MEASUREMENT OF LIQUID-FLUID INTERFACIAL TENSION BY THE PENDANT DROP METHOD USING IMAGE ANALYSIS

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Abstract. *In this work, a simple method for the measurement of liquid-fluid interfacial tension is presented. This method, supported by digital image analysis, can be used to provide a valuable physical property to technological applications of all kind as oil recovery, painting and cosmetic, etc. It consists in fitting numerically a theoretical profile obtained from a solution of the Young-Laplace equation of capillarity to the experimental pendant drop profile. Some preliminary results were obtained in the water-air system under different illumination conditions. It is shown that the pedant drop method is capable of giving a satisfatory accuracy in the experiments.*

Keywords*: Surface and Interfacial Tension, Pendant Drop Method, Image Analysis.*

1. INTRODUCTION

The liquid-fluid interfacial tension results from the disbalance of intermolecular forces at interfacial regions, in which exists an abrupt variation of the density. As a consequence, the resulting force on a molecule near the liquid-fluid interface is different from the force experienced by a molecule in a completely homogeneous region, where the resulting force is null. Therefore, this property can provide information about molecular interactions occurring at interface, in other words, how strong the cohesive and adhesion forces between the interacting fluids are. Hence, the measurement of liquid-fluid interfacial tension is very important in surface science. Beyond of the scientific aspects, the liquid-fluid interfacial tension has great technological importance in industries related to oil recovery, painting, cosmetic, etc. A very common technique used to measure the liquid-fluid interfacial tension is known as pendant drop method (Bashforth and Adams (1883), Andréas et al. (1938)). Its popularity is due to the requirement of small quantities of liquids and its applicability to many experimentally difficult situations of measurement, e.g., such as time, pressure and temperature dependence (Cheng et al., 1990).

The pedant drop method consists of taking a photograph of a suspended drop on the tip of a needle or capillary. Under equilibrium conditions, the capillary force is counterbalanced by the gravitational force, defining a physical configuration which can be described by a special form of Young-Laplace equation. The calculation of the interfacial tension is based on fitting the theoretical profile obtained from a solution of the Young-Laplace equation to the experimental pendant drop profile.

In this work, the influence of illumination on the measured values is analyzed. The analysis is performed by considering a water drop immersed in the air, for which the values of interfacial tension are well established in the literature.

2. THEORETICAL BACKGROUND

The theoretical basis of the pendant drop method for the calculation of liquid-fluid interfacial tension can be found in Anastasiadis et al. (1987) and Hartland and Hartland (1976). Under equilibrium conditions, the capillary force is counterbalanced by the gravitational force. The drop profile, $p(x,z)$, is the solution of a special form of the Young-Laplace equation, which can be written in a convenient dimensionless form as (see Figure 1):

$$\frac{d\phi}{dS} = \frac{2}{B} - Z - \frac{\sin\phi}{X}, \quad \frac{dX}{dS} = \cos\phi \quad \text{and} \quad \frac{dZ}{dS} = \sin\phi, \tag{1}$$

with the boundary conditions at the drop apex given by $X = Z = S = \phi = 0$ and $\sin\phi / X = 1/B$. In the above equations, the shape parameter, B, is defined by

$$B^2 = \frac{b^2 g \Delta\rho}{\gamma} = \left(\frac{b}{a}\right)^2 , \qquad (2)$$

where b is the radius of curvature at the drop apex, a is the capillary length, $\Delta\rho$ is the density difference, g is the gravity and γ is the interfacial tension. The variables X, Z and S are the dimensionless form of the corresponding dimensional variables x, z and s and they are related to each other through the following equations: $x = Xa$, $z = Za$ and $s = Sa$.

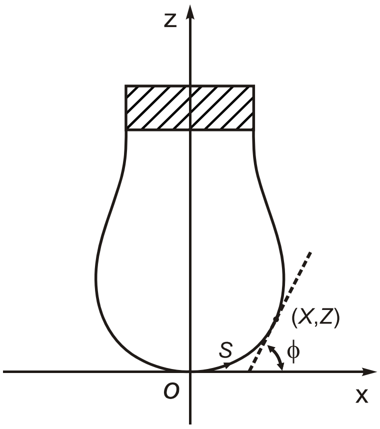


Figure 1. Schematic illustration of coordinates system and notation of symbols of the drop profile.

The calculation of the interfacial tension is based on fitting the theoretical profile obtained from a solution of the Young-Laplace equation to the experimental one. By mean of a drop shape comparison procedure, which optimizes the parameters B and a, is possible to determine the interfacial tension when the density difference and local gravity are known.

