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A non-gradient based algorithm for the determination of surface tension from a pendant drop: Application to low Bond number drop shapes

Nicolas J. Alvarez [a], Lynn M. Walker [a], Shelley L. Anna [a,b,*]

[a] Department of Chemical Engineering, Center for Complex Fluids Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
[b] Department of Mechanical Engineering, Center for Complex Fluids Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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ABSTRACT

The pendant drop method is one of the most widely used techniques to measure the surface tension between gas–liquid and liquid–liquid interfaces. The method consists of fitting the Young–Laplace equation to the digitized shape of a drop suspended from the end of a capillary tube. The first use of digital computers to solve this problem utilized nonlinear least squares fitting and since then numerous subroutines and algorithms have been reported for improving efficiency and accuracy. However, current algorithms which rely on gradient based methods have difficulty converging for almost spherical drop shapes (i.e. low Bond numbers). We present a non-gradient based algorithm based on the Nelder–Mead simplex method to solve the least squares problem. The main advantage of using a non-gradient based fitting routine is that it is robust against poor initial guesses and works for almost spherical bubble shapes. We have tested the algorithm against theoretical and experimental drop shapes to demonstrate both the efficiency and the accuracy of the fitting routine for a wide range of Bond numbers. Our study shows that this algorithm allows for surface tension measurements corresponding to Bond numbers previously shown to be ill suited for pendant drop measurements.

1. Introduction

When a fluid is suspended from a capillary and surrounded by another fluid such that gravity acts along the axis of the capillary to distend the nominally spherical interface, the shape of the interface depends on the surface tension, γ, the characteristic size of the bubble or drop, R_0, and the density difference between the two fluids, $\Delta\rho$. The Bond number, given by

$$\beta = \Delta\rho g R_0^2/\gamma, \tag{1}$$

is a dimensionless group describing the relative magnitude of forces due to gravity and surface tension. If the density difference between the fluids is known and the size can be measured, then the surface tension can be determined from a measurement of the interface shape. This method of measuring surface tension, first realized by Andreas and coworkers [1], has come to be known as the pendant drop method. The method was suggested earlier by Worthington [2,3] and Ferguson [4], but measurements of drop coordinates proved difficult at that time. Andreas et al. overcame these issues by reformulating the Young–Laplace equation in a new coordinate system.

Using the formulation of Andreas et al., the Young–Laplace equation is integrated to obtain a theoretical drop shape, which is then compared with an experimental drop shape to determine the surface tension between the two fluids. Before the availability of digital computers, drop shapes were analyzed by examining the ratio of radii of the drop at different axial positions, whose values were tabulated along with corresponding surface tension values [5]. This analysis, known as the selected plane method, is still carried out today when rough estimates (i.e. within 1 mN/m) of surface tension are of interest. However, when accuracy is required it is necessary to solve a nonlinear least-squares problem to fit a calculated drop shape to a measured drop shape. In addition, the selected plane method only works for drops that fall within a selected range of Bond numbers.

Although the particulars of the nonlinear least-squares fitting algorithms found in the literature might differ, the general procedure for each method remains the same. For instance, an image is first recorded by a CCD camera and digitized. An edge detection method is used to extract the shape of the drop interface. The coordinates of the interface are then used to calculate the error between computed theoretical shapes and the measured shape. The error is computed via an objective function, defined as the shortest distance between an experimental point and a point on the calculated interface. The procedure is repeated until the theoretical shape corresponding to the minimum error is found. The param-

* Corresponding author at: Department of Mechanical Engineering, Center for Complex Fluids Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA.
E-mail address: sanna@andrew.cmu.edu (S.L. Anna).

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eters that result from the fitting analysis are then assumed to be the parameters governing the shape of the experimental drop.

The most extensively utilized fitting routine for pendant and sessile drop studies is known as Axisymmetric Drop Shape Analysis (ADSA) [6]. Since the initial publication of this approach, there have been many improvements and adaptations for different applications [7,8]. The first version used a Newton–Raphson routine with incremental loading, a method that systematically increments the parameter space after each Newton–Raphson iteration. However, this algorithm was found to be computationally expensive and convergence is not guaranteed, especially when starting from a poor guess [7]. To improve convergence, del Rio et al. combined the Newton–Raphson method with the Levenberg–Marquardt algorithm which helped improve the likelihood of convergence. However, major limitations to the ADSA algorithm remain, as summarized recently by Hoorfar and Neumann [8]. For example, the authors found that ADSA-based algorithms are ill-suited for certain drop shapes that are close to spherical. A spherical drop of water analyzed using the ADSA algorithm yields a surface tension value near 79.32 mN/m, compared with the expected value of 72.28 mN/m [8]. The discrepancy between these two values is relatively large compared with typical pendant drop measurements, which are normally within 0.5 mN/m of the expected value at optimum conditions. To mitigate these discrepancies, a shape parameter, which is a measure of how close the shape is to spherical, is used to determine whether ADSA can be appropriately applied to a given drop. Generally speaking, the minimum Bond number at which the ADSA algorithm can be successfully applied is approximately $\beta \approx 0.2$.

