On the shape of a lightweight drop on a horizontal plane

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Abstract

The shape of a drop on a flat horizontal plane is obtained by including the first order of correction by the weight. The sphere solution of the weightless drop is used to introduce a new polar coordinate by which the perturbative expression for a region of a drop can be extended analytically to the entire surface of a drop having both concave and the convex parts. A comparison with experimental data is presented.

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1. Introduction

To the interface of two media $a$ and $b$ is assigned an energy per area of interface, the so-called interfacial energy coefficient $\gamma_{ab}$. For example, the liquid–vapor parameter $\gamma_{lv} \equiv \gamma$ describes the energy content coming from the fact that liquid molecules near the surface have fewer neighbors than those in the bulk. The corresponding coefficient is called the surface tension. The shape of a drop of liquid on a solid surface, in the idealized case (absence of impurities and pinning effects), is determined by the quantities (i) the surface tension $\gamma$, (ii) the adhesion coefficient $\sigma$, (iii) the shape of the solid surface, and due to the weight, (iv) the drop’s volume.

The adhesion coefficient is defined by the surface tension, and the solid–liquid and the solid–vapor interfacial energies as

$$\sigma \equiv \gamma_{sv} + \gamma - \gamma_{sl}. \tag{1}$$

At the solid–liquid–vapor point of contact, the contact angle $\vartheta$ in the equilibrium condition is given by the Young equation

$$\cos \vartheta = \frac{\sigma}{\gamma} - 1. \tag{2}$$

The above relation determines $\vartheta$ for $0 \leq \sigma \leq 2\gamma$. Three classes of possibilities for the contact angle are presented in figure 1. The cases with $\sigma \approx 2\gamma$ and $\sigma \ll \gamma$ correspond to the highest and the lowest spreading of the drop on the solid surface, respectively. Hence, the term ‘complete wetting’ befits the case with $\sigma \approx 2\gamma$.

At every point on the drop surface the Young–Laplace relation holds [1, 2]

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right). \tag{3}$$

in which $\Delta p \equiv p_l - p_v$ is the difference pressure across the surface and $(R_1, R_2)$ are two principal radii of curvature of the surface at a point. At each point of the drop’s surface the total curvature $R_1^{-1} + R_2^{-1}$ is determined in terms of the surface equation and its derivatives. Provided by the hydrostatic laws, $\Delta p$ can be expressed in terms of the surface equation as well. So the Young–Laplace relation is a partial differential equation which, accompanied by appropriate boundary conditions, determines the shape of the drop’s surface.

Equivalently, the shape of a drop can be obtained by minimizing the energy of a static system. While the surface tension tends to decrease the surface area of the drop, the adhesion coefficient tends to increase the surface area of the contact region, and gravity tends to lower the center of mass of the drop. The competition between these effects determines the shape of the drop. For a drop with volume $V$ and density $\varrho$, one can give an estimation for each of the effects. The order of the drop’s size is estimated by $L = V^{1/3}$. In many practical cases, the surface tension and the adhesion coefficient, although with opposite effects, may be considered at the same order, meaning that $\gamma$ and $\sigma$ are comparable. So the contribution of the interfacial energies, which is proportional to the area, is estimated by $\gamma L^2$. The contribution of the weight to the energy is given by...
expression for a region of a drop can be extended analytically introducing a new polar coordinate by which the perturbative weight. The sphere solution of the weightless drop is used to is obtained by including the first order of correction by the method to include the effect of the gravity on the shape of drops (or vanishing surface tension drops) are theoretically studied for more than a century. The early numerical solutions are based on the match between the calculated drop profiles and the experimental data on the drop profiles has been the subject of important for practical purposes. In fact, one of the most profiles of resting drops in different situations are particularly in this direction, in [2] the singular perturbation technique developed over the years, among them are those by the authors of [7–10] for small drops (small Bond number). As large drops (or vanishing surface tension drops) are theoretically an infinitely large and thin film of liquid subjected to the boundary conditions at the outer edge, the limit of large Bond number falls and has been studied in the context of singular perturbation problems [11]. Based on the similarity between the truncated oblate spheroid and the drop’s shape, an approximated profile is suggested in [12] for the shape of the drop. In [13] a new numerical treatment of the problem is given based on a variational method to minimize the total energy of the drop, by which the use of the tables in [3] is more direct than the earlier treatments. As another effort in this direction, in [14] the singular perturbation technique is used to obtain the asymptotic expressions describing the shape of small sessile and pendant drops. The study of the profiles of resting drops in different situations are particularly important for practical purposes. In fact, one of the most common methods to measure the surface tension of liquids is based on the match between the calculated drop profiles and the measured drop shapes. Over the years, the optimization of matching methods between the calculated profiles and the experimental data on the drop profiles has been the subject of several research works [15–17].

