to take the pendant drop problem beyond a simple interface, introducing an interfacial shell with solid-like behavior in addition to the surface tension. Due to the presence of the elastic shell, at any given point of the interface, the two principal interfacial stresses are no longer necessarily equal to one other. Using the assumption of an incompressible volume preserving interfacial layer, their isochoric model interface was characterized by a single parameter, the Young's modulus. The deviations between a Young–Laplace fit and the resulting elastic shape were studied by Ferri et al. [24] theoretically and experimentally. They investigated the influence of the interfacial shear modulus on the fit error of the Young–Laplace equation. However, when solving the inverse problem they used only the isotropic Young–Laplace equation to obtain the surface tension. With the assumption of Poisson ratio $\nu = 0$ (when compression and shear modulus are equal, see Appendix A. for definitions) the authors obtained the surface shear modulus G. This seems a very strong assumption, as the shear modulus G captures the reaction of the interface to a change in shape (deviatoric stress), and is at the heart of the anisotropic stress distribution at the interface. Close to the neck of the capillary the interfacial fluid elements will always deform and coupling G artificially to K by supposing $\nu = 0$ may not give physically realistic results for all interfaces.

Work by Knoche et al. [25] extended Carvajals analysis of elastic interfaces to two parameter models, using a Young's modulus and the Poisson ratio. Their work investigates hydrophobin (HFBII) and polymerized octadecyltrichlorosilane (OTS) layers under compression and also relates the number of wrinkles of the membrane to the bending modulus. Knoche et al. observed large uncertainties on the Poisson ratio ν, for example for HFBII drops. Their 2-parameter model is only valid in the small-strain limit.

Vaccari et al. studied elastic biofilms with a pendant drop and also analyzed the shear modulus with micro-rheology particle tracking. Their curve fitting also led to a wide spread of data for the Poisson ratio. Danov et al. [26] showed that in these cases the analysis of material properties relies on the knowledge on the unstrained reference state. They developed a method which they called Capillary Meniscus Dynamometry (CMD) to determine the anisotropic stress state at the interface, however no attempt was made to extract material properties from the stress state.

The work of Carvajal [23] also included a discussion on the most favorable experimental conditions. The precision of the pendant drop method faces stronger inherent limitations than other established techniques like the Langmuir trough. For example, the actual straining of the interface (albeit a complex deformation, as first shown by Petkov et al. [27]) is better prescribed in the Langmuir trough. In a pendant drop this will only be obtained as a result of the analysis used to extract the material parameters. This increased uncertainty generally requires larger strains and in return might actually be outside the linear regime, which is assumed in most of the approaches used so far. Moreover, experimental determinations of the surface deformation via optical methods also require substantial area deformations.

When the surface stress becomes very large it will be capped at the surface tension of the bare interface and wrinkles form to relax the compressive stress. Knoche et al. [25] were able to accurately predict where wrinkles would form based on elastic theory. As we are however, interested in a precise determination of the linear response, the issues of wrinkling and bending of the interface will not be pursued here. The current state of the art can be found in Ref. [25].