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Laplacian drop shapes and effect of random perturbations on accuracy of surface tension measurement for different drop constellations

Sameh M.I. Saad, A. Wilhelm Neumann *

Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8, Canada

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ABSTRACT

Theoretical drop shapes are calculated for three drop constellations: pendant drops, constrained sessile drops, and unconstrained sessile drops. Based on total Gaussian curvature, shape parameter and critical shape parameter are discussed as a function of different drop sizes and surface tensions. The shape parameter is linked to physical parameters for every drop constellation. The as yet unavailable detailed dimensional analysis for the unconstrained sessile drop is presented. Results show that the unconstrained sessile drop shape depends on a dimensionless volume term and the contact angle. Random perturbations are introduced and the accuracy of surface tension measurement is assessed for precise and perturbed profiles of the three drop constellations. It is concluded that pendant drops are the best method for accurate surface tension measurement, followed by constrained sessile drops. The unconstrained sessile drops come last because they tend to be more spherical at low and moderate contact angles. Of course, unconstrained sessile drops are the only option if contact angles are to be measured.

Contents

1. Introduction

Drop shape techniques are widely used for the measurement of surface tension and contact angle. Depending on specific purpose or given experimental constraints, different experimental constellations are considered: pendant drops (PD) [1–8], sessile drops (SD) [9–14], constrained sessile drops (CSD) [15–19], captive bubble (CB) [20–23] and liquid bridges (LB) [24,25] are of interest. The most commonly used of these are pendant drops and unconstrained sessile drops (SD). All these approaches have considerable power and versatility in that they are equally applicable to static and many dynamic situations.

* Corresponding author. Tel.: +1 416 978 1270; fax: +1 416 978 7753.
E-mail address: neumann@mie.utoronto.ca (A.W. Neumann).

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Adsorption kinetics on a static drop [26–32] can be followed as well as dynamic changes, as long as fluid dynamic effects do not interfere [33–36]. One such example is the use of CSD as a film balance in the study of lung surfactant films [37–41]. As the average period of human breathing is often approximately 3 s, the surface area of the drop has to undergo cyclical changes at that frequency in order to mimic the function of the human lung.

Compared to these efforts comparatively little has been done on the question of reliability and accuracy of the data produced by these techniques. Efforts to date were largely motivated by one reasonably obvious limitation of drop shape techniques. As drops become very small, they tend towards a spherical shape. This is due to the fact that the shape of such a drop is determined essentially by surface tension overpowering the effect of gravity. But the whole methodology depends ultimately on deducing the as yet unknown surface tension from the known effect of gravity, from a determination of the deformation of the drop shape. In other words, for very small drops, a very large change in surface tension would be required to bring about an appreciable change in drop shape. In practical terms this means that the technique becomes insensitive to surface tension.

This aspect of applicability of drop shape methods has been studied to some extent, but only for pendant and constrained sessile drops [42–44]. At the heart of these studies is the idea of a shape parameter that measures the deviation of the shape of a given drop from the spherical shape, or, more generally, the zero gravity shape. These shape parameters, calculated from the experimental drop profiles, are then compared with the values of the surface tension calculated from drops of pure liquids, for a large range of drop sizes. As expected, as the drop size decreases, a point is reached where the determined value of the surface tension deviates strongly from the known, constant surface tension. This point is called the "critical shape parameter"; for drops smaller than this value, surface tension cannot be measured for a given value of accepted error. This shape parameter is expressed in terms of a dimensionless drop volume and the Bond number, i.e. essentially the ratio of gravity to surface tension. Thus, the shape parameter will not only avoid erroneous work with a given set-up, but also provide design guidelines as well [42–44].

It has to be kept in mind that the above strategy depends on a given experimental setup. The quality of the results also depends on such matters as optics, lighting and resolution of the digital camera. It is well known that an increase in resolution will increase the accuracy of the measurement. But it has been shown that for a given drop image for a drop with a shape parameter exceeding the critical shape parameter an accuracy of the surface tension of the order of 0.01 mJ/m^2 for ordinary liquids under ambient conditions can be attained with suitable and optimized edge detection algorithms [42–44].

