Measure liquid surface tension by fitting lying droplet profile

Hao Tang
School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

Abstract

This study developed a simple method to measure liquid surface tension based on curve fitting technique. In this study, the explicit lying droplet profile function in terms of surface tension was derived by solving 2-D Young-Laplace equation exactly, and the derived profile function was superior to the existing approximate profile functions. By fitting the derived profile function with the detected droplet profile image data, the liquid surface tension was then obtained. The proposed method does not rely on any new instrument, it is quite different in principle and simpler than the traditional methods.

Keyword: surface tension; curve fitting; Young-Laplace equation; lying droplet profile

1. Introduction

Aroused by the unbalanced force of the surface molecules, liquid surface tension, is defined as the force per unit length perpendicular to the boundary between two adjacent parts of the surface. Surface tension is closely related to the liquid behaviors such as adsorption, adhesion, wetting and lubrication. Therefore, it has always been an important physical quantity to evaluate the performance of surfactants, dispersants, emulsifiers, lubricants and other similar products.

Since the last century, research on the measurement methods of liquid surface tension have been relatively rich. And most of these methods are developed to measure the static surface tension of stationary surfaces in equilibrium, such as Du Noüy ring method [1],
Wilhelmy plate method [2], Spinning drop method [3], Pendant drop method [4], Capillary rise method [5], etc. As listed in Table 1, these methods are usually based on the force nature of surface tension, which means to design a special instrument to keep the liquid in equilibrium or stable, then directly obtain the surface tension by solving the force balance equation. However, the designed instrument can be complicated, and many variables are usually involved in the measurement (some need to be recorded or controlled, and others need to be measured). Therefore, this study presents a simpler method to measure liquid surface tension, no extra instrument is needed in the measurement, and the proposed method only requires the profile of lying droplet with known density.

Table 1 Typical method to directly measure the static surface tension (σ) of liquid.

| Method                        | Main principle                                                                 | Variables involved                                      | Variables need recording/controlling | Variables need measuring |
|-------------------------------|-------------------------------------------------------------------------------|---------------------------------------------------------|-------------------------------------|--------------------------|
| Du Noüy ring method [1]       | Balance among pulling force, liquid tension, gravity and buoyant force of the ring: \( F = G_{ring} - F_b + 2\pi (r_i + r_o) \sigma \) | 1. gravity of the ring, \( G_{ring} \)  
2. inner radius of the ring, \( r_i \)  
3. outer radius of the ring, \( r_o \) | 1. pulling force, \( F \)  
2. buoyant force of the ring below liquid surface, \( F_b \) |
| Wilhelmy plate method [2]     | Balance between pulling force and liquid tension: \( F = \sigma (2w + 2d) \cos \theta \) | 1. plate width, \( w \)  
2. plate thickness, \( d \) | 1. contact angle, \( \theta \)  
2. pulling force, \( F \) |
| Spinning drop method [3]      | Balance between liquid tension and centrifugal forces: \( \sigma = \rho_1 - \rho_2 \), \( \omega^2 R^3/4 \) | 1. droplet density, \( \rho_1 \)  
2. fluid density, \( \rho_2 \)  
3. angular velocity, \( \omega \) | 1. cylinder radius, \( R \) |
| Pendant drop method [4]       | Balance between liquid tension and droplet gravity: \( mg = \pi d \sigma \sin \theta \) | 1. droplet mass, \( m \)  
2. tube diameter, \( d \) | 1. contact angle, \( \theta \) |
| Capillary rise method [5]     | Jurin's law (Balance between liquid tension and droplet gravity): \( h = (2 \sigma \cos \theta) / (\rho g r) \) | 1. liquid density, \( \rho \)  
2. capillary radius, \( r \) | 1. liquid column height, \( h \)  
2. contact angle, \( \theta \) |
| Method in this study          | Young-Laplace equation (Balance among liquid tension, droplet gravity and air pressure). | 1. droplet density  
2. droplet profile | — |
validated and compared with other approximate profile functions, finally the surface tension of the droplet is obtained by fitting the profile function with the droplet edge curve data from its image. Generally, the method proposed in this study is quite different and much simpler than the traditional methods in Table 1.

2. Explicit profile function of lying droplet

To obtain the profile function of a lying droplet on a horizontal surface, a rotationally symmetric lying droplet on a horizontal plane is considered and its cross-section view is presented in Fig. 1.

![Fig. 1 A lying droplet on a horizontal plane](image)

For a 2-D space condition, the droplet profile curve function can be expressed by the 2-D Young-Laplace equation [6-8]

\[ \kappa \sigma_{lg} = \Delta p \]  

where \( \kappa \), \( \sigma_{lg} \), \( \Delta p \) represent the curvature, liquid-gas surface tension and pressure difference respectively.

