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Total Gaussian curvature, drop shapes and the range of applicability of drop shape techniques

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ABSTRACT

Drop shape techniques are used extensively for surface tension measurement. It is well-documented that, as the drop/bubble shape becomes close to spherical, the performance of all drop shape techniques deteriorates. There have been efforts quantifying the range of applicability of drop techniques by studying the deviation of Laplacian drops from the spherical shape. A shape parameter was introduced in the literature and was modified several times to accommodate different drop constellations. However, new problems arise every time a new configuration is considered. Therefore, there is a need for a universal shape parameter applicable to pendant drops, sessile drops, liquid bridges as well as captive bubbles. In this work, the use of the total Gaussian curvature in a unified approach for the shape parameter is introduced for that purpose. The total Gaussian curvature is a dimensionless quantity that is commonly used in differential geometry and surface thermodynamics, and can be easily calculated for different Laplacian drop shapes. The new definition of the shape parameter using the total Gaussian curvature is applied here to both pendant and constrained sessile drops as an illustration. The analysis showed that the new definition is superior and reflects experimental results better than previous definitions, especially at extreme values of the Bond number.

Contents

1. Introduction

Drop shape techniques, based on the shape of a pendant drop, sessile drop or captive bubble, are extensively used for surface tension measurement. Early efforts in the analysis started by analyzing the shapes of pendant drops and predicting the shapes for a given surface tension value [1]. Later, certain dimensions of the shape were tabulated along with the corresponding surface tension value. Consequently, the surface tension can be calculated by interpolation using these tables [2]. More sophisticated methodology was later developed based on comparing a number of selected and measured points on the drop periphery

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to calculated drop shapes and hence determining the surface tension [3,4].

Axisymmetric Drop Shape Analysis (ADSA) [5–9] is a drop shape technique now extensively used for surface tension and contact angle measurement. ADSA, based on the shape of liquid/fluid interfaces, is complex but is adaptable to a variety of experimental circumstances including pendant drops, sessile drops and bubbles. ADSA was developed to use minimum input information: specifically a number of arbitrary chosen drop profile points and the density difference across the interface. It requires no correction factors nor information about the drop apex. Briefly, ADSA matches the drop/bubble profile extracted from experimental images to a theoretical Laplacian curve for known surface tension values using a nonlinear optimization procedure [5–7]. An objective function is used to evaluate the discrepancy between the theoretical Laplacian curve and the actual profile. This objective function is the sum of the squares of the normal distances between the measured points (i.e. experimental curve) and the calculated curve [7]. The optimization procedure minimizes the objective function and, hence, finds the surface tension value corresponding to the extracted profile from experimental drop images. Besides measuring the surface tension and contact angle, ADSA has also been used to study adsorption films [10–15], solid surface tension [16,17], lung surfactants [18–21], relaxation kinetics [22–24], interfacial chemical reactions [25–28] as well as to study the density of polymer melts [29].

The shape of the drop/bubble depends on the balance between surface tension and external forces, e.g. gravity. This balance is reflected mathematically in the Laplace equation of capillarity. When gravitational and surface tension effects are comparable, then, in principle, one can determine the surface tension from an analysis of the shape of the drop/bubble. The surface tension tends to round the drop, whereas gravity deforms it, i.e. gravity elongates a pendant drop or flattens a sessile drop. Whenever the surface tension effect is much larger than the gravitational effect, the shape tends to become spherical in the case of both pendant and sessile drops/bubbles. Theoretically, each drop shape corresponds to a certain surface tension value. For well deformed shapes, a slight change in surface tension causes a significant change in the shape. However, for nearly spherical drop/bubble shapes, a significant change in surface tension causes only a slight change in the shape. In that situation, the sensitivity of surface tension to changes in drop shape is low.

