New identities for sessile drops

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Abstract

A new set of mathematical identities is presented for axi-symmetric sessile drops on flat and curved substrates. The geometrical parameters, including the apex curvature and height, and the contact radius, are related by the identities. The validity of the identities are checked by various numerical solutions both for flat and curved substrates.

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1 Introduction

The study of drops with the effect of gravity being balanced with the surface tension goes back to more than a century [1], followed by renewal updates extending and refining the original treatment [2,3]. More recent efforts have concentrated on presenting approximate analytical solutions or developing more efficient methods for numerical solutions [5–20].

Heuristically, the balance between the surface effects and the bulk ones would fix the profile of a drop. While the gravity lowers the center of mass, the surface tension (γ) tends to decrease the surface, and the adhesion coefficient (σ) tends to increase the surface of the contact region. For a drop with volume V, density ϱ and comparable surface effects (i.e. σ ∼ γ), the so-called Bond number defined by the dimensionless combination $V^{2/3} \rho g/\gamma$ would determine whether weight has the dominant contribution or not.

Mathematically, at every point of the drop’s surface the Young-Laplace relation holds,

$$\gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta p \quad (1)$$

where $(R_1, R_2)$ are two principal radii of curvature at the point, and $\Delta p \equiv p_l - p_v$ is the pressure jump across the liquid-vapor interface. As the hydrostatic laws express $\Delta p$ in terms of the surface equation, the Young-Laplace relation is the differential equation by which, together with the boundary conditions, the drop’s profile is determined. As one of the boundary conditions, the contact angle (θ) is fixed by the Young equation

$$\cos \theta = \frac{\sigma}{\gamma} - 1. \quad (2)$$

The purpose here is to present a set of mathematical identities for sessile drops. In particular, for the cases of sessile drops on flat and curved substrates, by direct integration of Young-Laplace relation over the entire surface of drop, exact identities are derived. The geometrical parameters of drop, including the height and curvature at the apex and the contact radius of the drop are related by the identities. The importance of the mentioned parameters is that, they are initially unknown, and are determined only after the complete solution is available. The validity of the identities are checked by various numerical solutions both for flat and curved substrates.

2 The mathematical setup and derivation

Using the cylindrical coordinate setup given in Fig. 1 the total curvature of the axi-symmetric surface $z = f(\rho)$ is given by

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{|f'|}{\sqrt{1 + f'^2}} \right), \quad (3)$$
where \( f' = df/d\rho \). On the other hand, the pressure jump in presence of gravity gets contribution from the weight of the drop’s layers as well, leading to

\[
\Delta p(z) = \Delta p_\gamma + \varrho g (h - z)
\]  \hspace{1cm} (4)

in which \( h \) is the height of the drop’s apex, and \( \Delta p_\gamma \) is a constant representing the pressure jump due to the surface tension. So, the Young-Laplace relation reads

\[
\mp \frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{f'_{\pm}}{\sqrt{1 + (f'_{\pm})^2}} \right) = 2\kappa + \frac{\varrho g}{\gamma} (h - f_{\pm}).
\]  \hspace{1cm} (5)

in which \( f_+ \) and \( f_- \) are denoting the upper and lower parts of the drop, respectively (see Fig. 1b), and \( \kappa := \Delta p_\gamma/(2 \gamma) \). At apex \( (h = f_+(0)) \) we have \( R_1 = R_2 \), and so by \( \kappa \), \( \kappa \) is simply the curvature at apex.

The main issue with equation (5) is that the parameters \( h \) and \( \kappa \) are not known at the first place, and would be determined only after the complete solution is available. So at starting point the main equation is not fully known. Further, the contact radius \( \rho_0 \) (Fig. 1), as the limiting value for the variable \( \rho \), is not known at first place. As will be seen shortly, by integrating the Young-Laplace relation an identity is obtained which relates the three unknown parameters in a very helpful way. Hereafter, the cases for flat and curved substrates are considered separately.