For the situation shown in Fig. 1, \( \kappa \) can be given by the curvature equation

\[ \kappa(x) = -\frac{d^2 z}{dx^2}/\left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^{3/2} \]  

And \( \Delta p \) is governed by the difference between air pressure and hydrostatic pressure,
which is given by

\[ \Delta p = \varrho g [\delta - z] - p_g \]  \hspace{1cm} (3)

in which \( p_g \), \( \varrho \), \( g \), \( \delta \) represent the air pressure, droplet density, gravitational acceleration and droplet height respectively.

Substituting Eqs. (2, 3) into Eq. (1) gives the differential equation of the droplet profile

\[-\sigma_{lg} \frac{d^2 z}{dx^2} \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^\frac{3}{2} = \varrho g [\delta - z] - p_g \]  \hspace{1cm} (4)

Additionally, the boundary conditions can be expressed by (\( \theta_0 \) is the contact angle in Fig. 1)

\[ \left. \frac{dz}{dx} \right|_{z=0,x>0} = -\tan \theta_0 \quad \left. \frac{dz}{dx} \right|_{z=0,x<0} = \tan \theta_0 \]  \hspace{1cm} (5)

\[ \left. \frac{dz}{dx} \right|_{z=\delta} = 0 \]  \hspace{1cm} (6)

\[ x \Big|_{z=\delta} = 0 \]  \hspace{1cm} (7)

Solving Eqs. (4~7) leads to the explicit expression for the profile function of a liquid droplet on a flat horizontal surface. And the surface tension \( \sigma_{lg} \) is one of the parameters in the explicit profile function, thus it can be obtained by fitting the profile function using the rectangular coordinate data set \([X, Z]\) from the image of the liquid droplet on the flat horizontal surface. It is worth mentioning that, to simplify the calculation, many researchers have made different assumption to solve Eqs. (4~7) or equivalent Young-Laplace equation and obtained good approximation function (containing parameter \( \sigma_{lg} \)) to describe the droplet profile [8-21]. However, these approximation functions are only applicable under particular circumstance, hence not all the droplet images can be used to fit the approximation function. Additionally, many of these approximation functions are
in the form of parameter equations \((x = x(u,v), z = z(u,v))\) or polar coordinate equations \((x = x(\omega, \theta), z = z(\omega, \theta))\), which is not convenient for curve fitting using the rectangular coordinate data \([X, Z]\) from the droplet image. Therefore, the exact and explicit solution \(x = x(z)\) for Eq. (4) with boundary conditions Eqs. (5~7) is derived in this study (the detailed derivation process is attached in the Appendix A), which is symmetric about the \(z\) axis and can be expressed by (in the first quadrant)

\[
x(z) = -\sqrt{\frac{B^2 - 4AC}{4A^2}} \text{EllipticE}\left[\sqrt{Az^2 + Bz + C}, \sqrt{\frac{4A}{4AC - B^2}}\right]
\]

\[
+ \left(\frac{B^2 + 2A - 4AC}{2A\sqrt{B^2 - 4AC}}\right) \text{EllipticF}\left[\sqrt{Az^2 + Bz + C}, \sqrt{\frac{4A}{4AC - B^2}}\right]
\]

where

\[
A = \frac{\rho g}{4\sigma_{lg}}
\]

\[
B = -\frac{1}{2} \left(\frac{1}{\delta} + \frac{\rho g \delta}{2\sigma_{lg}} - \frac{\cos \theta_0}{\delta}\right)
\]

\[
C = \frac{1 - \cos \theta_0}{2}
\]

A known droplet volume is necessary to determine the real size of droplet from its image, and the volume \(V\) of the rotationally symmetric lying droplet can be given by

\[
V = \int_0^\delta \pi [x(z)]^2 dz
\]

the radius \(r\) of the droplet-plane contact circle is

\[
r = x(0)
\]

3. Validation experiment

Validation experiment is necessary to check the validity of the obtained explicit profile function. The numerical and experimental profile of droplet lying on the horizontal plane
were compared with the theoretical profile to check the validity of the obtained analytical solution of Eq. (1) in this study.

