Axisymmetric Drop Shape Analysis: Computational Methods for the Measurement of Interfacial Properties from the Shape and Dimensions of Pendant and Sessile Drops

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Numerous methodologies have been developed for the measurement of interfacial tensions and contact angles, as outlined in Refs. (8, 9). Of these, axisymmetric drop shape analysis (ADSA) methods are considered to be the most powerful because of their accuracy, simplicity, and versatility (3, 10). They are also very suitable for automated computer implementation by means of digital image analysis (2).

ADSA methods are based on the numerical fit between the shape of experimental drops (or bubbles) and the mathematical model given by the classical Laplace equation of capillarity. They are applicable to pendant and sessile drops in a very wide range of surface tensions, for any fluid–liquid system that can be represented by the Laplace equation of capillarity. Early efforts in the analysis of axisymmetric drops to determine surface tensions were those of Bashforth and Adams (11) and Maze and Burnet (12), who developed the numerical strategy on which modern methods are based, i.e., the numerical integration of the Laplace equation and the use of nonlinear least-squares optimization techniques. The most powerful and widely used method to date is that of Rotenberg et al. (1), called axisymmetric drop shape analysis—profile (ADSA-P). Jennings and Pallas (10) developed a similar method, built on Rotenberg and colleagues’ work, in an attempt to make the method computationally more efficient, but they introduced numerical simplifications that affect the accuracy of the method.

Another advantage of ADSA methods is that contact angles, as well as volume and surface area, can be computed simultaneously. This led to the development of axisymmetric drop shape analysis—diameter (ADSA-D), which computes contact angles based on the volume and diameter of sessile drops with known surface tension (13, 14). ADSA-D is particularly powerful for low contact angles (e.g., $\theta_c < 20^\circ$) where other methods present difficulties.

Another popular method for estimating surface tensions is the one developed by Malcolm and Elliott (15), which uses a semiempirical equation to approximate surface ten-
FIG. 1. Coordinate system used in the numerical solution of the Laplace equation for axisymmetric liquid–fluid interfaces.

s

\( x(0) = z(0) = \theta(0) = V(0) = A(0) = 0, \) [1f]

where \( b \) is the curvature at the origin of coordinates and \( c = (\Delta \rho) g / \gamma \) is the capillary constant of the system. \( \theta \) is the tangential angle which, for sessile drops, becomes the contact angle \( \theta_c \) at the three-phase contact line. Although the surface area \( A \) and the volume \( V \) are not required to define the Laplacian profile, they are included here because of their importance and the fact that they can be integrated simultaneously with little computational overhead. It should also be noted that since at the apex of the drop,

\[ \sin \frac{\theta}{x} = b \quad \text{at} \quad s = 0, \]

then Eq. [1c] becomes

\[ \frac{d\theta}{ds} = b \quad \text{at} \quad s = 0, \] [1g]

which avoids a division by zero, and there is no need to use analytical approximations to initialize the integration as done by Dimitrov et al. [21].

For given values of \( b \) and \( c \), a unique shape of a Laplacian fluid–liquid interface can be obtained by simultaneous integration of the above initial value problem. However, there is no known analytical solution for this problem, except for very limited cases, and a numerical integration scheme must be used, as implemented in the axisymmetric liquid–fluid interfaces (ALFI) computer program described below.

There exist several numerical methods to solve systems of ordinary differential equations for initial value problems and considerable research is still devoted to this subject [22]. The three major types of methods most commonly used are the Runge–Kutta, Burlisch–Stoer extrapolation, and predictor–corrector methods [23]. For simple equations and when efficiency is of no concern, fixed stepsize implementations are often used, but they are not suitable when accuracy and computational efficiency are important. Hartland and Hartley [24] used a fourth-order Runge–Kutta method with truncation error control to solve the Laplace equation [1]. Rotenberg et al. [1] and Jennings and Pallas [10] implemented a second-order implicit Euler method. After testing and comparing other methods, it was found that the Burlisch–Stoer scheme with adaptive stepsize control is

\[ \frac{dV}{ds} = \pi x^2 \sin \theta, \] [1d]

\[ \frac{dA}{ds} = 2\pi x, \] [1e]
computationally efficient but it can fail for large drops with very low surface tension.

A more efficient and flexible method is the fifth- and sixth-order Runge–Kutta–Verner pair, as implemented by Hull, Enright, and Jackson in the DVERK FORTRAN numerical routines (25, 26). Some important features of this code are its defect-based error and stepsize control that allows large integration steps with controlled accuracy, its flexible design that allows the calling program to interrupt and continue the integration after any step, and its capability to produce continuous approximations to the solution on each step using very accurate interpolations. These features are important to improve the speed and accuracy of ADSA computations, where numerous integrations are required, as described later.