Although ADSA has been widely used, it is well-documented that its performance or that of any other drop shape technique deteriorates as the drop/bubble shape becomes close to spherical [30]. The same problem has also been observed by other researchers who were using numerical optimizations for the measurement of interfacial tensions [31–34]. In their study, the surface tension values calculated from large pendant drops of pure liquids were consistent and accurate. However, as the volume of the drop decreased and the drop shape became close to spherical, the surface tension value deviated from the true value. This limitation is not only an inherent characteristic of specific ADSA-type algorithms but also exists in the same way for a different type of drop shape technique called Theoretical Image Fitting Analysis (TIFA). TIFA operates without using edge detection; the image analysis is tied to the optimization process in TIFA, and it is not a separate module as in ADSA [35,36]. Similar to ADSA-type algorithms, the TIFA algorithm shows accurate results for large well deformed drops but deviates dramatically for near spherical drops [37].

There is a need to define and quantify a measure of the deviation of a drop/bubble shape from a spherical shape, or more generally, the zero Bond number shape. In this context, the Bond number is a dimensionless number expressing the ratio of body forces to surface tension forces. This measure of deviation from the spherical shape has to be a geometrical one that reflects the total deformation of the drop/bubble shape. This measure also has to be universal in the sense that it must be applicable to any drop/bubble shape configuration such as pendant drops, constrained sessile drops, unconstrained sessile drops, captive bubbles, or liquid bridges. In other words, this measure of deviation should not depend on any specifics of the configuration, such as the diameter of the drop holder. This measure of deviation is often called “shape parameter”. It will be shown below that a geometric parameter called total Gaussian curvature is best suited for this task.

From the experimental point of view, the above definition of the shape parameter is not sufficient to perform accurate surface tension measurements. In fact, that definition merely indicates the deviation or the deformation of the drop shape but does not suggest how to put that parameter to practical use. For example, in the case of constrained sessile drops, it would not allow the prescription of an appropriate diameter of the drop holder to allow surface tension measurement in a specified range of surface tensions of interest.

Therefore, in addition to a definition for the shape parameter, we need to know how much deviation of the drop shape from a spherical shape is required so that a drop shape technique would work properly and consistently with such well deformed drops/bubbles. This minimum requirement is called “critical shape parameter” and is expected to be different for every experimental drop shape configuration. Thus, the shape parameter, which characterizes the drop shape purely in geometric terms, must also be linked to physical and geometrical quantities that are specific to each experimental configuration, such as constrained sessile drop and pendant drop.

To summarize, there are in fact two definitions for the shape parameter that are needed: One strictly geometrical to provide a quantitative measure of the deviation of the shape of a given experimental drop shape from spherical. The second definition is basically an expression of a functional relationship that relates the drop shape to the physical properties of the drop (surface tension and density) and geometric boundary conditions, such as the diameter of the drop holder. By comparing these two expressions for the shape parameter, the point can be found where, with decreasing drop size, the surface tension value calculated from ADSA starts to deviate from the correct and known surface tension. This point determines the critical shape parameter. Below the critical shape parameter, surface tension measurement is unreliable, probably erroneous. Such definitions and procedures are, in fact, not ADSA specific and can be employed with other drop shape techniques, like TIFA.

It will become apparent, below, that the usually considered axisymmetric drops and bubbles in pendant as well as sessile configurations, and axisymmetric liquid bridges all fall into one of only four categories. All of these categories share the universal definition of the geometry-based shape parameter which provides a quantitative measure of the deviation of the shape of a given experimental drop shape from the spherical shape. However, each category will have a unique functional relationship that relates the drop shape to the physical properties of the drop and geometric boundary conditions. For example, it turns out that both pendant drops and constrained sessile drops possess shapes that depend solely on the same five physical and geometrical parameters that in turn can be expressed in only two dimensionless groups: Bond number and a dimensionless volume. Thus, the shape parameter for this category will also depend on these two dimensionless groups. Detailed analysis will be given below.

Other constellations, such as unconstrained sessile drops, captive bubbles and constrained and unconstrained liquid bridges, would fall into different categories with unique geometrical boundary conditions. Although all these categories share the universal definition of the geometry-based shape parameter, each category has a different functional relationship that relates the drop shape to the unique geometric boundary conditions. For example, the contact angle will influence the shape of an unconstrained sessile drop and the distance between the usually upper constraining drop holder (pedestal) and the lower extended solid surface will affect the shape of a liquid bridge. Therefore, the physical shape parameter for these categories will depend on unique sets of dimensionless groups. More details will be given below.