It is the purpose of this note to develop a perturbation method to include the effect of the gravity on the shape of the drop’s surface. Here, in particular, the shape of the drop is obtained by including the first order of correction by the weight. The sphere solution of the weightless drop is used to introduce a new polar coordinate by which the perturbative expression for a region of a drop can be extended analytically to the entire surface of a drop having both concave and the convex parts.

\[ \rho V g L = \rho g L^4, \]  
with \( \rho \) being the gravitational acceleration constant. Comparing these contributions, one can differentiate three regions:

- \( L \ll \sqrt{\gamma/\rho g} \): the effect of weight is small;
- \( L \sim \sqrt{\gamma/\rho g} \): the weight and the interfacial energies have comparable effects;
- \( L \gg \sqrt{\gamma/\rho g} \): the effect of weight is dominant.

In other words, the comparison between the length \( \ell \equiv \sqrt{\gamma/\rho g} \) and \( L \) or equivalently the value of the Bond dimensionless parameter \( L^2 \rho g / \gamma \) would determine the regime. For a weightless drop only the contribution from the surface tension exists. Minimizing the area for a fixed volume, the shape of the drop’s surface turns out to be part of a sphere. The problem of a drop on a horizontal surface with the effect of surface tension being balanced with gravity has been studied for more than a century. The early numerical solutions go back to 1883 [3], with updates by different authors [4–6]. Different perturbative treatments of the problem have been developed over the years, among them are those by the authors of [7–10] for small drops (small Bond number). As large drops (or vanishing surface tension drops) are theoretically an infinitely large and thin film of liquid subjected to the boundary conditions at the outer edge, the limit of large Bond number falls and has been studied in the context of singular perturbation problems [11]. Based on the similarity between the truncated oblate spheroid and the drop’s shape, an approximated profile is suggested in [12] for the shape of the drop. In [13] a new numerical treatment of the problem is given based on a variational method to minimize the total energy of the drop, by which the use of the tables in [3] is more direct than the earlier treatments. As another effort in this direction, in [14] the singular perturbation technique is used to obtain the asymptotic expressions describing the shape of small sessile and pendant drops. The study of the profiles of resting drops in different situations are particularly important for practical purposes. In fact, one of the most common methods to measure the surface tension of liquids is based on the match between the calculated drop profiles and the measured drop shapes. Over the years, the optimization of matching methods between the calculated profiles and the experimental data on the drop profiles has been the subject of several research works [15–17].

It is the purpose of this note to develop a perturbation method to include the effect of the gravity on the shape of the drop’s surface. Here, in particular, the shape of the drop is obtained by including the first order of correction by the weight. The sphere solution of the weightless drop is used to introduce a new polar coordinate by which the perturbative expression for a region of a drop can be extended analytically to the entire surface of a drop having both concave and the convex parts.
changing the sign of its derivative, or its corresponding $\psi_0$ by (6). With the integration of (8)
\[ \mp \rho \psi_{0\pm} = K_0 \rho^2 + a_\pm, \]
where $a_\pm$ are the constants of integration. By the above reasoning, in the present case $a_+ = a_-$. Also $a_\pm$ should be set to zero in order that $\psi_{0\pm}$ does not blow up at $\rho = 0$, for which by definition $|\psi(\rho)| \leq 1$. One then has
\[ f_{0\pm}^2/1 + f_{0\pm}'^2 = \psi_0^2 \rho^2 \]
and so
\[ df_{0\pm}/d\rho = \pm \frac{\rho_0 \rho}{\sqrt{1 - \psi_0^2 \rho^2}} \]
for which by the integration we find that
\[ z = f_{0\pm}(\rho) = \pm \frac{1}{\sqrt{\psi_0^2 - \rho^2 + z_0}}, \]
which represents a sphere with radius $R = \psi_0^{-1} > 0$ whose center is located on the $z$-axis at $z = z_0$. As mentioned, in the case of $\vartheta < 90^\circ$, only the positive sign has meaning, and both $\pm$ signs should be kept in the case of $\vartheta > 90^\circ$.