ALFI was written, implementing the Hull–Enright–Jackson numerical integration scheme, to generate Laplacian profiles of pendant and sessile drops of any size and surface tension by numerically integrating the initial value problem [1]. The following are some of the features of ALFI:

- The volume \( V \) and surface area \( A \) are computed simultaneously with the drop profile with negligible computational overhead. These properties are useful in applications such as the ADSA film balance (27).
- The integration can be stopped when any given values of \( s, \theta, x, z, V, \) or \( A \) are reached, allowing the computation of drop profiles of any specified contact angle, volume, surface area, or size. The integration also terminates if \( \theta \) reaches 180° (sessile drops) or becomes negative (pendant drops).
- The inflection point of pendant drops is accurately computed, which is useful for testing and evaluating drop profile methods.
- The origin of the coordinate system can be translated and rotated arbitrarily, and the coordinates can be scaled in the horizontal and vertical directions. This feature permits the comparison between theoretical and experimental drop profiles which have generally an arbitrary origin of coordinates, can be vertically misaligned due to a vertical misalignment of the video camera, and have an arbitrary magnification.
- The profile coordinates can be randomly perturbed in the normal direction, allowing the simulation of experimental errors, which can be used to evaluate ADSA methods.

ALFI has been found very useful not only in producing tables and plots of Laplacian data as done by Hartland and Hartley (24) and by Bashforth and Adams (11), but it is also a very important tool to test and evaluate drop shape analysis methods, as described later.

As mentioned before, ALFI generates complete Laplacian profiles from values of \( b \) and \( c \) by integrating the initial value problem [1]. The inverse process of determining \( b \) and \( c \) (from which \( \gamma \) and contact angle \( \theta_c \) can be easily computed) based on drop profile characteristics is a more difficult task and forms the basis of the ADSA methods described in the following sections.

### 3. CONTACT ANGLE MEASUREMENTS FROM DIAMETER AND VOLUME OF SESSILE DROPS (ADSA-D)

The ADSA-D methodology to compute contact angles \( \theta_c \) from the contact or maximum diameter \( D \) (usually measured from a picture of the drop looking from above) and volume \( V \) of sessile drops with known surface tension \( \gamma \) was originally developed by Skinner et al. (13) and Moy et al. (14). The basic scheme of their implementation was to generate Laplacian profiles by integration of [1] for different values of \( b \), comparing the measured and the computed volumes at the given diameter, until convergence, employing a Newton iteration. However, this approach, also known as single shooting, has numerical deficiencies and can fail if the initial values are distant from the solution. In this section, a boundary-value-problem approach to ADSA-D is described, which is numerically more stable and easier to implement.

As in the original ADSA-D, there are two cases to consider—(1) \( \theta_c \geq 90^\circ \) and (2) \( \theta_c < 90^\circ \)—which represent two separate boundary-value problems since in the first case the maximum diameter corresponds to the equatorial diameter of the drop (at \( \theta = 90^\circ \)) and in the second case the maximum diameter corresponds to the three-phase contact line (at \( \theta = \theta_c \)) (see Fig. 2).

#### a. Contact Angle Greater than or Equal to 90°

Rewriting equations [1a]–[1c] as functions of \( x \), considering the curvature \( b \) as a new variable, and with the boundary conditions as seen in Fig. 2a, the Laplace equation can be written as the following boundary-value problem for \( \theta_c 

\[ \frac{d\theta}{dx} = \frac{1}{\cos \theta} \left( 2b + cz - \frac{\sin \theta}{x} \right) \]  
[2a]

\[ \frac{dz}{dx} = \tan \theta, \]  
[2b]

\[ \frac{db}{dx} = 0, \]  
[2c]

\[ z(0) = \theta(0) = 0, \quad \theta(R) = \frac{\pi}{2} \]  
[2d]

where \( R = D/2 \) is the maximum (equatorial) radius. Problem [2] completely defines the Laplacian shape: its solution gives directly the profile shape for \( 0 \leq x \leq R \), and the constant value of the apex curvature \( b \). The contact angle
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additional numerical integration since the contact angle can be obtained simply from \( \theta_c = \theta(R) \).

To initialize ADSA-D it is necessary to determine, for given values of \( V_c \) and \( R \), whether \( \theta_c \leq 90^\circ \) (problem [2]) or \( \theta_c < 90^\circ \) (problem [3]). On occasion, the user can give this information as input, but in many cases, especially for \( \theta_c \) near 90°, it is not known. The approach implemented in the program is (1) if the user knows whether the drop is wetting (\( \theta_c \leq 90^\circ \)) or nonwetting (\( \theta_c > 90^\circ \)), solve the respective problem and exit; otherwise, (2) assume \( \theta_c \approx 90^\circ \) and solve problem [2] for the given \( R \), and compute volume \( V_{90} \) at \( \theta = 90^\circ \) by numerically integrating [1]. If \( V_{90} \leq V_c \) the initial assumption was correct, compute \( \theta_c \), and exit; otherwise, (4) solve problem [3] for \( \theta_c \approx 90^\circ \).

