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A simple formula for the estimation of surface tension from two length measurements for a sessile or pendant drop

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ABSTRACT

We present a very simple formula for the determination of surface tension from only two length measurements for pendant or sessile liquid drops (together with knowledge of their density). The formula is derived from an analytic theory of Morse and Witten for the shape of a drop under a small applied force. ~~We show that, asymptotically, the theory is exact in the limit of small deformation.~~ We also discuss its validity in the presence of measurement accuracy.

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Surface tension; pendant and sessile drops; analytic theory

1. Introduction

The history of the measurement of the surface tension of a liquid by the observation of the shape of a liquid drop in equilibrium under gravity (or the conditions for its instability) goes back well into the nineteenth century. The most notable milestone was the contribution of Bashforth and Adams [1] which is still widely cited, in both the present context and the methodology of the numerical solution of ordinary differential equations. Their objective was to provide extensive and accurate tables, by means of which the value of surface tension could be extracted from shape measurements.

Many methods follow the same general approach, later translated into modern computational form. While reliable, they are still elaborate and somewhat obscure, since they generally involve 'black box' commercial or open software for computation of shape using image analysis. Here we offer a complementary method – an extremely simple and transparent alternative, grounded in analytic theory.

This should prove to be a useful and instructive adjunct to the principal current methods. It yields an immediate value for the surface tension, by means of a simple formula, requiring only *two* length measurements related to the drop profile. The same method can be applied to both sessile and pendant drops, and also bubbles.

The new formula is based on the theory of Morse and Witten [2], which provides an explicit analytic formula for drop shape, in a linear approximation. That is, it is exact in the limit of high surface tension (or small drop size). We will indicate the regime in which this approximation is reasonably accurate.

Evaluation of surface tension of a *sessile* drop, based on a simple formula which only involved a pair of length measurements (maximum drop diameter and height of drop from

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top to equator), appears to date back to Worthington in 1885 [3]. He improved upon an initial (cruder) formula by Quincke (1858) [4], which only involved one length. Various further simple formulae were suggested, and are reviewed in the book by Rusanov and Prokhorov [5], but all these approximations have one thing in common: that they only apply for wide (flat) sessile drops, corresponding to drop diameters exceeding 1.5 cm in the case of water. Rusanov and Prokhorov proceed to state that in order to calculate surface tension for the case of sessile drops of smaller dimensions, 'one needs to use numerical methods' [5].

The analysis of *pendant* drops using a pair of length measurements dates back to Andreas et al. [6] in 1938, who used the maximum drop diameter and the drop diameter, as measured at that distance away from the apex. Surface tension may then be computed from tabulated values obtained from numerical solutions of the Laplace-Young equation [7,8], together with numerical approximations and interpolations [9]. (The table initially provided by Andreas et al. [6] was based on experimental measurements of drop shapes.)

For a sessile drop the above choice for measurements of drop dimensions is not possible. The maximum drop diameter (measured at a horizontal plane), and the distance of this plane from the apex provides an alternative pair of dimensions, suitable for the characterisation of both pendant and sessile drops. The pair features in the (cumbersome) second order perturbation solutions of the Laplace-Young equation, as derived by O'Brien and van den Brule [10] for the computation of surface tension. It is also used in our method described below.

None of the above methods, we believe, have the transparency and analytic basis of what is described here. Our method can be applied in either two or three dimensions for both pendant and sessile drops. The 2d case may be of limited practical value, but we will also present the resulting equation for line-tension in that case.

All of what we present applies equally well to the case of a bubble in a liquid under gravity, with obvious changes.

2. Application of the Morse–Witten theory to pendant and sessile drops

To demonstrate the essence of the method, Figure 1 shows examples of both sessile and pendant liquid drops. We will derive a formula for their values of surface tension γ in terms of the two distances L_x (maximum 'equatorial' drop radius) and L_y (distance of this equator to the drop apex), which are indicated in Figure 1. This assumes knowledge of $\Delta\rho g$, the product of density difference and acceleration due to gravity. The boundary condition at a contacting plane or nozzle outlet is irrelevant, provided it is not such as to break the rotational symmetry of the drop.

To this we apply the analytic results of Morse and Witten [2]. These were not motivated by our present objective: rather they were aimed at developing a method of simulating the interactions of multiple bubbles (or drops) and exploring the form of that interaction in the limit of slight contact [12]. To our knowledge, their results have never been adduced to provide insights or methods for surface tension methods, as below, or indeed introduced into the general theory of sessile and pendant drops. This may be attributed to the difficulty of the theoretical framework presented by Morse and Witten [13]. Despite this, its essential results are simple, compact, and easily applied.