3. THE EXPERIMENTAL DROP PROFILE

As mentioned above, it is necessary to take a photograph of the pendant drop to extract the experimental drop profile using some edge detection algorithm. The experimental setup used is shown in the Figure 2. It is composed by a video-based goniometer (Model OCA20 provided by DataPhysics Instruments GmbH) connected to the computer which is responsible by the numerical calculations. First of all, an image of the pendant drop is captured using a frame grabber which generates a grayscale image with 768 x 574 pixels. After that, the experimental drop profile is extracted by a binarization procedure. The threshold gray level used in the binarization is equal to half the color range.

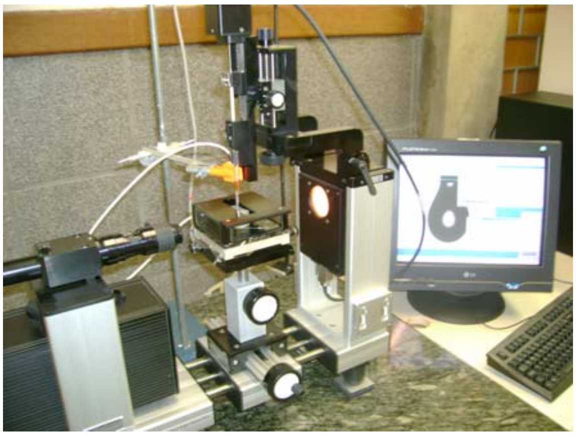
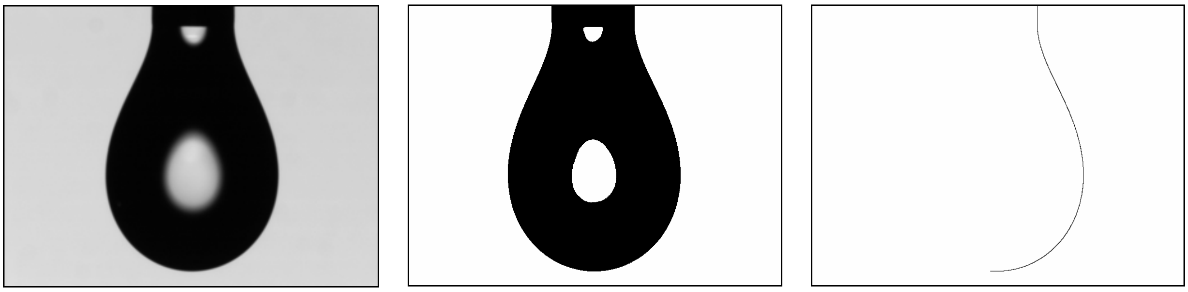


Figure 2. Experimental setup used to take the drop image.

Using a simple algorithm to perform a scanning on the binary image, it becomes possible to determine the drop apex position (x_0, z_0) and getting the experimental drop profile, $p(x, z)$. In this work, it is supposed that the experimental procedure results an axisymmetrical drop. Hence, by simplicity, it is necessary to consider only one side of the drop on the calculations. In the Figure 3 is illustrated the original image, the binarizated image and the experimental drop profile.



(a) (b) (c)

Figure 3. Extraction of the drop profile from a grayscale image. In (a) it is shown the original grayscale image, in (b) the binarizated image and in (c) the extracted drop profile.

The drop profile, $p(x,z)$, is composed by coordinate points in units of pixel. To convert $p(x,z)$ to physical units some physical dimension must be known. The natural choice is to use the needle (or capillary) external diameter which is visible in the Figure 3(a) e 3(b), whose value is known *a priori* or can be determined with a micrometer. From the needle diameter, the image resolution is obtained, i.e., the physical dimension associated to each pixel. In all experiments the needle diameter corresponds to 1.65 mm.

4. SOLUTION OF THE YOUNG-LAPLACE EQUATION

4.1 Numerical solution

The dimensionless form of the Young-Laplace equation represented by Equations 1 can be solved numerically for a given shape parameter, *B*. Some solutions of those equations for different values of *B* are shown in the Figure 4.

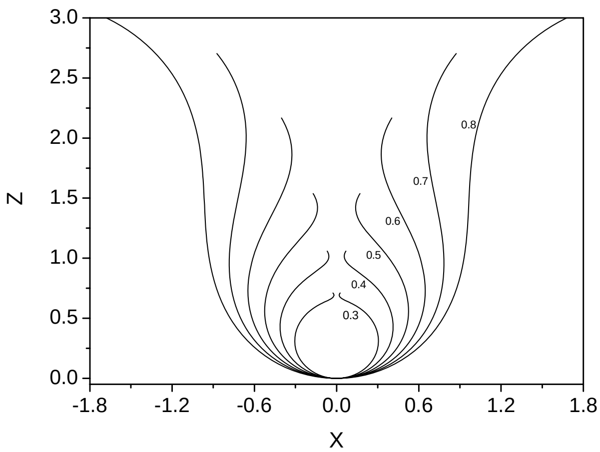


Figure 4. Solutions of the dimensionless form of the Young-Laplace equation for different values of *B*.