The nonlinear problems [2] and [3] must be solved numerically. Numerical methods to solve boundary-value problems can be divided into two main categories (28, 29): initial value or shooting methods, and finite difference or collocation methods. The original implementation of ADSA-D used a variation of the single shooting method, which is known to have stability drawbacks. Multiple shooting methods are more stable but, after some tests, they were found to be inefficient for Laplacian problems, particularly for well-deformed drop shapes. A more efficient approach is the use of finite-difference methods with collocation formulas, as implemented in the COLSYS FORTRAN library by Ascher and Bader (28), which uses collocation at Gaussian points to approximate the solution.

FIG. 2. Boundary conditions for ADSA-D boundary-value problems [2] and [3]. (a) Contact angle greater than or equal to 90°; (b) contact angle less than 90°.

\( \theta_c \) can then be computed by integrating Eq. [1], for the known values of \( b \) and \( \gamma \), past the maximum diameter, stopping when the computed volume reaches the drop volume, \( V_c \). This problem thus requires a boundary-value problem solver plus a numerical integration.

b. Contact Angle Less than 90°

Similarly, as seen in Fig. 2b, the Laplace equation for \( \theta_c < 90^\circ \) can be written as the following boundary-value problem:

\[
\frac{d\theta}{dx} = \frac{1}{\cos\theta} \left( 2b + cz - \sin\theta \right), \quad [3a]
\]

\[
\frac{dz}{dx} = \tan\theta, \quad [3b]
\]

\[
\frac{dV}{dx} = \pi x^2 \tan\theta, \quad [3c]
\]

\[
\frac{db}{dx} = 0, \quad [3d]
\]

\[
z(0) = \theta(0) = V(0) = 0, \quad V(R) = V_c. \quad [3e]
\]

Here \( V_c \) is the total volume of the drop. Problem [3] completely defines the Laplacian shape. There is no need for an

4. SURFACE TENSION MEASUREMENTS FROM HEIGHT AND DIAMETER OF SESSILE AND PENDANT DROPS (ADSA-HD)

Several methods to approximate \( \gamma \) from the height \( H \) and diameter \( D \) of sessile drops, based on semiempirical equations and/or Laplacian tables, have been developed in the past (15, 16). However, these methods are restricted to special cases (e.g., sessile drops with \( \theta_c \approx 180^\circ \)) and their accuracy is limited for a certain range of height/diameter ratios (20), even when perfect numerical data are used.

In this section a boundary-value-problem approach to this
A definition of the problem can be applied to pendant and sessile drops. Here, the problem is presented, which is exact (to a specified numerical tolerance) and general: it is applicable to sessile drops (wetting and nonwetting) and pendant drops, and it can be used with any measured height and diameter, not necessarily the equatorial diameter and maximum height.

The most general case, as shown in Fig. 3, can be defined by the following boundary-value problem, written as a function of the tangential angle, with both the apex curvature $b$ and the capillary parameter $c$ as unknown constants:

\[
\begin{align*}
\frac{dx}{d\theta} &= \cos \theta \left( 2b + cz - \frac{\sin \theta}{x} \right)^{-1}, \quad [4a] \\
\frac{dz}{d\theta} &= \sin \theta \left( 2b + cz - \frac{\sin \theta}{x} \right)^{-1}, \quad [4b] \\
\frac{db}{d\theta} &= 0, \quad [4c] \\
\frac{dc}{d\theta} &= 0. \quad [4d]
\end{align*}
\]

\[x(0) = z(0) = 0, \quad x(\theta_1) = R, \quad z(\theta_2) = H. \quad [4e]\]

Here $R = D/2$. Problem [4] completely defines the drop shape; its solution determines the profile coordinates for any $\theta$, as well as the (constant) values of $b$ and $c$ from which $\gamma$ and other drop properties, e.g., $\theta_0$, $V$, and $A$, can be readily computed by the numerical integration of [1]. The same definition of the problem can be applied to pendant and sessile (wetting and nonwetting) drops. The only limitation is that, for pendant drops, the boundary conditions at $\theta_1$ and $\theta_2$ must be measured before the inflection point ($\theta_{inf}$ in Fig. 3) for the problem to have a unique solution. In the general case, problem [4] is a three-point boundary-value problem; if $H$ and $D$ are measured at the same location, i.e., $\theta_1 = \theta_2$, it becomes a two-point boundary-value problem.

As in the ADSA-D implementation (see above), the COLSYS library can be used to solve problem [4], taking advantage of its ability to handle multiple-point boundary conditions. The algorithm in this case is initialized using an elliptical fit that satisfies the boundary conditions [4e], an initial curvature equal to the curvature of the fitted ellipse at the origin, and the capillary parameter is initialized with a user-supplied value, which can be a very rough estimate, as seen in Section 9. A continuation algorithm has also been implemented in case COLSYS fails initially.