For the numerical droplet profile, it was obtained by numerically solving Young-Laplace equation in terms of the above parameters $A, B, C$ (see Eq. (15) in Appendix A.) using $ode15s$ function of MATLAB R2018b. It should be noted that when the contact angle $\theta_0 > 90^\circ$, the initial value at $z = \delta$ ($\frac{dz}{dx}|_{z=\delta} = 0, x|_{z=\delta} = 0$) is not enough to calculate the whole numerical profile because the computation would diverge at $\frac{dz}{dx} = \infty$ [22]. Therefore, the initial value at $z = 0$ is also used as a complement to the original boundary condition, which is

$$
\frac{dz}{dx}|_{z=0,x>0} = -\tan\theta_0 \left( \frac{dz}{dx}|_{z=0,x<0} = \tan\theta_0 \right)
$$

(5)

$$
x|_{z=0} = r
$$

(14)

For the experimental profile, the silicon plate and Dutch Twilled Weave were used as the substrates in the experiment (silicon plate (10mm $\times$10mm$\times$0.5mm) was purchased from Zhejiang Lijing Optoelectronics Technology Co., Ltd. Dutch Twilled Weave (DTW, 200$\times$1400) was purchased from GKD-GEBR. KUFFERATH AG). The experimental profile of the deionized water droplet of a controlled volume on the flat horizontal substrate were recorded by Dataphysics OCA20 at temperature of 5.0 °C.

For the theoretical profile, the parameters in profile function Eq. (8) were obtained by three steps: (1) recording the image of a rotationally symmetric droplet (with controlled volume) lying on the substrate, (2) extracting the droplet profile using the $edge$ function of MATLAB R2018b to get the droplet profile points $[X,Z]$ in rectangular coordinate, (3) fitting the profile points $[X,Z]$ based on Eq. (8) using the $fit$ function of MATLAB.
R2018b to obtain parameters $A, B, C$. The least-square algorithm was used in the profile fitting process, hence the R-squared ($r^2$) and root mean squared error (RMSE) were provided as the Goodness-of-fit statistics [23].

As shown in Fig. 2, the numerical and theoretical droplet profiles are in exact accordance with each other, regardless of the droplet size or wettability. This is because no approximation was used in the derivation of Eq. (8). The validity of the theoretical profiles with different parameter values also differs the obtained solution Eq. (8) in this study from the existing approximate solutions of Young-Laplace equation [8-21]. Therefore, the proposed profile droplet function is an ideal replacement of the numerical solution of Eq. (4).

**Fig. 2** Comparison of the numerical and theoretical droplet profile
The experimental and theoretical droplet profiles are shown in Fig. 3. And the corresponding droplet attributes are recorded in Table 2. As we can see, the theoretical droplet profile is in great agreement with the experimental data, which further validates the correctness of the obtained explicit profile function.

### Table 2 Drop properties and shape parameters.

| No. | Droplet Properties | Volume (μL) | Substrate |
|-----|--------------------|-------------|-----------|
| E1-1|                    | 1           | Silicon   |
| E1-2|                    | 5           | Silicon   |
| E1-3|                    | 10          | Silicon   |
| E1-4|                    | 1           | DTW       |
| E1-5|                    | 5           | DTW       |
| E1-6|                    | 10          | DTW       |

4. **Superiority of the derived profile function**

The superiority of the derived profile function lies on “exact” and “explicit”. “Explicit” means the reduction of computational complexity. Young-Laplace equation is an implicit differential equation, and it can only be solved numerically using the finite element algorithm or other complicated differential algorithm. However, the explicit solution of
Young-Laplace equation is suitable for the simple least-square algorithm, thus it is easier to be solved.

“Exact” means the derived profile function leads to the most accurate results. As aforementioned, many approximate functions have been derived from Young-Laplace equation, among which the circle function [24] and ellipse function [25] are most frequently used. Therefore, this study compared the fitting results from circle and ellipse function with that from the derived profile function Eq. (8). Considering the most common application nowadays of fitting droplet profile function is contact angle measurement, so the contact angles from different fitting method were also provided (the contact angle from the derived profile function fitting was obtained by solving Eq. (11) with the fitted value of parameter \( C \).)

Table 3 Fitting results of different functions.