It is useful to check the number of parameters involved. The parameters $\Delta \rho_0$, or equivalently $\rho_0$, and $z_0$ are unknown in the first place. Following a simple geometrical argument in the sphere (see figure 2), we have
\[ \cos \vartheta = -\frac{z_0}{R}, \]
by which we have $z_0 > 0$ for $\vartheta > 90^\circ$ and $z_0 < 0$ for $\vartheta < 90^\circ$, corresponding to the center above and below the solid surface, respectively. So given the relation for the volume
\[ V = \frac{\pi}{6} R^3 (1 - \cos \vartheta)^2 (2 + \cos \vartheta) \]
$z_0$ and $R$ are fixed. The parameters $\rho_0$ and $\rho_1$ in figure 2, as the contact and equatorial radii, respectively, can be obtained once the equation of the sphere is solved for $z = 0$ and $z = z_0$. yielding
\[ \rho_0 = R \sin \vartheta, \quad \rho_1 = R. \]
The place of the drop’s apex in the spherical solution is
\[ r_0 = R + z_0. \]

Before proceeding, let us introduce an identity for later use. The difference pressure in the presence of gravity gets a contribution from the weight of the drop’s layers as well. So we have for the ratio
\[ \frac{\Delta p(z)}{\gamma} = 2\kappa + \frac{\varrho g}{\gamma} (h - f(\rho)) \]
in which $h$ is the height of the drop’s apex, and $\kappa$, similar to its counterpart $\kappa_0$, represents the difference pressure due to the surface tension but here in the presence of gravity. The contribution of the surface tension pressure to the presence of gravity is different and simply can be understood as the area of the drop that is changed due to the effect of weight. Hence the surface tension contribution to the energy of the drop is different due to the gravity. So, the Young–Laplace relation reads
\[ \mp \frac{1}{\rho} \frac{d}{d\rho} (\rho \psi_{\pm}) = 2\kappa + \frac{\varrho g}{\gamma} (h - f_{\pm}). \]
Integrating the above for the upper and lower parts gives the following:
\[ \rho_1 = \left( \kappa + \frac{\varrho g}{2\gamma} h \right) \rho_1^2 - \frac{\varrho g}{\gamma} \int_0^{\rho_1} \rho f_+(\rho) d\rho, \]
\[ \rho_1 - \rho_0 \sin \vartheta = \left( \kappa + \frac{\varrho g}{2\gamma} h \right) (\rho_1^2 - \rho_0^2) - \frac{\varrho g}{\gamma} \int_{\rho_0}^{\rho_1} \rho f_-(\rho) d\rho \]
in which we have used
\[ \frac{f_+'(\rho')}{\sqrt{1 + f_+'^2(\rho')}} \bigg|_{\rho = \rho_0} = -\tan \vartheta \sqrt{1 + \tan^2 \vartheta} = \sin \vartheta \]
for $\vartheta > 90^\circ$. Subtracting (19) and (20) gives
\[ \kappa + \frac{\varrho g}{2\gamma} h = \frac{\sin \vartheta}{\rho_0} + \frac{\varrho g V}{2\pi \gamma \rho_0^2} \]
in which we have used the relation for the volume of the 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 (22) is valid for the acute contact angle ($\vartheta < 90^\circ$), as well. Note that in obtaining (22) no approximation is used, and so it is an exact relation.