5. SURFACE TENSION MEASUREMENTS BY DROP PROFILE FITTING OF SESSILE AND PENDANT DROPS (ADSA-P)

The ADSA-P methodology to determine interfacial properties by means of a numerical fit of several arbitrary drop profile coordinates to the Laplace equation was originally developed by Rotenberg et al. (1) using a four-parameter nonlinear least-squares fit with a Newton optimization scheme and incremental loading or parameter continuation. This method has been used successfully to measure interfacial tensions in a variety of systems for several years (4) but it has presented convergence problems for some systems with ultralow interfacial tension and very flat drop shapes because of the limitations of Newton’s method when the initial parameters are distant from the solution. A new version of ADSA-P is presented in this section, implementing additional optimization parameters and more efficient and globally stable numerical methods. Also, the original optimization parameters have been redefined, using the curvature at the apex $b$ instead of the radius of curvature ($R_0 = b^{-1}$) and making the parameters independent of each other, which simplifies the algebra and the numerical analysis.

Similarly to the original ADSA-P, the strategy used is to construct and minimize an objective function $E$, defined as the sum of the weighted squared normal distances between any $N$ profile coordinates and the Laplacian profile (problem [11]), as seen in Fig. 4:

\[
E = \sum_{i=1}^{N} w_i e_i, \quad [5a]
\]

\[e_i = \frac{1}{2} d_i^2 = \frac{1}{2} [(x_i - X_i)^2 + (z_i - Z_i)^2]. \quad [5b]\]

Here, $w_i$ is a weighting factor, $(X_i, Z_i)$ are the measured drop coordinates, and $(x_i, z_i)$ are the Laplacian coordinates closest to $(X_i, Z_i)$. Currently, $w_i$ is set equal to 1.0 until more studies are available on the effect of weighting factors. By introducing the generally unknown origin $(x_0, z_0)$ and
angle of rotation of the system of coordinates \( \alpha \), and scaling factors on both coordinates \((X_s, Z_s)\), the individual error can be written (dropping the subscript \(i\)) as

\[
e = \frac{1}{2}(e_x^2 + e_z^2),
\]

\[
e_x = x - x_0 - X_sX \cos \alpha + Z_sZ \sin \alpha, \quad [5d]
\]

\[
e_z = z - z_0 - X_sX \sin \alpha - Z_sZ \cos \alpha. \quad [5e]
\]

The objective is therefore to compute the set of \( M \) optimization parameters \( a \) that minimizes [5], where \( a = [b \ c \ x_0 \ z_0 \ \alpha \ X_s \ Z_s]^T \) or any subset of it. This definition is more general than the four parameters used by Rotenberg et al. and is similar to the parameter set used by Jennings and Pallas (10). It should be noted though that only one of the scaling factors, \( X_s \) or \( Z_s \), can be optimized simultaneously with \( b \) and \( c \) for the solution to be unique. Generally one of the scaling factors is known from the experimental setup and can be held constant while optimizing the other to correct for the aspect ratio to calibrate the optical system. The rotational angle \( \alpha \) can also be optimized to correct for the rotational misalignment of the camera for calibration purposes, but it can be held constant once the system has been calibrated, provided the camera has not been moved.

The optimization problem can be written as

\[
\min_a E(a) = \sum_{i=1}^{N} w_i e_i(a).
\]

Problem [6] is a multidimensional nonlinear least-squares problem that requires an iterative optimization procedure. When the minimum has been found, the optimization parameters determine the Laplacian profile that best fits the given profile, from which \( y \) and other properties can be readily computed.

Evaluating \( E \) for a trial set of \( a \), i.e., for each optimization iteration, involves determining the minimum (normal) distance from the Laplacian curve to each experimental point. This is done using a one-dimensional Newton–Raphson iteration to solve, for each \( i \)th point,

\[
f(s) = \frac{de}{ds} = e_x \cos \theta + e_z \sin \theta = 0.
\]

This procedure requires several numerical evaluations of the initial value problem [1] for each data point, and in previous versions of ADSA-P it required several numerical integrations of [1] (approximately \( 3N \) integrations) that made the evaluation of \( E \) computationally expensive. With the implementation of the numerical integration package of Hull, Enright, and Jackson, DVERK, only one integration of [1] is necessary to evaluate \( E \) for any given set of the parameters \( a \), and any intermediate values are computed with the inexpensive and equally accurate function approximation routine of DVERK, called INTRP (26).

In the work of Jennings and Pallas the residuals are computed using a linear interpolation in an attempt to reduce computational time. However, this approach introduces larger errors on sections of the drop with larger curvature and is not suitable for highly curved surfaces. The Newton–Raphson approach implemented in ADSA-P is exact, to the given numerical tolerance, for all curvatures and drop profiles.

There exist several numerical methods to solve optimization problems. Among them, Newton’s method is well known for its second-order convergence if the initial values are very close to the solution, but it is unpredictable otherwise, particularly for multidimensional problems. To overcome this problem, several Newton-like algorithms have been developed with more advanced convergence strategies. The original ADSA-P used Newton’s method with incremental loading to approach the solution, but this approach is computationally expensive and its convergence is not guaranteed. Jennings and Pallas (10) used a modified Gauss–Newton method with restricted step. Another method commonly used for nonlinear least-squares optimization is the Levenberg–Marquardt algorithm which can be described as a trust-region implementation of the Gauss–Newton method (30).