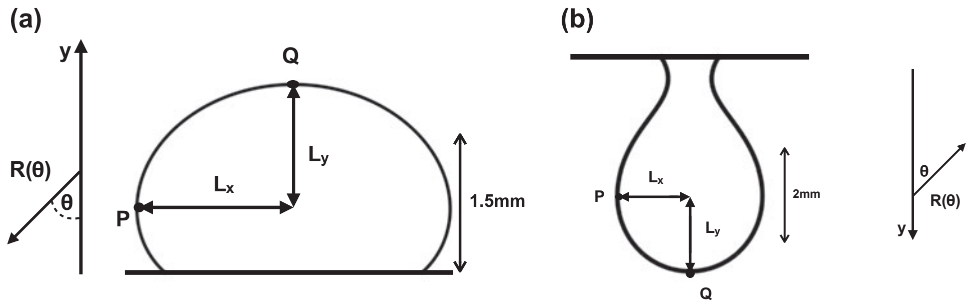

Figure 1. Examples of profiles of sessile and pendant drops (computed by integrating the Laplace equation using standard numerical methods [11]) with relevant notation. Measurements of both L_x and L_y are sufficient to obtain an estimate of surface tension (for given value of $\Delta\rho g$). (Left) Sessile water drop: $\Delta\rho g = 9810\,\mathrm{kg/m^3}$, volume $4\pi/3(3\,\mathrm{mm})^3$ and surface tension of water, $\gamma = 72\,\mathrm{mN/m}$ result in values $L_x = 2.645\,\mathrm{mm}$ and $L_y = 2.235\,\mathrm{mm}$. Using Equation (5) we arrive at an estimate of surface tension as 71.7 mN/m, underestimating the exact value by about 0.4%. (Right) For a pendant water drop of volume $4\pi/3(2\,\mathrm{mm})^3$ measurements of $L_x = 1.474\,\mathrm{mm}$ and $L_y = 1.593\,\mathrm{mm}$ result in an estimate of surface tension as 71.9 mN/m, using Equation (5). The exact value is thus underestimated by about 0.2%.

To describe the profile of a deformed drop we use spherical coordinates R and θ (the third coordinate being irrelevant on grounds of symmetry). The analysis of Morse and Witten [2] gives the radius $R(\theta)$ as

$$R(\theta) = R_0 + \Delta R(\theta), \tag{1}$$

where R_0 is the radius of the unperturbed drop and $\Delta R(\theta)$ is its displacement in response to an applied force F, acting at $\theta = 0$.

To linear order in F the displacement is given by [2]

$$\Delta R(\theta) = \frac{F/\gamma}{4\pi}\left\{\frac{1}{2} + \frac{4}{3}\cos\theta + \cos\theta \ln\left[\sin^2(\theta/2)\right]\right\}. \tag{2}$$

In the case considered here, F is the gravitational (or buoyancy) force of the undeformed sphere in the Morse and Witten theory given by $F = \pm\frac{4}{3}R_0^3\pi\,\Delta\rho g$, where the '+' sign is for sessile and the '−' sign for pendant drops. We note that Morse and Witten [2] only considered the case in which $F \geq 0$, corresponding to a sessile drop (or a drop contacting another drop). The possibility of also studying pendant drops appears to be a new application of the theory.

Note also that the theory is framed in terms of an applied *point* force, which is in itself unphysical and introduces a divergence in the profile, associated with the logarithmic term in Equation (2), and visible in Figure 2. However, this force may be replaced by the distributed force at a flat boundary in either case of Figure 2, without affecting the solution away from the boundary. The remaining solution for the displacement $\Delta R(\theta)$ is small for all angles θ, for small F.

In general our method can be applied in various situations, such as Figure 1(a) or Figure 1(b) which feature finite contact angles, provided an equator exists. In this case, the