| No. | Eq. (8) Fitting | Circle Fitting | Ellipse Fitting | Deviation | Eq. (8) Fitting | Circle Fitting | Ellipse Fitting | Deviation |
|-----|----------------|---------------|----------------|-----------|----------------|---------------|----------------|-----------|
|     | \( r^2 \) | RMSE (mm) | Contact Angle | \( r^2 \) | RMSE (mm) | Contact Angle | \( r^2 \) | RMSE (mm) | Contact Angle | Deviation |
| E1-1 | 0.997 | 0.015 | 72.8° | 0.997 | 0.015 | 72.8° | 0.997 | 0.015 | 71.7° | -1.1° |
| E1-2 | 0.998 | 0.021 | 69.7° | 0.998 | 0.022 | 67.1° | 0.998 | 0.021 | 69.5° | -0.2° |
| E1-3 | 0.997 | 0.033 | 68.2° | 0.997 | 0.034 | 66.1° | 0.997 | 0.033 | 67.9° | -0.3° |
| E1-4 | 0.991 | 0.020 | 122.9° | 0.988 | 0.023 | 120.1° | 0.988 | 0.023 | 119.5° | -3.4° |
| E1-5 | 0.996 | 0.022 | 125.5° | 0.994 | 0.027 | 117.6° | 0.996 | 0.023 | 122.9° | -2.6° |
| E1-6 | 0.997 | 0.023 | 127.5° | 0.994 | 0.035 | 115.6° | 0.997 | 0.024 | 123.5° | -4.0° |

\( a \) Deviation represents the difference between contact angle from Eq. (8) fitting and that from circle/ellipse fitting.

The fitting results and visual comparison of different fitting methods are shown in Table 3 and Fig. 4 respectively. Table 3 illustrates the Goodness-of-fit (\( r^2 \) and RMSE) from Eq. (8) fitting are just slightly superior to that from circle or ellipse fitting. Fig. 4 demonstrates the fitted curves from different fitting methods are mostly consistent with the detected droplet profile, especially when droplet volume or contact angle are small.
Fig. 4(E1-1~E1-4). However, what distinguishes Eq. (8) fitting from circle and ellipse fitting is the precise measurement of contact angle. It is noticed from Table 3 that the deviation of contact angle from circle and ellipse fitting can be large, even if both droplet volume and contact angle are small (E1-1~E1-4). Therefore, choosing the exact profile function Eq. (8) to fit the droplet contour for contact angle measurement can be necessary.

Fig. 4 Detected droplet profile and curves by fitting different function.

5. Surface tension measured by the derived profile function

Similar to the measurement of contact angle, the liquid surface tension $\sigma_{lg}$ was also obtained by fitting the derived profile function Eq. (8), then solving the Eq. (9) with droplet density $\rho$ and gravitational acceleration $g$. Table 4 gives a comparison between literature surface tension value of typical liquid against air and that measured by the above described method. To check the reproducibility of the proposed method, the measurements of the same droplet are repeated for ten times in the experiment. As shown in Table 4, the measured surface tension agrees well with the literature value. The standard deviations, all below 0.22 mN/m, are better than that of pendant drop method [4].
implying the proposed method is reproducible. And the deviations between literature and measured surface tension value (mainly attributed to the edge detection error when processing images [26]) are in the range of -1.00~1.00 mN/m, which are similar to the counterpart of pendant drop method research [4], indicating the results from the proposed method is acceptable.

Table 4 Literature and measured surface tension value of typical liquid.

| Type              | Density (g/cm³) | Surface tension (mN/m) |
|-------------------|----------------|------------------------|
|                   | Literature value | Measured value (mean value ± standard deviation) | Deviation c |
| Water (at 5°C)    | 1.000           | 74.9 [27]              | 74.14±0.005 | -0.76 |
| Water (at 20°C)   | 0.998           | 72.74 [28]             | 72.69±0.038 | -0.05 |
| n-Hexadecane      | 0.773           | 27.47 [28]             | 27.64±0.217 | 0.17  |
| Acetone           | 0.791           | 23.10 [29]             | 22.67±0.064 | -0.43 |
| Diethylene Glycol | 1.118           | 44.80 [30]             | 45.47±0.109 | 0.67  |
| Epoxy E51         | 1.100           | 45.00 [31]             | 44.52±0.027 | -0.48 |
| Diiodomethane     | 3.325           | 50.80 [32]             | 51.71±0.001 | 0.91  |
| Ethanol           | 0.787           | 22.10 [33]             | 22.98±0.002 | 0.88  |
| Formamide         | 1.133           | 58.20 [34]             | 57.93±0.006 | -0.27 |

b Mean value and standard deviation are obtained from ten consecutive measurements of the same droplet.

c Deviation represents the difference between literature and measured surface tension value.

6. Conclusion

This study presents the profile function of the lying droplet, then proposes a liquid surface tension measurement method by fitting the profile function. The lying droplet profile function is exact, explicit and fit for curve fitting. And the proposed method is accurate and more maneuverable than other methods.