In this version of ADSA-P, a combination of the Newton and Levenberg–Marquardt methods were implemented. Very often, as in the case of time-dependent studies, the results from a previous run can be used as initial values and Newton’s method can be used to take advantage of its fast convergence. The FORTRAN linear algebra packages LAPACK and BLAS were used to solve the system of equations to compute the Newton iteration steps. The Newton optimization is aborted as soon as divergence is detected or if the Hessian matrix is found to be nonpositive-definite (27).
If good initial values are not available or if Newton’s method fails, the Levenberg–Marquardt method is used. This method takes advantage of numerical properties particular to least-squares problems, is known to be globally convergent, and needs only first-order derivatives to build the Jacobian matrix. The numerical implementation chosen here is the Levenberg–Marquardt with derivative (LMDER) routines from the FORTRAN MINPACK library developed by Moré and Wright (31).

Both the first derivatives needed to construct the Jacobian matrix used by LMDER and the second derivatives needed to construct the Hessian used by Newton’s method are computed with the same degree of accuracy as the objective function by simultaneous numerical integration of the derivatives together with the integration of [1], as described in Ref. (1). This involves the simultaneous numerical integration of a system of 11 first-order ordinary differential equations for the LMDER routines and 20 for the Newton method.

Of the seven possible optimization parameters, the most difficult one to initialize is the capillary parameter \( c \). It can be initialized with either a call to ADSA-HD, with results from a previous run (e.g., time-dependent studies), or with user-supplied values. The effect of this initial value on the performance of the program is evaluated in Section 10. Good initial values for \( b \), \( x_0 \), and \( z_0 \) can be found by a least-squares elliptical fit of several points near the drop apex, and the rotational angle \( \alpha \) and the scaling factors \( X_s \) and \( Z_s \) are generally known from the experimental setup.

6. TESTING AND EVALUATION PROCEDURE

The evaluation of ADSA methods requires that drop profiles of known surface tension and apex curvature be given as input data, so the numerical results can be compared with the known values of the parameters. Since experimental values of surface tension and curvature are generally uncertain or unknown, the evaluation of ADSA numerical methods is best done by means of “synthetic” or theoretical drops, obtained by numerical integration of the Laplace equation. Another advantage of using synthetic drop profiles is that the sensitivity of the methods can be easily measured by perturbing the input data to simulate experimental errors, and comparing the results with the known exact solution.

The following sections describe how the ALFI program was used to generate synthetic profiles to test and evaluate the ADSA methods presented above. The computational times were measured on a Sun SPARCstation 10 (60-MHz SuperSPARC CPU) and are presented here only as reference. Comparative or even faster performance can be obtained on other computer systems, e.g., Intel Pentium personal computers.

7. TESTING AND EVALUATION OF ALFI

The numerical profiles obtained with ALFI agree, within a specified numerical precision, with those published by Hartland and Hartley (24) and with other numerical integration schemes tested; they are not reproduced here. By tracing the numerical integration steps, it was found that, as the numerical integration routine DVERK automatically adjusts the stepsize along the profile to control the estimated numerical errors, small steps are usually needed near the drop apex and increasingly larger steps (compared to the total arc length) afterward.

Several drop profiles, both sessile and pendant, were generated during the testing and evaluation of the programs. Figure 5 shows some selected profiles with a variety of drop shapes, with the corresponding parameters shown in Table 1. The capillary parameter \( c = 13.45 \text{ cm}^2 \) used for some of the profiles corresponds to a value typical of a water–air system. The computational performance of ALFI is of the order of 0.05 s to produce 100 plotting points for each drop. A numerical tolerance of \( 10^{-8} \) was used to generate the drop profiles.

8. TESTING AND EVALUATION OF ADSA-D

ADSA-D requires as input \( c \), \( R \), and \( V \) of a sessile drop, and returns the contact angle \( \theta_c \). Table 2 shows the results of running ADSA-D for sessile drops S1–S5 with arbitrarily

![Figure 5](https://via.placeholder.com/150)
selected contact angles. The input values were obtained from the data generated by ALFI for the respective contact angles. A numerical tolerance of 10^{-6} was used in the computations. It can be seen that ADSA-D returns the correct contact angle with negligible errors in all the cases. Table 2 also shows the computational time required to run ADSA-D. Its performance is always satisfactory, with better performance for contact angles less than 90° (less than 0.5 s). In all the cases tested, the method succeeded in the first call to the boundary problem solver COLSYS; i.e., parameter continuation was not required.