### 2.1 Flat substrate

The boundary conditions for \( \vartheta > 90^\circ \) are:

\[
f'_+(0) = 0 \quad \hspace{1cm} \hspace{1cm} (6)
\]

\[
f'_-(\rho_0) = -\tan \vartheta, \quad \hspace{1cm} (7)
\]

\[
f_-(\rho_0) = 0. \quad \hspace{1cm} (8)
\]
We mention $f_+' < 0$ and $f_- > 0$. In case with $\vartheta < 90^\circ$ (7) and (8) are valid for $f_+$. In what follows we mainly consider the case with $\vartheta > 90^\circ$. The generalization to case with $\vartheta < 90^\circ$ is rather straightforward. Integrating the Young-Laplace relation for the upper and lower parts of drop leads to

$$\rho_1 = \left(\kappa + \frac{\varrho g}{2\gamma} h\right) \rho_1^2 - \frac{\varrho g}{\gamma} \int_0^{\rho_1} \rho f_+ (\rho) d\rho$$

$$\rho_1 - \rho_0 \sin \vartheta = \left(\kappa + \frac{\varrho g}{2\gamma} h\right) (\rho_1^2 - \rho_0^2) - \frac{\varrho g}{\gamma} \int_{\rho_0}^{\rho_1} \rho f_- (\rho) d\rho$$

in which we have used

$$\frac{f_- \prime}{\sqrt{1 + f_- \prime^2}} \bigg|_{\rho_0} = -\frac{\tan \vartheta}{\sqrt{1 + \tan^2 \vartheta}} = \sin \vartheta$$

for $\vartheta > 90^\circ$. Subtracting (9) and (10) leads to the identity

$$\kappa + \frac{\varrho g}{2\gamma} h = \frac{\sin \vartheta}{\rho_0} + \frac{\varrho g V}{2\pi \gamma \rho_0^2}$$

in which we have used the relation for the volume of drop,

$$\frac{V}{2\pi} = \int_0^{\rho_1} \rho f_+ (\rho) d\rho - \int_{\rho_0}^{\rho_1} \rho f_- (\rho) d\rho.$$ 

It is easy to show that identity (12) is valid for the acute contact angle ($\vartheta < 90^\circ$) as well. It is emphasized in (12) no approximation is used, hence it is an exact relation.

It would be useful to check the above identity for the case with absence of gravity, in which, as only the surface effects are present, the drop’s surface is part of sphere. By direct insertion it can be seen that the following satisfies the Young-Laplace relation (5),

$$z = f_{0,\pm} (\rho) = \pm \sqrt{R^2 - \rho^2} + z_0$$

representing a sphere with radius $R$ whose center is located at $z = z_0$. Following a simple geometrical argument in the sphere (see Fig. 1), we have

$$\rho_0 = R \sin \vartheta, \quad z_0 = -R \cos \vartheta.$$ 

As on the surface of a sphere the curvature is constant, we have $\kappa = 1/R$. By setting $g = 0$ in the identity (12), it is simply satisfied by the given values.

### 2.2 Curved substrate

In the lines similar to the case for the flat case, we can derive the identities for curved substrate as well. The main differences, as follow, appear in the
boundary condition, and in the way that volume of drop comes to the play. The possible situations are represented in Figs. 2 & 3. Here the angle between the drop’s surface at contact point and the horizontal line, denoted by \( \tilde{\theta} \) in Figs. 2 & 3, appears as part of the boundary conditions. First let us consider cases shown in Fig. 2. For cases with obtuse angle, the boundary conditions read:

\[
\begin{align*}
  f'_+(0) &= 0 \\  f'_-(\rho_0) &= -\tan \tilde{\theta}.
\end{align*}
\]  

(16)  

(17)

Again, in case with \( \theta < 90^\circ \) [17] is valid for \( f_+ \). In what follows we mainly consider the case with \( \theta > 90^\circ \). The generalization to case with \( \theta < 90^\circ \) is rather straightforward. Integrating the Young-Laplace relation for the upper and lower parts of drop leads to

\[
\begin{align*}
  \rho_1 &= \left( \kappa + \frac{\sigma g}{2\gamma} h \right) \rho_1^2 - \frac{\sigma g}{\gamma} \int_0^{\rho_1} \rho f_+(\rho) d\rho \\
  \rho_1 - \rho_0 \sin \tilde{\theta} &= \left( \kappa + \frac{\sigma g}{2\gamma} h \right) (\rho_1^2 - \rho_0^2) - \frac{\sigma g}{\gamma} \int_{\rho_0}^{\rho_1} \rho f_-(\rho) d\rho
\end{align*}
\]

(18)  

(19)