Appendix A. Derivation of the exact and explicit solution

For ordinary differential equation

\[-\sigma_g \frac{d^2 z}{dx^2} \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^\frac{3}{2} = \varrho g [\delta - z] - p_g\] (4)
with boundary conditions

\[
\begin{align*}
\frac{dz}{dx}igg|_{z=0, x>0} &= -\tan\theta_0 \left( \frac{dz}{dx}igg|_{z=0, x<0} = \tan\theta_0 \right) \\
\frac{dz}{dx}igg|_{z=\delta} &= 0 \quad (5) \\
\frac{dz}{dx}igg|_{z=0, x<0} &= -\tan\theta_0 \left( \frac{dz}{dx}igg|_{z=0, x>0} = \tan\theta_0 \right) \\
\frac{dz}{dx}igg|_{z=\delta} &= 0 \quad (6)
\end{align*}
\]

\( x|_{z=\delta} = 0 \quad (7) \)

Let

\[
p = \frac{dz}{dx} \quad (A1)
\]

Then

\[
\frac{d^2z}{dx^2} = \frac{dp}{dx} = \frac{dp}{dz} \frac{dz}{dx} = p \frac{dp}{dz} \quad (A2)
\]

Substituting Eqs. (A1, A2) into Eq. (5) gives

\[
-\frac{p}{[1 + p^2]^2} dp = \frac{\rho g (\delta - z) - p_g}{\sigma_{ig}} \; dz \quad (A3)
\]

Integrating both sides gives

\[
\frac{1}{\sqrt{1 + p^2}} = \frac{\rho g \delta - p_g}{\sigma_{ig}} z - \frac{\rho g}{2\sigma_{ig}} z^2 + c \quad (A4)
\]

The function \( z(x) \) decreases with \( x \) in the first quadrant, hence \( p \leq 0 \), substituting

\[
p = \frac{dz}{dx} \quad \text{into Eq. (A4)} \quad \text{and solving} \quad \frac{dz}{dx} \quad \text{gives}
\]

\[
\frac{dz}{dx} = -\sqrt{1 - \left[ \frac{\rho g \delta - p_g}{\sigma_{ig}} z - \frac{\rho g}{2\sigma_{ig}} z^2 + c \right]^2} \quad (A5)
\]

Then substituting the first boundary condition \( \frac{dz}{dx}igg|_{z=0, x>0} = -\tan\theta_0 \) into Eq. (A5) gives

\[
c = \cos\theta_0 \quad (A6)
\]

substituting the second boundary condition \( \frac{dz}{dx}igg|_{z=\delta} = 0 \) and Eq. (A6) into Eq. (A5) gives
\[ \frac{\varrho g \delta - p_g}{\sigma_{tg}} = \frac{1 - \cos \theta_0}{\delta} + \frac{\varrho g \delta}{2\sigma_{tg}} \tag{A7} \]

Substituting Eqs. (A6, A7) into Eq. (A5) and separating variables gives

\[ \frac{\left( \frac{1 - \cos \theta_0}{\delta} + \frac{\varrho g \delta}{2\sigma_{tg}} \right) z - \frac{\varrho g}{2\sigma_{tg}} z^2 + \cos \theta_0}{\sqrt{1 - \left[ \left( \frac{1 - \cos \theta_0}{\delta} + \frac{\varrho g \delta}{2\sigma_{tg}} \right) z - \frac{\varrho g}{2\sigma_{tg}} z^2 + \cos \theta_0 \right]^2}} dz = -dx \tag{A8} \]

Let

\[
\begin{align*}
A' &= -\frac{\varrho g}{2\sigma_{tg}} \\
B' &= \frac{1 - \cos \theta_0}{\delta} + \frac{\varrho g \delta}{2\sigma_{tg}} \\
C' &= \cos \theta_0
\end{align*}
\tag{A9}
\]

Substituting Eq. (A9) into Eq. (A8) and integrating both sides gives

\[ \int \frac{A'z^2 + B'z + C'}{\sqrt{1 - (A'z^2 + B'z + C')^2}} dz = -\int dx \tag{A10} \]

Let

\[ z = \frac{-B' - \sqrt{B'^2 - 4A'(C' - t)}}{2A'} \tag{A11} \]

thus

\[ dz = \frac{-dt}{2\sqrt{A'} \sqrt{t - \frac{4A'C' - B'^2}{4A'}}} \tag{A12} \]

Then, let

\[ m = \frac{4A'C' - B'^2}{4A'} \tag{A13} \]

Substituting Eqs. (A11, A12, A13) into Eq. (A10) gives

\[ \frac{1}{2\sqrt{A'}} \int \frac{t}{\sqrt{1 - t^2 \sqrt{t - m}}} dt = \int dx \tag{A14} \]

Let

\[ t = 1 - 2v^2 \tag{A15} \]
hence

\[ dt = -4v dv \]  \hspace{1cm} (A16)