To evaluate the sensitivity of the method to experimental errors, each input parameter can be perturbed by a small amount δ, comparing the resulting contact angles with the original one. In practice, V can be measured with a micrometer syringe with an accuracy of 10^{-5} cm^3 (0.01 μl). D can be measured using digital image analysis with an accuracy better than 0.15% (approximately one pixel on a 640 × 480 image), and c can be obtained with an accuracy better than 1.0%. These experimental errors would produce the contact angle errors shown in Table 3, where each row shows the error obtained by perturbing each input parameter (keeping the others constant) and the last row is the maximum combined error obtained by perturbing all the input parameters. The tests show that the method is not very sensitive to experimental errors for small contact angles, for which the best results are obtained (e.g., an error of less than 0.5° for contact angles less than 30° and less than 1° for contact angles less than 90°). For contact angles greater than 90° the method is more sensitive and more accurate measurements are required for good results.

These results agree with the experimental results obtained by Skinner et al. in the evaluation of the original ADSA-D method (13). The effect of nonaxisymmetry of the drops was also addressed by Skinner et al. The larger errors for contact angles greater than 90° are due to the faster angular change of the drop profiles below the maximum diameter, which causes larger changes in contact angle for small perturbations of any parameter, especially for large values of c. Note that drop S5 with θ_e = 180°, which produced the largest errors, corresponds to a very large value of c. Also, for drop S1 with θ_e = 5° the maximum error is due to the very small volume of the drop, but with a more accurate volume measurement the error would be negligible.


The only input required by ADSA-HD is coordinate information (x, y, z) of one or two arbitrarily selected profile points, from which c (therefore γ) is computed. See Eq. (4). The points of maximum diameter and maximum height are usually chosen since they are easier to measure, but the method is not limited to any particular locations. In practice these coordinates can be accurately measured from a digital image.

Table 4 shows the results and performance of ADSA-HD for the sessile and pendant drops of Fig. 5 using arbitrarily selected boundary points. D, H, θ_1, and θ_2 are the input data, t is the computational time required to run the program, c is the output capillary constant, and c_{error} is the output error. A tolerance of 10^{-6} was used, and the initial value of c was always given with an error greater than or equal to 25% of the exact solution, e.g., c_{init} = 0.1, 10, 500 for c = 1, 13.45, 1000, respectively. Every run shown in the table converged in the first iteration (i.e., no parameter continuation was required) in less than 0.5 s, except for pendant drop P3 which required two continuation iterations, hence the longer computational time. It can be seen that the method is not very sensitive to the initial estimate of c. The program succeeded for all the sessile and pendant drops tested with relative numerical errors within the specified tolerance.

To evaluate the sensitivity of the method to experimental errors, the input values of H and D were perturbed by 0.15%
of the original values (approximately one pixel on a 640 × 480 digital image), and the resulting value of \( c \) was compared with the original one. These results are shown in Table 5. It can be seen that the sensitivity of the method varies from drop to drop, with errors of less than 1% for some drops but higher errors in other cases. This behavior depends on the slope of the multidimensional topology of the given problem and seems to be unpredictable, but it can be evaluated by perturbing the input data by the estimated measurement errors as described above. Further tests show that, for a given drop, the error becomes smaller when the input data are measured at larger angles \( \theta_1 \) and \( \theta_2 \); e.g., the error obtained using data points near \( \theta = 180^\circ \) for drop S4 is approximately 1%.

### 10. Testing and Evaluation of ADSA-P

ADSA-P differs from the other ADSA methods in that it requires as input an arbitrary number \( N > M \) of profile coordinates, where \( M \) is the number of optimization parameters. To test the accuracy of the algorithm, synthetic drops S1–S5 and P1–P5 were given as input to the program, using \( N = 21 \) points and a numerical tolerance of \( 10^{-8} \). The results are shown in Table 6. It can be seen that the numerical errors are negligible.

As mentioned earlier, the ADSA-P optimization algorithm requires as input the initial values of the optimization parameters, which, except for the capillary constant \( c \), can be estimated using an elliptical least-squares fit. To evaluate the global convergence and the sensitivity of the method to the initial value of \( c \), a wide range of initial values were given as input to the program and the results are shown in Table 7 for both Newton and Levenberg–Marquardt optimization methods. It can be seen that the Levenberg–Marquardt method succeeds for any initial value of \( c \) without a significant increase in computational time, while the Newton method succeeds only if the initial value is very close to the exact solution (±10% in this particular case). However, when successful, the Newton method is considerably faster than the Levenberg–Marquardt method.

Figure 6 shows the computational performance of the methods when different numbers of data points \( N \) are used. For the Newton optimizations, initial values of 0.9 \( c \) were used. It can be seen again that the Newton method is considerably faster but it failed to converge for drops S1, S4, and S5, while the Levenberg–Marquardt method succeeded in all the cases.