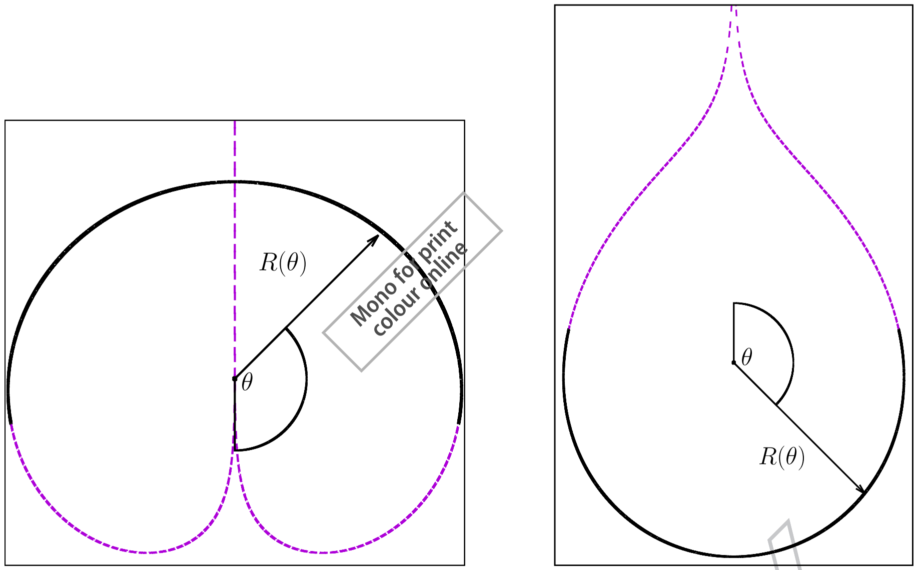

Figure 2. Examples of profiles of sessile and pendant drops, obtained from the result of Morse and Witten, Equations (1) and (2). Only the parts indicated by thick solid lines represent the physical drops of Figure 1. Note that our derived equation for surface tension, Equation (5), applies regardless of the boundary conditions imposed within the other part of the profiles (and also regardless of the volume that is enclosed).

configuration can be extended past the contact plane to create the standard Morse-Witten setup as shown in Figure 2 with a small force $F = \pm\frac{4}{3}\pi R_0^3 \Delta\rho g$.

In the following we adopt the Morse-Witten result, Equation (2), to arrive straightforwardly at a method of estimating surface tension γ.

At the equator (point P in Figure 1) the profile of the drop is vertical for our chosen coordinate system. The corresponding angle θ_P is thus determined from

$$\frac{\mathrm{d}}{\mathrm{d}\theta}(R(\theta)\sin\theta)|_{\theta=\theta_P} = 0, \tag{3}$$

where $R(\theta)$ is given by Equation (2). Solving for θ_P, where we write $\theta_P = \pi/2 + \delta\theta_P$ and Taylor expand cosine and sine terms to first order in $\delta\theta_P$, we can compute the location of P=(P_x,P_y). We thus obtain $L_x = P_x$ and $L_y = R(\pi) - P_y$, with the following expression for L_x and L_y,

$$L_x = R_0\left(1 + \frac{F/(\gamma R_0)}{8\pi}\right)$$
$$L_y = R_0\left(1 - \frac{F/(\gamma R_0)}{4\pi}(\ln 2 - 1/2)\right). \tag{4}$$

We proceed by computing the sum and difference of L_x and L_y, resulting in $L_x - L_y = (\ln 2/4\pi)F/\gamma$ and $Lx + L_y = 2R_0 - (\ln 2 - 1)/(4\pi)F/\gamma$. Setting $F = \pm\frac{4}{3}R_0^3\pi\Delta\rho g$, as above, we can eliminate R_0 to arrive at the following ~~exact~~ expression for surface tension, which we denote by γ_{MW}, since it is based on Morse-Witten theory,