Substituting Eqs. (A15, A16) into Eq. (A14) gives

\[
\frac{1}{\sqrt{A'(1-m)}} \int \frac{2v^2 - 1}{\sqrt{1-v^2} \sqrt{1 - \frac{2}{1-m} v^2}} dv = \int dx
\]  \hspace{1cm} (A17)

Utilizing the transformation

\[
\frac{2v^2 - 1}{\sqrt{1-v^2} \sqrt{1 - \frac{2}{1-m} v^2}} = -(1-m) \frac{1 - \frac{2}{1-m} v^2}{\sqrt{1-v^2}} - \frac{m}{\sqrt{1-v^2} \sqrt{1 - \frac{2}{1-m} v^2}}
\]  \hspace{1cm} (A18)

Then Eq. (17) is transformed to

\[
-\sqrt{A'(1-m)} \left(1-m\right) \int \frac{2}{\sqrt{1-v^2} \sqrt{1 - \frac{2}{1-m} v^2}} dv
\]

\[
-\frac{m}{\sqrt{A'(1-m)}} \int \frac{1}{\sqrt{1-v^2} \sqrt{1 - \frac{2}{1-m} v^2}} dv = x + c'
\]  \hspace{1cm} (A19)

Using elliptic integral Elliptic $E[\varphi, \eta]$ and Elliptic $F[\varphi, \eta]$, Eq. (A19) can be expressed by

\[
-\sqrt{A'(1-m)} \left(1-m\right) \text{Elliptic } E \left( v, \sqrt{\frac{2}{1-m}} \right)
\]

\[
-\frac{m}{\sqrt{A'(1-m)}} \text{Elliptic } F \left( v, \sqrt{\frac{2}{1-m}} \right) = x + c'
\]  \hspace{1cm} (A20)

in which

\[
\text{Elliptic } E(x; k) = \int_{0}^{x} \frac{\sqrt{1 - k^2 t^2}}{\sqrt{1 - t^2}} dt
\]  \hspace{1cm} (A21)
Elliptic \( F(x; k) = \int_0^x \frac{1}{\sqrt{(1-t^2)(1-k^2t^2)}} dt \) \hspace{1cm} (A22)

Substituting Eqs. (A9, A11, A13, A15) into Eq. (A20) gives

\[
\begin{aligned}
\nu &= \sqrt{\frac{qg}{4\sigma_{lg}} - \frac{1}{2}\left(\frac{1}{\delta} + \frac{qg\delta}{2\sigma_{lg}} - \frac{\cos\theta_0}{\delta}\right) z + \frac{1 - \cos\theta_0}{2}} \\
\sqrt{1-m} &= \sqrt{-\frac{4qg}{\sigma_{lg}} - \frac{2qg}{\sigma_{lg}}(\cos\theta_0 - 1) + \left(\frac{1}{\delta} + \frac{qg\delta}{2\sigma_{lg}} - \frac{\cos\theta_0}{\delta}\right)^2} \\
-\sqrt{\frac{(1-m)}{A'}} &= -\sqrt{-\frac{2\sigma_{lg}}{qg}(1 - \cos\theta_0) + \left(\frac{\sigma_{lg}}{qg}\right)^2 \left(\frac{1}{\delta} + \frac{qg\delta}{2\sigma_{lg}} - \frac{\cos\theta_0}{\delta}\right)^2}
\end{aligned}
\hspace{1cm} (A23)

And then substituting the third boundary condition \( x|_{z=\delta} = 0 \) into Eqs. (A20, A23) gives

\[ c' = 0 \] (A24)

To further simplify the analytical solution, let

\[
A = \frac{qg}{4\sigma_{lg}} 
\hspace{1cm} (9)
\]
\[
B = -\frac{1}{2}\left(\frac{1}{\delta} + \frac{qg\delta}{2\sigma_{lg}} - \frac{\cos\theta_0}{\delta}\right) 
\hspace{1cm} (10)
\]
\[
C = \frac{1 - \cos\theta_0}{2} 
\hspace{1cm} (11)
\]

And then, substituting Eqs. (A24, 8, 9, 10) into Eqs. (A20, A23) gives the analytical expression for the shape of a liquid droplet on a flat horizontal surface

\[
x(z) = -\sqrt{\frac{B^2 - 4AC}{4A^2}}\text{Elliptic E} \left[ \sqrt{Az^2 + Bz} + C, \sqrt{\frac{4A}{4AC - B^2}} \right] \\
+ \left(\frac{B^2 + 2A - 4AC}{2A\sqrt{B^2 - 4AC}}\right)\text{EllipticF}\left[ \sqrt{Az^2 + Bz} + C, \sqrt{\frac{4A}{4AC - B^2}} \right]
\hspace{1cm} (8)
\]