### 3. The shape of a lightweight drop

Here we consider the first correction of gravity to the shape of a drop, supposedly applicable to drops with tiny weight or equivalently small volume. It is clear from (18) that the effect of weight, as mentioned earlier, appears in the combination $\varrho g / \gamma$. With the help of volume $V$, it is useful to introduce the Bond dimensionless parameter $\lambda \equiv V^{1/3} / \varrho g / \gamma$. This supposedly small parameter helps us to develop a perturbative expansion for the contribution of gravity to the shape of the drop. At the first order of correction one has
\[ z = f(\rho) = f_0(\rho) + \lambda f_1(\rho), \]
where $f_0(\rho)$ is the sphere solution found in the previous section. By inserting the above into (6), one finds for $\psi_0(\rho)$
\[ \psi_0(\rho) = \frac{f_0'}{\sqrt{1 + f_0'^2}} = \frac{f_0'}{\sqrt{1 + f_0'^2}} + \lambda \frac{f_1'}{\left(1 + f_0'^2\right)^{1/2}} + O(\lambda^2). \]
The combination $\kappa + \varrho g h$ in the right-hand side of (18) can easily be rearranged based on the effect of gravity using the identity (22). As it is expected that the contact radius $\rho_0$ is changed under the effect of gravity, at the first order of perturbation in $g$, by replacing $\rho_0 = R \sin \vartheta + \delta \rho_0$, the identity is given in the form
\[ \kappa + \frac{\varrho g}{2\gamma} h \simeq \frac{1}{R} - \frac{\delta \rho_0}{R^2 \sin \vartheta} + \frac{\varrho g V}{2\pi \gamma R^2 \sin^2 \vartheta}. \]
We will find later that $\delta \rho_0 > 0$, as expected. By inserting (25) and (26) into (18) and using the fact that $f_0$ satisfies the equation with $\lambda = 0$ (equation (8)), for the case of $\vartheta < 90^\circ$ or the upper half of the case of $\vartheta > 90^\circ$ the Young–Laplace relation reads

$$\frac{d}{d\rho} \left[ \rho f'_1(\rho) \right] = \frac{1}{V^{2/3}} \rho (a + f_0(\rho)) \quad (27)$$

in which

$$a = 2\gamma \frac{\delta \rho_0}{\rho R^2 \sin^2 \vartheta} - \frac{V}{\pi R^2 \sin^2 \vartheta} \quad (28)$$

Using $f_0(\rho) = \sqrt{R^2 - \rho^2 + \zeta_0}$, integrating (27) from 0 to $\rho$ gives

$$\rho \frac{f'_1(\rho)}{(1 + f'_0(\rho))^{3/2}} = \frac{1}{V^{2/3}} \left( \frac{1}{2}(\zeta_0 + a) - \frac{1}{3}(R^2 - \rho^2)^{3/2} + \frac{1}{3}R^3 \right) \quad (29)$$

Again using the expression for $f_0(\rho)$, we find that

$$f'_1(\rho) = \frac{R^3}{V^{2/3}} \left[ \frac{(\zeta_0 + a) + \lambda f'_1(\rho) + \lambda \cos \vartheta}{2(R^2 - \rho^2)^{3/2}} - \frac{1}{3 \rho} + \frac{R^3}{3 \rho(R^2 - \rho^2)^{3/2}} \right] \quad (30)$$

It is useful to note that for the above expression, the limit $\rho \to 0$ exists and is zero, as expected. However, we mention that the above expression diverges in the limit $\rho \to R$, indicating that the present form of the perturbative solution fails for drops with contact angle close to or greater than $90^\circ$. We will come back to this issue later. The above expression can be used to find the corrected value of the contact radius $\rho_0$ or equivalently $\delta \rho_0$. Subject to the condition that the drop intercepts the solid surface with contact angle $\vartheta$ and also the constraint on the volume of the drop, the expression (30) should satisfy the following:

$$- \tan \vartheta = f'_1(\rho_0) = f'_0(\rho_0) + \lambda f'_1(\rho_0) + \lambda \cos \vartheta \quad (31)$$

$$V = \pi \int_0^{\rho_0} \rho^2 f'_0(\rho) \, d\rho \approx - \pi \int_0^{\rho_0} \rho^2 f'_0(\rho) \, d\rho$$