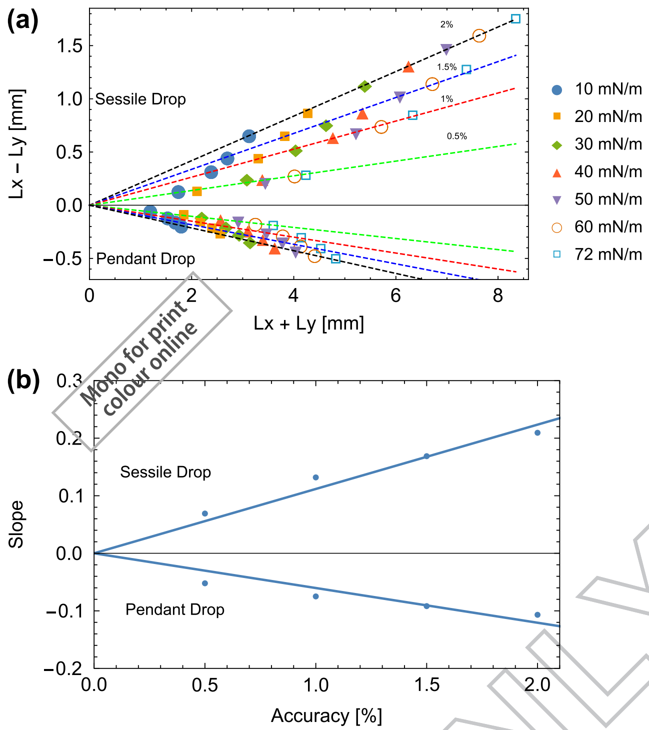

Figure 3. (a) Variation of the difference of our two length measurements ($L_x - L_y$) as a function of their sum ($L_x + L_y$) for numerical solutions, carried out over a range of values of surface tensions equal to and below that of water. Dashed lines mark the respective accuracy of the estimate γ_{MW}. (b) Slope of the lines of constant accuracy as a function of accuracy, see Equation (6). For details, see text.

$$\gamma_{MW} = \frac{\Delta\rho g \ln 2}{24} \frac{(L_x + L_y)^3}{|L_x - L_y|} \left[1 \mp 3c + 3c^2 \mp c^3\right], \quad (5)$$

with $c = \left(\frac{1-\ln 2}{\ln 2}\right) \frac{|L_x - L_y|}{L_x + L_y}$ ($\mp$: $-$ for sessile drop, $+$ for pendant). There are no terms with order higher than c^3. This expression is accurate in the limit $\gamma^{-1} \to 0$, as will be shown below. For practical purposes the c^2 and c^3 terms are negligible.

Figure 1 shows examples of the application of Equation (5) to estimate surface tension for test cases representing sessile and pendant water drops. Shown are accurate solutions of the Laplace-Young equation, computed by standard numerical methods [11], for $\Delta\rho g = 9810\,\mathrm{kg/m^3}$, ~~volume $4\pi/3 \times (3\,\mathrm{mm})^3$~~ and surface tension of water, $\gamma = 72\,\mathrm{mN/m}$. Determination of L_x and L_y from these solutions results in estimates of surface tension from Equation (5) as $\gamma_{MW} = 71.7\,\mathrm{mN/m}$ (sessile drop) and $\gamma_{MW} = 71.9\,\mathrm{mN/m}$ (pendant drop), corresponding to 0.4 and 0.2% errors, respectively.

To investigate the variation of accuracy of our estimate γ_{MW} compared to the exact result, we have carried out simulations for a range of drop volumes and surface tensions (γ) (for a fixed density of water). We present our results in Figure 3(a) in terms of the variation of $L_x - L_y$ with $L_x + L_y$, the relevant combinations in Equation (5). Drop volumes for the simulations were chosen such that γ_{MW} (Equation 5) was within either 0.5%, 1%,

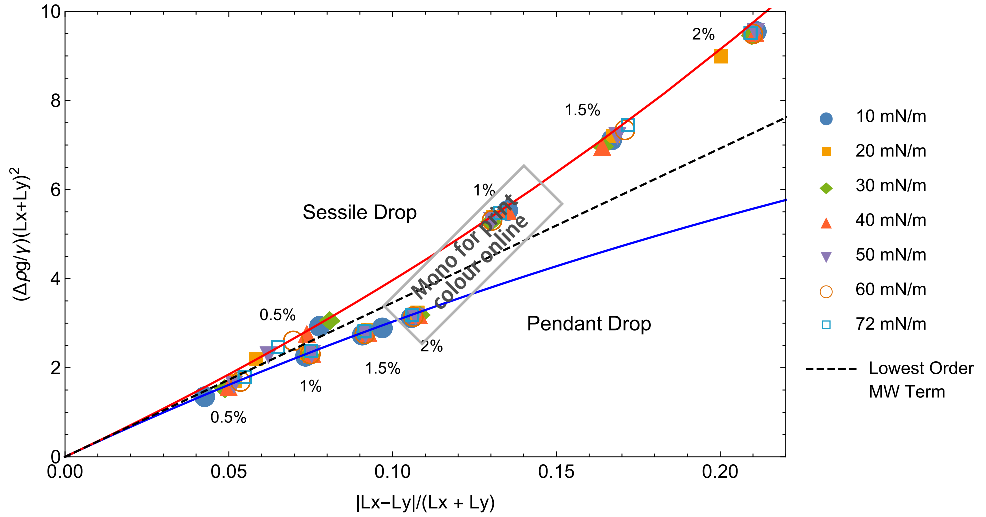

Figure 4. A dimensionless plot of the data in Figure 3(a). Solid lines are obtained from Equation (5), with the sessile case in red and pendant case in blue. The dashed line is the prefactor of ~~Equation (5)~~. The percentages indicated refer to the percentage error in the estimate of γ using the measured L_x and L_y.