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### Table 3

<table>
<thead>
<tr>
<th>Drop</th>
<th>( \theta_1 ) (deg)</th>
<th>( \theta_2 ) (deg)</th>
<th>( t ) (s)</th>
<th>( c ) (cm(^{-2}))</th>
<th>( c_{\text{error}} ) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>6.5652</td>
<td>4.578</td>
<td>90</td>
<td>120</td>
<td>13.45</td>
</tr>
<tr>
<td>S2</td>
<td>1.1152</td>
<td>0.503</td>
<td>10</td>
<td>10</td>
<td>13.45</td>
</tr>
<tr>
<td>S3</td>
<td>0.0965</td>
<td>0.0793</td>
<td>80</td>
<td>80</td>
<td>13.45</td>
</tr>
<tr>
<td>S4</td>
<td>0.4849</td>
<td>0.1278</td>
<td>30</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>S5</td>
<td>0.1401</td>
<td>0.0664</td>
<td>90</td>
<td>180</td>
<td>1000.0</td>
</tr>
</tbody>
</table>

---

### Table 4

<table>
<thead>
<tr>
<th>Drop</th>
<th>( D/2 ) (cm)</th>
<th>( H ) (cm)</th>
<th>( \theta_1 ) (deg)</th>
<th>( \theta_2 ) (deg)</th>
<th>( t ) (s)</th>
<th>( c ) (cm(^{-2}))</th>
<th>( c_{\text{error}} ) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.6562</td>
<td>0.4578</td>
<td>90</td>
<td>120</td>
<td>0.35</td>
<td>13.45</td>
<td>&lt;1.0e-07</td>
</tr>
<tr>
<td>S2</td>
<td>1.1152</td>
<td>0.503</td>
<td>10</td>
<td>10</td>
<td>0.47</td>
<td>13.45</td>
<td>&lt;1.0e-07</td>
</tr>
<tr>
<td>S3</td>
<td>0.0965</td>
<td>0.0793</td>
<td>80</td>
<td>80</td>
<td>0.35</td>
<td>13.45</td>
<td>4.0e-07</td>
</tr>
<tr>
<td>S4</td>
<td>0.4849</td>
<td>0.1278</td>
<td>30</td>
<td>30</td>
<td>0.35</td>
<td>1.0</td>
<td>&lt;1.0e-07</td>
</tr>
<tr>
<td>S5</td>
<td>0.1401</td>
<td>0.0664</td>
<td>90</td>
<td>180</td>
<td>0.45</td>
<td>1000.0</td>
<td>9.8e-05</td>
</tr>
</tbody>
</table>

---

### Table 5

<table>
<thead>
<tr>
<th>Drop</th>
<th>( R ) (nm)</th>
<th>( H ) (nm)</th>
<th>( c ) (cm(^{-2}))</th>
<th>( c_{\text{error}} ) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.11</td>
<td>0.050</td>
<td>7.13</td>
<td>8.85</td>
</tr>
<tr>
<td>S2</td>
<td>0.41</td>
<td>0.35</td>
<td>7.42</td>
<td>9.16</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.52</td>
<td>0.40</td>
<td>14.57</td>
<td>18.07</td>
</tr>
</tbody>
</table>

---

\( ^a \) Each row represents the error obtained by perturbing the parameters \( R \) and \( H \), simulating typical experimental errors. The maximum error corresponds to the worst-case scenario of perturbing both \( R \) and \( H \).
TABLE 6
Numerical Results of ADSA-P for Sessile (S) and Pendant (P) Drops Using \( N = 21 \) Points

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c (\text{cm}^{-2}) )</td>
<td>13.45</td>
<td>13.45</td>
<td>13.45</td>
<td>1.0</td>
<td>1000.0</td>
</tr>
<tr>
<td>( e_{\text{c}} ) (cm²)</td>
<td>7.0e-08</td>
<td>7.6e-06</td>
<td>2.7e-04</td>
<td>8.1e-07</td>
<td>8.3e-05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c (\text{cm}^{-2}) )</td>
<td>−13.45</td>
<td>−13.45</td>
<td>−13.45</td>
<td>−1.0</td>
<td>1000.0</td>
</tr>
<tr>
<td>( e_{\text{c}} ) (cm²)</td>
<td>2.4e-06</td>
<td>2.0e-06</td>
<td>1.3e-04</td>
<td>3.6e-06</td>
<td>3.6e-03</td>
</tr>
</tbody>
</table>

To simulate the effect of experimental errors on ADSA-P, ALFI was used to randomly perturb the Laplacian profiles with a maximum normal perturbation of approximately one pixel of a 640 × 480 digital image. Sessile drops of various contact angles and pendant drops from the apex to the inflection point were used, as seen in Table 8. The inflection points of the pendant drops were used only for convenience; ADSA-P is not limited by nor needs information about the inflection point. It can be seen that the larger errors correspond to sessile drops of low contact angle and pendant drop P3, which does not have an equatorial diameter or a "neck." Otherwise, the accuracy is better than 1% for sessile drops with \( \theta_c > 90^\circ \) and better than 0.5% for pendant drops with a neck, particularly when using \( N \approx 50 \) points.