Although improvements on these methods continue to be developed, there are fundamental limitations to gradient-based techniques such as ADSA. For instance, the convergence of gradient optimization methods assumes a continuous objective function. Although continuity of the error equation may be assumed for theoretical drops with no distortion in the pixel positions, the assumption may not be valid for experimental drop shapes where pixel positions may be shifted due to threshold effects, imperfect edge detection routines, and random noise [9].

The inability of pendant drop measurements to be conducted below $\beta \approx 0.2$ places a significant restriction on interfacial tension measurements for liquid–liquid pairs. For example, in the case of silicone oil and water, the density difference, $\Delta\rho \approx 10^{-2}$ g/cm^3. To achieve a Bond number greater than $\beta \approx 0.2$ would require a drop size on the order of centimeters. While this might not represent a significant impedance for static measurements, the timescale to reach equilibrium in dynamic studies of surfactant adsorption scales with drop radius, and a centimeter-scale drop will increase the timescale by an order of magnitude compared with typical pendant drop measurements [10]. In addition, in experiments where microgravity is simulated using density matched fluids $\Delta\rho \approx 10^{-3}$ g/cm^3, which further limits both static and dynamic studies as the drop would have to be extremely large and timescales to reach equilibrium very long. Therefore, an algorithm that can avoid the restriction on Bond number would facilitate studies of liquid–liquid interfaces that are currently too difficult to measure.

The present paper describes a new, non gradient-based algorithm that utilizes the Nelder–Mead simplex method for the determination of surface tension from the measured shape of a pendant drop or bubble. Numerous test cases are constructed to validate the efficiency and robustness of the algorithm, even when only poor initial guesses are available. In addition, one of the main concerns of using a non-gradient based optimization routine is that convergence could take an extended period of time. Therefore, we have documented the computational time of the algorithm to ensure its efficiency in dynamic surface tension studies where many frames (i.e. 100–1000) need to be analyzed. Furthermore, we demonstrate the ability of the new algorithm to fit nearly spherical drop shapes, both theoretically and experimentally, overcoming a major limitation of existing algorithms.

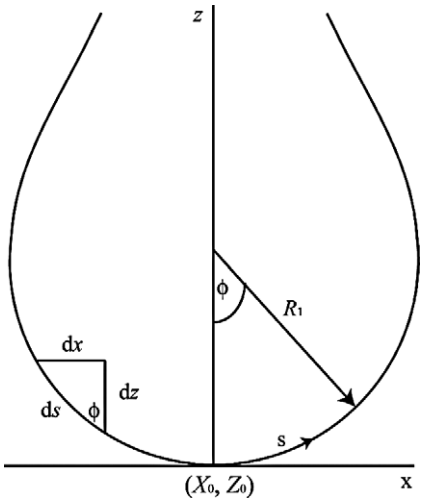

Fig. 1. The coordinate system for a pendant drop, where x is the horizontal coordinate, z is the vertical coordinate, ϕ is the angle of rotation from the apex (X_0, Z_0), and s is the arc length. R_1 is the principal radius of curvature in the plane of the paper and R_2 is the principal radius of curvature in a plane perpendicular to the paper and the axis of symmetry, such that $R_2 = x/\sin\phi$.

2. Relationship between surface tension and the shape of a pendant drop

The pressure jump ΔP across a fluid interface at any point is a function of the two principal radii of curvature, given by the Young–Laplace equation, $\Delta P = \gamma(1/R_1 + 1/R_2)$, where γ is the interfacial tension, and R_1 and R_2 are the two principle radii of curvature. If gravity is the only additional force acting on the drop, then the pressure jump is given by $\Delta P = \Delta P_0 + \Delta\rho g z$, where $\Delta\rho$ is the density difference between the two fluids. Using geometrical arguments and a change of coordinate system, illustrated schematically in Fig. 1, the Young–Laplace equation becomes a set of three ordinary differential equations [1],

$$\frac{dx}{ds} = \cos\phi,$$
$$\frac{dz}{ds} = \sin\phi,$$
$$\frac{d\phi}{ds} = 2 - \beta\cdot z - \frac{\sin\phi}{x}, \tag{2}$$

where x is the horizontal coordinate, z the vertical coordinate, ϕ is the angle of rotation measured from the apex, and s is the arc length. Equations (2) are subject to the initial conditions

$$x(s=0) = z(s=0) = \phi(s=0) = 0, \tag{3}$$

where β is the Bond number defined earlier, Eq. (1), in which R_0 is taken to be the radius of curvature at the apex.

Numerous techniques, summarized by del Rio and Neumann [7], have been employed to solve the system of differential equations given by Eqs. (2) and (3). In the present paper, we have chosen to use a version of the well-known Runge–Kutta approach, specifically the fourth and fifth order Runge–Kutta–Dormand–Prince pair, which is an efficient solver allowing for intermediate step sizes to be calculated with almost no increase in computational time [11]. This scheme increases the accuracy of the fitting routine without increasing computational time for the numerous