A very simple method to solve the Equations 1 was implemented. The method works basically according to the following procedure. Values of *X*, *Z* and ϕ are given at the origin (drop apex) of the coordinates system through the boundary conditions mentioned above. After that, new values of these three variables are estimated at the distance ΔS (here, $\Delta S = 0.001$) from the origin using a non-infinitesimal form of the Equations 1. Using the estimated values of *X*, *Z* and ϕ, new values of these variables are calculated along the drop profile and so on. Defining a maximum number of points, the entire drop profile is constructed for a given *B*.

4.2. Estimative of the shape parameter and capillary length

A good estimative of the shape parameter, *B*, and capillary length, *a*, will improve the fitting of the theoretical drop profile to the experimental one, because the demanding time necessary to satisfy the convergence criterion will be smaller. In this work, it is implemented the method of Song and Springer (1996a) which introduces a more versatile method to estimate the shape parameter based on a numerical solution of Equations 1. They used the ratio of x_φ or z_φ of two independent points on the profile, where these coordinates fulfill the following relation:

$$\left(\frac{z_\varphi - z_0}{x_\varphi - x_0}\right) = \tan\varphi\,. \tag{3}$$

According to Song and Springer (1996a), the shape parameter can be estimated by the relation:

$$B^2 = \frac{b_0 + b_1.r + b_2.r^2 + b_4.r^4}{1 + c_1.r + c_2.r^2 + c_4.r^4}\,, \tag{4}$$

where r is the ratio $z_{\varphi 1}/z_{\varphi 2}$ or $x_{\varphi 1}/x_{\varphi 2}$ of any two different φ values and b_i and c_i $(i = 0,1,2,4)$ are the fitting coefficients in the Table 1.

Table 1 – The fitting coefficients in Equation (4) for B = 0.25 – 0.8 (from Song and Springer (1996a)).

r	z_{60}/z_{30}	x_{60}/x_{30}	z_{45}/z_{30}	z_{45}/z_{30}
b_0	-90.513	-83.617	0.00418	6.31248
b_1	30.171	83.617	0.0	0.0
b_2	0.0	0.0	-0.15528	-4.73420
b_4	0.0	0.0	0.28856	0.0
c_1	-0.09398	-17.011	0.0	0.0
c_2	4.43275	36.905	-0.83765	-0.97208
c_4	0.0	0.0	0.20228	-0.51322

After the calculation of an initial shape parameter, the estimative of capillary length, *a*, is done using a least-squares fitting, in a way that *a* is determined by minimization of

$$\sum_{i,j}\left\{\left[(x_i - x_0) - X_j a\right]^2 + \left[(z_i - z_0) - Z_j a\right]^2\right\}, \tag{5}$$

with respect to *a*. With the estimative of *a* and the knowledge of density difference, $\Delta\rho$, it is possible to calculate a good value for interfacial tension, γ, using the capillary length definition, $a = \sqrt{\gamma/\Delta\rho g}$.

4.3. Optimization

The procedure mentioned above makes possible to estimate values for the shape parameter, capillary length, and consequently, for the interfacial tension. These initial values can be very useful in the more accurate determination of the interfacial tension in which the theoretical drop profile fits to the experimental one as better as possible. To optimize the value of the interfacial tension, it was used the minimization of the mean-squared shortest distance of points on theoretical and experimental profiles, *E*, according to Rotenberg et al. (1983). In this work, *E* is only a function of the shape parameter and capillary length, i.e., $E = E(B,a)$. It is interesting to keep in mind the function *E* can be dependent on others parameters as apex drop position, aspect ratio, etc., further on those considered.

5. RESULTS

To evaluate the influence of the illumination on the measurement of the interfacial tension, it was considered the water-air system under different light conditions. The experiment room was adapted for measurements under low external luminosity, in a manner the glass windows (covered with a thin dark film) allow the entrance of only one lux (unit of illuminance) orthogonally to the glass surface measured with a luximeter. It is possible to control the intensity of the light source in the goniometer by adjusting the potentiometer within a range, which allows varying the illuminance from 0 to 386 lux at the position where the drop is formed.

The Figure 5 exhibits the variation of the interfacial tension for different illumination adjustments. As it can be seen, when higher values of the illuminance are imposed, higher values of interfacial tension are obtained. Based on the values of the water-air interfacial tension related in the literature (see Table 3), it is concluded that lower values of illuminance must be used in the experiments.