$$- \pi \lambda \int_0^{\rho_0} \rho^2 f'_1(\rho) \, d\rho \quad (32)$$

in which $\rho_0 = R \sin \vartheta + \delta \rho_0$. We mention that, due to the presence of $\lambda$, it is sufficient to insert the unperturbed values of the previous section in the expression for $f'_1$. It is easy to check that, thanks to the identity (22), the first in the above is automatically satisfied. By the second condition the change in the contact radius is found to be

$$\delta \rho_0 = \frac{\rho_0 R^3}{6\gamma} \frac{(1 - \cos \vartheta)^2}{(2 + \cos \vartheta)} > 0 \quad (33)$$

from which the constant $a$ is obtained:

$$a = - R \frac{(1 - \cos \vartheta)(3 + \cos \vartheta)}{(2 + \cos \vartheta)} \quad (34)$$

Once again the relation (30) can be integrated, leading to

$$f_1(\rho) = \frac{R^3}{V^{2/3}} \left[ \frac{3(\zeta_0 + a) + 2R}{6\sqrt{R^2 - \rho^2}} - \frac{1}{3} \ln \left( \frac{R + \sqrt{R^2 - \rho^2}}{2R} \right) \right] + b \quad (35)$$

where $b$ is a constant, which should be determined by the condition

$$0 = f_1(\rho_0) = f_0(\rho_0) + \lambda f_1(\rho_0) + \lambda \cos \vartheta \quad (36)$$

Using the above we find that

$$b = \frac{R^3}{V^{2/3}} \left[ \frac{\cos \vartheta}{2(2 + \cos \vartheta)} + \frac{2}{3} \ln \cos \frac{\vartheta}{2} \right] \quad (37)$$

In the case of $\vartheta > 90^\circ$, (35) represents the correction only for the upper half of the drop. It is seen that both (30) and (35) diverge as $\rho \to R$. So the perturbative solution in the present form fails in the vicinity of the circle $\rho = R$. For $\vartheta > 90^\circ$ one has to find the solution for the convex part (lower half part) as well, represented by the $f_{1-}$. This can also be done along similar lines for the concave part; however, the boundary conditions are different. It is easy to see that in this case, just like we had for the upper part, $f_{1-}(\rho)$ diverges for $\rho \to R$.

One way out of the divergent behavior of $f_{1\pm}(\rho)$ near $\rho = R$ is to change the role of the function $z$ and the variable $\rho$, working with $\rho = h(z)$, for $\rho > 0$. One can then find valid perturbations near $\rho = R$ (the maximum of $\rho$); however, this time the solution diverges at the top of the drop ($\rho \to 0$). This shows that the appearance of the divergent behavior in the perturbative expressions for the shape of the drop is not an intrinsic one, but a coordinate artifact. From all these, there are three functions $f_{1\pm}(\rho)$ and $h_1(z)$, which should be joined smoothly to give the correction of the gravity to the shape of the drop in all regions.

A better way is to use polar coordinates suggested by the sphere solution of the weightless drop. Choosing the bottom of the circle corresponding to the weightless drop as the origin and measuring the angle from the $z$-axis, one has (Figure 3)

$$r(\theta) \cos \vartheta - d = z = f(\rho) = f_0(\rho) + \lambda f_1(\rho) \quad (38)$$

where $d = R - \zeta_0 = R(1 + \cos \vartheta)$, by (13). A perturbative expansion for $r(\theta)$ is then

$$r(\theta) = r_0(\theta) + \lambda r_1(\theta) \quad (39)$$

where

$$r_0(\theta) = 2R \cos \vartheta \quad (40)$$

Putting

$$\rho = r(\theta) \sin \vartheta = R \sin(2\theta) + \lambda r_1(\theta) \sin \vartheta \quad (41)$$
in (38), one obtains

$$\lambda^0 : \quad r_0(\theta) \cos \theta - R + z_0 = f_0(\rho) \bigg|_{\rho=R \sin(2\theta)};$$

$$\lambda^1 : \quad r_1(\theta) \cos \theta = \left[ r_1(\theta) \sin \theta \frac{df_0}{d\rho} + f_1(\rho) \right]_{\rho=R \sin(2\theta)}.$$  \hspace{1cm} (43)