Figure 2: The four possible situations for drop on curved substrate \( s(\rho) \), and definition of the angle \( \tilde{\theta} \) (single-arc), as the angle between the drop and horizontal line at the contact point. The contact angle is represented by double-arc. Other parameters are the same as Fig. 1.
in which, as mentioned before, $\tilde{\vartheta}$ is the angle between the drop’s surface at contact point and horizontal line (Fig. 2), for which we have

$$\frac{f'}{\sqrt{1 + f'^2}}\bigg|_{\rho_0} = -\frac{\tan \tilde{\vartheta}}{\sqrt{1 + \tan^2 \vartheta}} = \sin \tilde{\vartheta}, \quad (20)$$

Subtracting (18) and (19) leads to the identity

$$\kappa + \frac{\rho g}{2\gamma} h = \frac{\sin \tilde{\vartheta}}{\rho_0} + \frac{\rho g}{2\pi \gamma \rho_0^2} (V + V_s) \quad (21)$$

in which we have used the following relations for the volumes,

$$\frac{V}{2\pi} = \int_0^{\rho_1} \rho f_+ (\rho) d\rho - \int_0^{\rho_0} \rho f_- (\rho) d\rho - \frac{V_s}{2\pi}, \quad (22)$$

$$\frac{V_s}{2\pi} = \int_0^{\rho_0} \rho s(\rho) d\rho, \quad (23)$$

in which $s(\rho)$ is the equation of the substrate (Fig. 2). It is easy to show that identity (21) is valid for the acute contact angle as well. Again, it is emphasized in (21) no approximation is used, hence it is an exact relation.

Now we come to the case shown in Fig. 3, in which $\rho = 0$ makes a dimple. For this case the Young-Laplace relation reads:

$$\frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{f'}{\sqrt{1 + f'^2}} \right) = 2\kappa - \frac{\rho g}{\gamma} (h - f_-), \quad (24)$$

by which after integration one finds

$$\rho_0 \sin \tilde{\vartheta} = \left( \kappa - \frac{\rho g}{2\gamma} h \right) \rho_0^2 + \frac{\rho g}{\gamma} \int_0^{\rho_0} \rho f_- (\rho) d\rho, \quad (25)$$

or, by the relations for volumes,

$$\kappa - \frac{\rho g}{2\gamma} h = \frac{\sin \tilde{\vartheta}}{\rho_0} - \frac{\rho g}{2\pi \gamma \rho_0^2} (V + V_s) \quad (26)$$

So, for case in Fig. 3 the identity finds a slightly different form than others.
3 Check of identities

In order to provide the numerical tests of the identities obtained in previous section, here a collection of numerical solutions is presented which covers all the situations for which the identities are claimed to hold. The outputs of numerical solutions, including the contact radius \( \rho_0 \), apex height \( h \) and curvature \( \kappa \), and in case for curved substrates the angle \( \vartheta \), are presented in Tabs. 1-4, by which the direct tests of identities are made possible. As illustrations, the plots of all of the numerical solutions are presented in Figs. 4-7.

Table 1: The geometrical values by the numerical solutions of Young-Laplace relation for drops with acute contact angle, plotted in Fig. 4. For all: \( V = 0.1 \text{ cm}^3 \), \( g = 980 \text{ cm/s}^2 \), \( \gamma = 70 \text{ dyn/cm} \).

| Cont. ang. | \( g \) g/cm\(^3\) | Bond no. | \( \rho_0 \) cm | \( h \) cm | \( \kappa \) cm\(^{-1}\) |
|------------|-----------------|----------|-----------------|------------|-----------------|
| \( \vartheta = 45^\circ \) | 0 | 0 | 0.526 | 0.218 | 1.345 |
| | 0.5 | 1.51 | 0.546 | 0.194 | 0.990 |
| | 1.0 | 3.02 | 0.564 | 0.175 | 0.729 |
| | 1.5 | 4.52 | 0.581 | 0.159 | 0.536 |

Figure 4: The plots of numerical solutions of Young-Laplace relation for drops on flat substrate with acute contact angle, given at Tab. 1 (scales: 1:1).