11. DISCUSSION

Recent advances in ADSA techniques have been presented in this paper: new versions of the ADSA-D and ADSA-P methods that overcome the main limitations of earlier versions, e.g., numerical instability and failure to converge for certain ultralow interfacial tensions and well-deformed drop shapes, and a new method called ADSA-HD that computes surface tension from the height and diameter of sessile and pendant drops. Advanced, general-purpose numerical methods that are well known for their numerical stability have been used, making the software more flexible and easier to implement. No numerical simplifications were made, to make the programs as accurate as possible. This strategy has proven successful as can be seen by the wide range of applicability of the methods, i.e., the wide range of surface tensions, drop sizes, and variety of drop shapes for which the programs succeed. Ultralow interfacial tensions and well-deformed drop shapes are no longer a limitation of the methods.

Numerical simulations, performed with the aid of a program that generates theoretical drop profiles (ALFI), show the applicability of the methods. Contact angles can be measured with an accuracy better than 1° with ADSA-D from the volume and diameter of sessile drops, and an accuracy of 0.1° is readily obtainable for drops with low contact angles, e.g., \( \theta_c < 30^\circ \). However, more accurate measurements are required to obtain accurate contact angles for drops near 180° contact angle. ADSA-HD can be used to estimate surface tension by measuring only height and diameter of a pendant or sessile drop with an accuracy of about 2% for drops with an equatorial diameter, i.e., sessile drops with \( \theta_c \geq 90^\circ \) and pendant drops with a neck. ADSA-P can be used for more accurate surface tension measurements, with which an accuracy better than 0.5% is readily obtainable, with better results for pendant drops with a neck and sessile drops with \( \theta_c > 90^\circ \).

Since the input required by ADSA programs consists of only a few drop profile coordinate measurements, they can be used with any kind of data acquisition, although digital image analy-
Computational Results of ADSA-P for Sessile (S) and Pendant (P) Drops after Perturbing Every Profile Coordinate by a Random Normal Distance, with a Maximum Perturbation Equivalent to Approximately the Distance between Two Consecutive Pixels in a 640 \times 480 Digital Image

<table>
<thead>
<tr>
<th></th>
<th>( N = 21 )</th>
<th></th>
<th>( N = 51 )</th>
<th></th>
<th>( N = 101 )</th>
<th></th>
<th>( N = 501 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( c (\text{cm}^{-2}) )</td>
<td>( \epsilon_{\text{true}} (%) )</td>
<td>( c (\text{cm}^{-2}) )</td>
<td>( \epsilon_{\text{true}} (%) )</td>
<td>( c (\text{cm}^{-2}) )</td>
<td>( \epsilon_{\text{true}} (%) )</td>
<td>( c (\text{cm}^{-2}) )</td>
</tr>
<tr>
<td>S1, 120(^\circ)</td>
<td>13.419</td>
<td>0.22</td>
<td>13.415</td>
<td>0.26</td>
<td>13.407</td>
<td>0.32</td>
<td>13.408</td>
</tr>
<tr>
<td>S2, 10(^\circ)</td>
<td>13.428</td>
<td>0.16</td>
<td>13.733</td>
<td>2.11</td>
<td>13.700</td>
<td>1.86</td>
<td>13.517</td>
</tr>
<tr>
<td>S3, 80(^\circ)</td>
<td>14.371</td>
<td>6.84</td>
<td>16.667</td>
<td>1.61</td>
<td>13.679</td>
<td>1.70</td>
<td>13.426</td>
</tr>
<tr>
<td>S4, 30(^\circ)</td>
<td>1.146</td>
<td>14.6</td>
<td>1.035</td>
<td>3.54</td>
<td>0.953</td>
<td>4.73</td>
<td>1.020</td>
</tr>
<tr>
<td>S5, 180(^\circ)</td>
<td>991.76</td>
<td>0.82</td>
<td>992.33</td>
<td>0.77</td>
<td>991.99</td>
<td>0.80</td>
<td>993.13</td>
</tr>
<tr>
<td>P1, 110(^\circ)</td>
<td>-13.432</td>
<td>0.14</td>
<td>-13.433</td>
<td>0.13</td>
<td>-13.428</td>
<td>0.16</td>
<td>-13.425</td>
</tr>
<tr>
<td>P2, 143(^\circ)</td>
<td>-13.425</td>
<td>0.18</td>
<td>-13.436</td>
<td>0.10</td>
<td>-13.447</td>
<td>0.02</td>
<td>-13.427</td>
</tr>
<tr>
<td>P3, 18(^\circ)</td>
<td>-13.179</td>
<td>2.02</td>
<td>-12.909</td>
<td>3.40</td>
<td>-13.077</td>
<td>2.77</td>
<td>-13.305</td>
</tr>
<tr>
<td>P4, 127(^\circ)</td>
<td>-0.995</td>
<td>0.52</td>
<td>-0.996</td>
<td>0.35</td>
<td>-0.997</td>
<td>0.27</td>
<td>-0.998</td>
</tr>
<tr>
<td>P5, 109(^\circ)</td>
<td>-997.03</td>
<td>0.30</td>
<td>-996.66</td>
<td>0.33</td>
<td>-997.93</td>
<td>0.21</td>
<td>-998.06</td>
</tr>
</tbody>
</table>

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REFERENCES