It is the purpose of this study to open a second venue into applicability and accuracy of drop shape techniques in order to solidify the promise of these methodologies. There are two very different goals to this study. The first goal is the study of theoretical profiles rather than experimental ones, by introducing possible errors into the very precise theoretical drop shapes and to analyze these modified profiles. In the first instance we expect to learn what errors can be caused by the experimentally observed scatter. This aspect will also provide a base for an evaluation of the impact that changes of experimental parameters, e.g. the brightness of the image, may have.

The second goal is a very practical one: With the work already performed in the area, we know the size of drops limiting the accuracy of surface tension very well, in the case of pendant drops (PD) and constrained sessile drops (CSD) [42–44]. This insight is intimately connected with fairly large arrays of experimental data, i.e. a large number of drop images as a function of drop size for drops of liquids of well known surface tension. For unconstrained sessile drops such information is not available yet. However, understanding drop size and shape requirements and hence the ability to determine surface tension reliably is crucially important, e.g., in metallurgy and other high temperature applications. In such situations a small sample of the material in question is typically placed on a smooth and flat surface under ambient conditions before high temperature and possibly vacuum or protective atmospheres are established. Simply put, we do not know how large a sessile drop and its contact angle has to be in order to allow a meaningful surface tension measurement. This is not an academic point. From the authors' work on contact angles [45,46], we know that the calculated surface tension is frequently erroneous. The progress to be made will have to be based on the comparison between the analysis of experimental, theoretical and distorted theoretical profiles.

The work to be presented here will be linked intimately to the concepts of shape and shape parameter. Therefore the study has to start with a review of this concept of shape and shape parameter [44]. For present purposes, these concepts are best considered in terms of the total Gaussian curvature, $\mathcal{K}$, of a given drop. Next, the shape parameter will have to be linked to physical parameters, including surface tension and gravity. Theoretical drop shapes will be generated and compared for similarities among shapes. Such theoretical shapes will then be run through axisymmetric drop shape analysis (ADSA), i.e. the software package that determines surface tension, contact angle and other physical parameters of the drop [47]. As input, the precise theoretical shape will be used without and with random perturbations. Critical shape parameters will be established for such perturbed drop shapes, as a function of the extent of the perturbation. These critical shape parameters will then be compared with the known experimental critical shape parameters for both pendant and constrained sessile drops. The results of this comparison will be applied to unconstrained sessile drops, for which the minimum requirements needed for drop size and contact angle to achieve an acceptable value for surface tension are unknown.

2. The shape parameter: a geometrical concept

It has been shown before that the curvature of any given drop, be it pendant, sessile or of the liquid bridge type, is characterized by a single, numerical, non-dimensional number, i.e. the total Gaussian curvature ($\mathcal{K}$) [44]. It is defined as the surface integral of the second (Gaussian) curvature (K),

$$\mathcal{K} = \iint_A K dA = \iint_A \left(\frac{1}{R_1}\right)\left(\frac{1}{R_2}\right) dA \tag{1}$$

where R_1 and R_2 are the principal radii of curvature.

The total Gaussian curvature is well suited to represent the curvature of a given drop and to be used in a unified approach for the shape parameter [44]. For experimental purposes, specifically for measuring surface tension, what matters is the deviation of a given drop shape from a spherical shape, i.e. the difference between the total Gaussian curvature of the Laplacian drop shape and the total Gaussian curvature of the respective best fit zero Bond number shape (the sphere in the case of pendant/sessile drops):

$$P_c = d\mathcal{K} = |\mathcal{K} - \mathcal{K}_s| \tag{2}$$

where $\mathcal{K}$ is the total Gaussian curvature of the pendant/sessile drop and $\mathcal{K}_s$ is the total Gaussian curvature of the respective best fit zero gravity shape; P_c is called the shape parameter.

In shape parameter analysis, the extracted experimental profile of sessile/pendant drop shapes is compared to a portion of the sphere (spherical cap). For a spherical cap with height, $H \leq 2R$, the surface area is: $A = 2\pi RH$. Therefore, the total Gaussian curvature can be easily calculated, as shown before [44]:

$$\mathcal{K}_s = \frac{2\pi H}{R}. \tag{3}$$

For an experimental profile of a pendant or a sessile drop (constrained or unconstrained), the Gaussian curvatures can be calculated from the

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