Table 2: The geometrical values by the numerical solutions of Young-Laplace relation for drops with obtuse contact angle, plotted in Fig. 5. For all: \( V = 0.1 \text{ cm}^3 \), \( g = 980 \text{ cm/s}^2 \), \( \gamma = 70 \text{ dyn/cm} \).

| Cont. ang. | \( g \) g/cm\(^3\) | Bond no. | \( \rho_0 \) cm | \( h \) cm | \( \kappa \) cm\(^{-1}\) |
|------------|-----------------|----------|-----------------|------------|-----------------|
| \( \vartheta = 135^\circ \) | 0 | 0 | 0.208 | 0.501 | 3.404 |
| | 0.5 | 1.51 | 0.264 | 0.420 | 2.799 |
| | 1.0 | 3.02 | 0.295 | 0.375 | 2.332 |
| | 1.5 | 4.52 | 0.317 | 0.343 | 1.954 |

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| Cont. angl. | $\vartheta$ | Bond $\rho_0$ | $h$ | $\tilde{\vartheta}$ | $\kappa$ |
|------------|-------------|-------------|-----|----------------|---------|
| Subst.     | g/cm$^3$    | no. cm      | cm  | deg. cm$^{-1}$  |         |
| $\vartheta = 45^\circ$ | 0 | 0 | 0.477 | 0.233 | 70.51 | 1.976 |
| Convex     | 0.5 | 1.51 | 0.517 | 0.175 | 72.32 | 1.417 |
| $s = -0.5 \rho^2$ | 1.0 | 3.02 | 0.562 | 0.129 | 73.33 | 0.967 |
| upp. Fig. 6| 1.5 | 4.52 | 0.631 | 0.073 | 77.23 | 0.577 |
| $\vartheta = 45^\circ$ | 0 | 0 | 0.537 | 0.216 | 32.88 | 1.011 |
| Concave    | 1.0 | 3.02 | 0.561 | 0.188 | 32.35 | 0.565 |
| $s = 0.5 \rho^2$  | 2.0 | 6.03 | 0.579 | 0.170 | 31.97 | 0.328 |
| mid. Fig 6 | 3.0 | 9.05 | 0.592 | 0.158 | 31.67 | 0.200 |
| $\vartheta = 20^\circ$ | 0 | 0 | 0.527 | 0.236 | 37.67 | 1.160 |
| Concave    | 1.0 | 3.02 | 0.512 | 0.258 | 36.94 | 0.751 |
| $s = 1.5 \rho^2$  | 2.0 | 6.03 | 0.504 | 0.269 | 36.53 | 0.526 |
| low. Fig. 7| 4.0 | 12.1 | 0.495 | 0.282 | 36.06 | 0.289 |

Table 3: The geometrical values by the numerical solutions of Young-Laplace relation for drops with acute contact angle, plotted in Fig. 6. For all: $V = 0.1$ cm$^3$, $g = 980$ cm/s$^2$, $\gamma = 70$ dyn/cm. For substrate $s(\rho) = \lambda \rho^2$, $V_s = 2\pi \lambda \rho^3/4$.

| Cont. angl. | $\vartheta$ | Bond $\rho_0$ | $h$ | $\tilde{\vartheta}$ | $\kappa$ |
|------------|-------------|-------------|-----|----------------|---------|
| Subst.     | g/cm$^3$    | no. cm      | cm  | deg. cm$^{-1}$  |         |
| $\vartheta = 135^\circ$ | 0 | 0 | 0.169 | 0.514 | 144.6 | 3.438 |
| Convex     | 0.5 | 1.51 | 0.233 | 0.414 | 148.1 | 2.827 |
| $s = -0.5 \rho^2$ | 1.0 | 3.02 | 0.268 | 0.359 | 150.0 | 2.346 |
| upp. Fig. 7| 1.5 | 4.52 | 0.293 | 0.319 | 151.3 | 1.959 |
| $\vartheta = 135^\circ$ | 0 | 0 | 0.259 | 0.487 | 120.5 | 3.327 |
| Concave    | 1.0 | 3.02 | 0.324 | 0.394 | 117.1 | 2.301 |
| $s = 0.5 \rho^2$  | 2.0 | 6.03 | 0.353 | 0.351 | 115.6 | 1.661 |
| low. Fig. 7 | 3.0 | 9.05 | 0.372 | 0.323 | 114.6 | 1.216 |

Table 4: The geometrical values by the numerical solutions of Young-Laplace relation for drops with obtuse contact angle, plotted in Fig. 7. For all: $V = 0.1$ cm$^3$, $g = 980$ cm/s$^2$, $\gamma = 70$ dyn/cm. For substrate $s(\rho) = \lambda \rho^2$, $V_s = 2\pi \lambda \rho^3/4$.

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