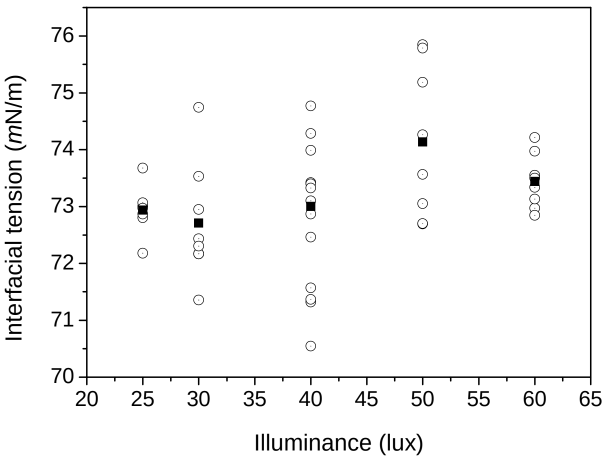


Figure 5. Influence of the illumination conditions on the measured values of water-air interfacial tensions. The mean values are represented by closed squares.

If a low viscosity fluid, e.g. water, is used in the experiments, it is observed the presence of drop oscillations when the system is not vibration free. To avoid any kind of problem associated to the system vibration, once this can insert lack of accuracy in the edge detection, the goniometer is put on a marble table together with some rubber wafers supporting the equipment. This solution showed to be efficient in the all cases considered.

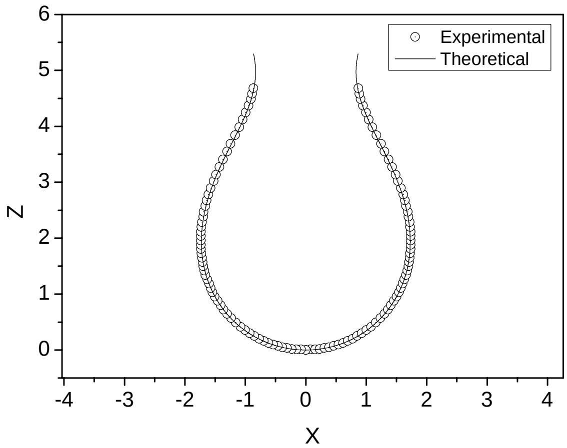


Figure 6. Theoretical and experimental drop profiles after the fitting process.

The experiments were carried out at room temperature of 24 ± 0.5°C by considering the water-air system. The illumination system was adjusted to 46 lux. The obtained results are shown in the Table 2. The Figure 6 exhibits the theoretical and experimental drop profiles after the fitting process when parameters *B* and *a* were optimized to fit those curves as better as possible. As it is seen, the superposition of them is very good.

Table 2 – Liquid-gas interfacial tension for pure water at 24 ± 0.5 °C.

Interfacial Tension (*m*N/m)*	**Standard Deviation** (*m*N/m)	**Minimum** (*m*N/m)	**Maximum** (*m*N/m)
72.8	0.7	72.1	73.6

* Mean value over 20 images

The Table 3 shows some values of interfacial tensions for water-air systems found in the literature. A comparison between these preliminary results and those from others authors shows the experimental setup and procedure adopted to extract the drop profile are suitable to provide satisfactorily accurate values for liquid-gas interfacial tensions. However, there are others factors which can affect the accuracy of the measurement (see e.g. Song and Springer (1996a, 1996b) for more details) what demands that each factor to be analyzed in a systematic way together with its dependency with a given experimental setup.

Table 3 – Values of the interfacial tension for water-air systems (from Pallas and Harrison (1990)).

Citation	**Interfacial Tension** (*m*N/m)	**Temperature** (^{o}C)
Pallas and Harrison (1990)	72.869	20
Neiderhauser and Bartell (1948)	72.00	25
Patterson and Ross (1979)	73.06	20
Sentis (1915)	72.86	20
Douglas (1950)	71.82	25
Smith and Sorg (1941)	73.0	25

6. CONCLUSIONS

Measurements of liquid-gas interfacial tensions were presented to the purpose of presenting a simple and intuitive technique to determine the liquid-fluid interfacial tension. The inspection of the theoretical background and experimental procedure shows the pendant drop method is applicable to different physical systems where the visualization of an axisymmetrical shape drop is possible. The preliminary results for the water-air interfacial tension show the illumination of the liquid drop can affect the measured value of the interfacial tension and some careful illumination conditions must be established. A comparison between these results and those found in the literature emphasizes the suitability of the method to provide satisfactorily accurate values for liquid-fluid interfacial tensions.

7. ACKNOWLEDGEMENTS

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