As the concave part always exists, we can use $f_0$, and $f_1$, in the above to find the unknown part $r_1(\theta)$,

$$r_1(\theta) = \frac{R^3}{V^{2/3} \cos \theta} \left( \frac{3(z_0 + a) + 2R}{6R} - \frac{2}{3} \cos(2\theta) \ln \cos \theta \right) + b \frac{\cos(2\theta)}{\cos \theta},$$

in which constant $a$ and $b$ are given by (34) and (37), respectively. In fact, the above expression is nothing but the analytically extended result for the concave part (35) to the entire surface of the drop. We mention that (44) has smooth behavior for the whole interval $0 \leq \theta < \frac{\pi}{2}$, which covers the convex part too. It is useful to define the angle $\theta_0$ as the polar angle at which the contact between the drop and the surface takes place. This angle is easily obtained by the following condition:

$$d \tan \theta_0 = \rho_0 R \sin \theta_0 + \delta \rho_0,$$

in which $\delta \rho_0$ is given by (33). For the spherical solution, $\theta_0 = \theta/2$.

It is a matter of interest to obtain the equatorial radius (maximum bulge) $\rho_1$ for the case of $\theta > 90^\circ$. It is obvious that by the spherical solution $\rho_1 = R$, happening at the angle $\theta_1 = 45^\circ$. In general, the equator is defined by the condition

$$0 = \rho'(\theta_1) = 2R \cos(2\theta_1) + \lambda \left[ \frac{d}{d\theta} \left( \sin \theta r_1(\theta) \right) \right]_{\theta=\pi/4}. \hspace{1cm} (46)$$

Using (41), at the first order of $\lambda$, we find that

$$\rho_1 = R + \lambda \sin \frac{\pi}{4} r_1 \left( \frac{\pi}{4} \right). \hspace{1cm} (47)$$

The equatorial plane intercepts the $z$-axis at

$$z_1 = r(\theta_1) \cos \theta_1 - d,$$

which is easy to find by using (46). For later use, the distance between the apex of the drop and the equatorial plane, $\tilde{h}$, is given explicitly

$$\tilde{h} = h - z_1 = R + \frac{\rho_1}{\rho} R^3 \left( \frac{3(z_0 + a) + 2R}{6R} + \frac{2}{3} \ln \sqrt{\frac{\sqrt{2}}{2}} \right). \hspace{1cm} (50)$$

4. Comparison with data

In order to assess the accuracy of the perturbative solution presented in this work, here the outputs of the solution are compared with some available data. However, it would be helpful to begin with a demonstration of the results. In figure 4, the sphere and the perturbative solution are plotted for two drops which are equal except in their contact angles.
As expected, the apexes of the perturbative solution are lower than the sphere ones, while the contact radii are increased in comparison with the sphere solution. Also for the case of \( \theta > 90^\circ \), the equatorial radius is larger than the radius of the sphere solution.

The outputs of the perturbative solution are compared with the data for drops with both acute and obtuse contact angles. In table 1 the collection for the case of \( \theta < 90^\circ \) for water drops is presented. The data include three drops on the carbon steel surface [12] and one drop on the poly(methyl methacrylate) (PMMA) surface by [17]. The comparison between the experimental values and the ones by the perturbative solution, except perhaps for the contact radius of the third sample on carbon steel, shows satisfactory agreement. The failure of good agreement with the third drop might be better justified once the peculiar behavior of the data with this drop is mentioned. For example, the contact radius of this drop is even less than the one of the sphere solution, and the height of the apex is larger than the one of the sphere solution. Both of these observations are in contrast with expectations from the effect of gravity on a real drop.

In table 2, the collection for the case of \( \theta > 90^\circ \) for mercury drops is presented. The data include four drops of mercury on a glass slide by [8]. Here the data are available for the equatorial and contact radii and the equator–apex difference \( h \) of the previous section. Again, except perhaps for the first drop, the agreement between experimental data and theoretical results is satisfactory. Just like the third water drop, also for the first drop here the data are in opposition to the expectation of the effect of gravity (less radii and larger height than the sphere solution). It is notable that in this collection the Bond parameter, as the perturbative expansion parameter, exceeds 1 (\( \lambda \approx 1.33 \)) for the last drop as the largest one.

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