Additionally, the Young-Laplace equation in terms of the above parameters \( A, B, C \)
can be obtained by substituting Eqs. (9, 10, 11) into Eq. (4), which is

\[
\frac{d^2z}{dx^2}\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2} = 2B + 4Az
\]  

(15)

References

[1] P.L. du Nouy, An interfacial tensiometer for universal use, J. Gen. Physiol. 7 (1925) 625-631. https://doi.org/10.1085/jgp.7.5.625.
[2] H. Butt, K. Graf, M. Kappl, Surface Forces, in: H. Butt, K. Graf, M. Kappl (Eds.) Physics and Chemistry of Interfaces, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003, pp. 80-117.
[3] H.H. Hu, D.D. Joseph, Evolution of a Liquid Drop in a Spinning Drop Tensiometer, J. Colloid Interf. Sci. 162 (1994) 331-339. https://doi.org/10.1006/jcis.1994.1047.
[4] F.K. Hansen, G. Rødsrud, Surface tension by pendant drop: I. A fast standard instrument using computer image analysis, J. Colloid Interf. Sci. 141 (1991) 1-9. https://doi.org/10.1016/0021-9797(91)90296-K.
[5] F. Ferrero, Wettability measurements on plasma treated synthetic fabrics by capillary rise method, Polym. Test. 22 (2003) 571-578. https://doi.org/10.1016/S0142-9418(02)00153-8.
[6] S. Shi, C. Lv, Wetting states of two-dimensional drops under gravity, Phys. Rev. E 98 (2018) 042802. https://doi.org/10.1103/PhysRevE.98.042802.
[7] S. Vafaei, M.Z. Podowski, Analysis of the relationship between liquid droplet size and contact angle, Adv. Colloid Interfac. 113 (2005) 133-146. https://doi.org/10.1016/j.cis.2005.03.001.
[8] S. Champmartin, A. Ambari, J.Y. Le Pommelec, New procedure to measure simultaneously the surface tension and contact angle, Rev. Sci. Instrum. 87 (2016) 055105. https://doi.org/10.1063/1.4948736.
[9] A. Ferguson, LXXXIX. On the shape of the capillary surface formed by the external contact of a liquid with a cylinder of large radius, Philos. Magaz. 24 (1912) 837-844. https://doi.org/10.1080/14786441208634877.
[10] V.A. Lubarda, K.A. Talke, Analysis of the Equilibrium Droplet Shape Based on an Ellipsoidal Droplet Model, Langmuir 27 (2011) 10705-10713. https://doi.org/10.1021/la202077w.
[11] A.P.P. K., S. S., Z.K. A. Approximate analytical solution to non-linear Young-Laplace equation with an infinite boundary condition. In: 2018 International Conference on Computing, Mathematics and Engineering Technologies (iCoMET). Sukkur, Pakistan: IEEE, 2018
[12] Y. Tang, S. Cheng, The meniscus on the outside of a circular cylinder: From microscopic to macroscopic scales, J. Colloid Interf. Sci. 533 (2019) 401-408. https://doi.org/10.1016/j.jcis.2018.08.081.
[13] K. Mazuruk, M.P. Volz, Dynamic stability of detached solidification, J. Cryst. Growth 444 (2016) 1-8. https://doi.org/10.1016/j.jcrysgro.2016.03.032.
[14] B. Prabhala, M. Panchagnula, V.R. Subramanian, S. Vedantam, Perturbation Solution of the Shape of a Nonaxisymmetric Sessile Drop, Langmuir 26 (2010) 10717-10724. https://doi.org/10.1021/la101168b.

[15] D. Megias-Alguacil, L.J. Gaukler, Accuracy of the toroidal approximation for the calculus of concave and convex liquid bridges between particles, Granul. Matter 13 (2011) 487-492. https://doi.org/10.1007/s10035-011-0260-9.

[16] L. Braescu, S. Epure, T. Duffar, Mathematical and Numerical Analysis of Capillarity Problems and Processes, in: T. Duffar (Ed.) Crystal Growth Processes Based on Capillarity: Czochralski, Floating Zone, Shaping and Crucible Techniques, 2010, pp. 465-524.

[17] A.V. Nguyen, New method and equations for determining attachment tenacity and particle size limit in flotation, Int. J. Miner. Process. 68 (2003) 167-182. https://doi.org/10.1016/S0301-7516(02)00069-8.