1.5%, or 2% of the value of γ set in the simulation. From Figure 3, we find that, for data with the same percentage accuracy ϵ, $L_x - L_y$ varies roughly linearly with $L_x + L_y$ i.e.

$$\frac{(L_x - L_y)}{(L_x + L_y)} = c\epsilon \tag{6}$$

where the constant $c = 0.11 \pm 0.01$ (sessile drop), and $c = -0.06 \pm 0.01$ (pendant drop). Given values for L_x and L_y, this allows the computation of the accuracy of the estimate of γ from Equation (5).

Figure 4 shows Equation (5) and the data from Figure 3(a) in the form of a plot of the dimensionless ratios $\Delta\rho g/\gamma(L_x + L_y)^2$ versus $|L_x - L_y|/(L_x + L_y)$. The small deviations between the theory based on the Morse–Witten result and the exact numerical values is an indication of the accuracy of the Morse–Witten approximation, Equation (5), for both sessile and pendant drops. ~~As expected, the Morse–Witten result is asymptotically exact in the limit of small deformation.~~

Having established the accuracy of the theory, what accuracy can we expect from applying Equation (5) to actual *physical measurements*? Images obtained with digital cameras result in a length resolution of at best 0.001 mm per pixel. It is straightforward to see that L_x can be determined to within $\pm$ 1 pixel, but there has been some discussion as to the accuracy of determining, L_y [5,14], which, when treated in the framework of *random* errors, is greatly magnified. When looking at a pixelated image, it is obvious that the accuracy in L_y is also ± 1 pixel. This *systematic* error is due only to the coarse-graining of the picture. The error in γ_{MW} is then given by $\Delta\gamma_{MW}(L_x, L_y) = \left(\left(\frac{\partial\gamma_{MW}}{\partial L_x}\right)^2 + \left(\frac{\partial\gamma_{MW}}{\partial L_y}\right)^2\right)^{1/2} \Delta L$ where ΔL is the accuracy in L_x or L_y.

To test our result we have applied Equation (5) to photographs of a pendant water drop published by [15]. Values for L_x and L_y were obtained using ImageJ, resulting in $\gamma_{MW} =$

69 mN/m. Note that in the published version of the image, the pixel resolution is only $\Delta L = 0.01$ mm. Evaluating $\Delta\gamma_{MW}$ we get ± 6 mN/m. Our value of $\gamma_{MW} = 69 \pm 6$ mN/m is then in agreement with the value of 72 mN/m given by the authors [15]. We intend to carry out our own experiments in due course.

3. Conclusion

Following the work of Rotenberg et al. [16] and Huh and Reed [17] in 1983, many papers were published that describe the evaluation of surface tension based on the comparison of an image of the entire drop profile with numerical solutions (see for example [15,18,19]). While such an approach will be more accurate for numerical evaluation, we believe that the method described here offers complementary advantages. It is based on an analytically tractable theory which is exact in the limit of small drop deformation, the mathematical procedure is brief and transparent, and it results in an equation for surface tension, Equation (5), which has a very simple form.

The formula can also be generalised to other pairs of measurements (e.g. the pair used by [7], see Section 1), by using non zero values on the RHS of Equation (3). This might mitigate measurement error, and it will also allow for an extension of our formula to the case of a sessile drop with contact angle greater than $\pi/2$ (where L_x doesn't exist). We will examine this in future work, in which we will apply our result to the analysis of experimental data for pure water and surfactant solutions, requiring a computational scheme to extract values of L_x and L_y from high resolution drop images. As we have shown above, the determination of these lengths ~~is~~ high accuracy is important for an accurate estimation of surface tension.

Finally, the derivation shown in Section 2 can also be carried out for two-dimensional drops, using the corresponding 2d equations of the Morse–Witten model [20]. This results in the following expression ~~(exact for the model)~~,

$$\tilde{\gamma}_{MW2d} = \frac{(\pi - 2)}{4} \Delta\tilde{\rho} g \frac{L^3}{|L_x - L_y|}. \quad (7)$$

Here $L = L_x$ for a pendant drop and $L = L_y$ for a sessile drop, $\tilde{\rho}$ denotes a 2d density (mass/area) and $\tilde{\gamma}_{MW}$ is a line tension (with dimension of a force).

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Disclosure statement

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