[18] A.V. Nguyen, Empirical Equations for Meniscus Depression by Particle Attachment, J. Colloid Interf. Sci. 249 (2002) 147-151. https://doi.org/10.1006/jcis.2002.8263.

[19] M. Kagan, W.V. Pinchewski, Meniscus and Contact Angle in an Eye-Shaped Capillary, J. Colloid Interf. Sci. 203 (1998) 379-382. https://doi.org/10.1006/jcis.1998.5488.

[20] D. Homentcovsch, J. Geer, T. Singler, Uniform asymptotic solutions for small and large sessile drops, Acta Mech. 128 (1998) 141-171. https://doi.org/10.1007/BF01251887.

[21] P.C. Wayner, Spreading of a liquid film with a finite contact angle by the evaporation/condensation process, Langmuir 9 (1993) 294-299. https://doi.org/10.1021/la00025a056.

[22] L.F. Shampine, M.W. Reichelt, The matlab ode suite, SIAM J. Sci. Comput. 18 (1997) 1-22. https://doi.org/10.1137/S1064827594276424.

[23] C. Onyutha, From R-squared to coefficient of model accuracy for assessing "goodness-of-fits", Geosci. Model Dev. Discuss. 2020 (2020) 1-25. https://doi.org/10.5194/gmd-2020-51.

[24] X. Z., F.L. F., A static contact angle algorithm and its application to hydrophobicity measurement in silicone rubber corona aging test, IEEE T. Dielect. El. In. 20 (2013) 1820-1831. https://doi.org/10.1109/TDEI.2013.6633713.

[25] Z. Xu, Automatic static contact angle algorithm forblurry drop images and its application in hydrophobicity measurement for insulating materials, IET Sci. Meas. Technol. 9 (2015) 113-121. https://doi.org/10.1049/iet-smt.2014.0072.

[26] I. Ríos-López, P. Karamaoynas, X. Zabulis, M. Kostoglou, T.D. Karapantsios, Image analysis of axisymmetric droplets in wetting experiments: A new tool for the study of 3D droplet geometry and droplet shape reconstruction, Colloid. Surface. A 553 (2018) 660-671. https://doi.org/10.1016/j.colsurfa.2018.05.098.

[27] M.S. Jhon, E.R. Van Artsdalen, J. Grosh, H. Eyring, Further Applications of the Domain Theory of Liquid Water: I. Surface Tension of Light and Heavy Water; II. Dielectric Constant of Lower Aliphatic Alcohols, J. Chem. Phys. 47 (1967) 2231-2234. https://doi.org/10.1063/1.1703297.

[28] P.S. Brown, B. Bhushan, Durable, superoleophobic polymer – nanoparticle composite surfaces with re-entrant geometry via solvent-induced phase transformation,
[29] V.A. Ganesh, S.S. Dinachali, S. Jayaraman, R. Sridhar, H.K. Raut, A. Góra, A. Baji, A.S. Nair, S. Ramakrishna, One-step fabrication of robust and optically transparent slippery coatings, RSC Adv. 4 (2014) 55263-55270. https://doi.org/10.1039/C4RA08655D.

[30] A.M. Munshi, V.N. Singh, M. Kumar, J.P. Singh, Effect of nanoparticle size on sessile droplet contact angle, J. Appl. Phys. 103 (2008) 084315. https://doi.org/10.1063/1.2912464.

[31] T. Sun, M. Li, S. Zhou, M. Liang, Y. Chen, H. Zou, Multi-scale structure construction of carbon fiber surface by electrophoretic deposition and electropolymerization to enhance the interfacial strength of epoxy resin composites, Appl. Surf. Sci. 499 (2020) 143929. https://doi.org/10.1016/j.apsusc.2019.143929.

[32] Z. He, M. Ma, X. Lan, F. Chen, K. Wang, H. Deng, Q. Zhang, Q. Fu, Fabrication of a transparent superamphiphobic coating with improved stability, Soft Matter 7 (2011) 6435-6443. https://doi.org/10.1039/CISM05574G.

[33] X. Chen, J.A. Weibel, S.V. Garimella, Water and Ethanol Droplet Wetting Transition during Evaporation on Omniphobic Surfaces, Sci. Rep.-UK 5 (2015) 17110. https://doi.org/10.1038/srep17110.

[34] M. Annamalai, K. Gopinadhan, S.A. Han, S. Saha, H.J. Park, E.B. Cho, B. Kumar, A. Patra, S. Kim, T. Venkatesan, Surface energy and wettability of van der Waals structures, Nanoscale 8 (2016) 5764-5770. https://doi.org/10.1039/C5NR06705G.