Compound pendant drop tensiometry for surface tension measurement at zero Bond number—Supporting Information

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Compound pendant drop theory

Here we provide a detailed derivation of the theory presented in the main text for the shape of a pendant drop with density ρ_d suspended from a surface (in this case a needle), with a particle of density ρ_p hanging axisymmetrically at its apex. The compound pendant drop system is surrounded by a bulk fluid phase with density ρ . A schematic of this configuration is shown in Fig. 1.

We now show that the shape of this system is characterized by a drop Bond number,

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Figure 1: A schematic representation of a particle attached to the interface of a pendant drop below a needle. Gravitational forces act on both the particle and the liquid drop, resulting in coupled drop deformations.

 Bo_d , and a particle Bond number, Bo_p , defined by

$$Bo_d \equiv (\rho_d - \rho) g a^2 / \gamma, \qquad Bo_p \equiv (\rho_p - \rho) g a^2 / \gamma.$$
(1)

Here, Bond numbers are directional, as defined by the sign of the density difference. The shape of the fluid interface is described by the axisymmetric Young–Laplace equation, which can be written as a system of first order differential equations for the coordinates rand z of the drop interface, together with the azimuthal angle ϕ , in terms of the arc length s, measured from the three phase contact at the particle. The dimensional Young–Laplace equations are

$$\frac{\mathrm{d}\phi}{\mathrm{d}s} = 2H_0 - (\rho_d - \rho)gz - \frac{\sin\phi}{r}$$
(2a)

$$\frac{\mathrm{d}r}{\mathrm{d}s} = \cos\phi \tag{2b}$$

$$\frac{\mathrm{d}z}{\mathrm{d}s} = \sin\phi. \tag{2c}$$

In the preceding expression, H_0 is the mean curvature at the particle contact. Scaling by

the particle radius a leads to the ordinary differential equations:

$$\frac{\mathrm{d}\phi}{\mathrm{d}\bar{s}} = 2\bar{H}_0 - \mathrm{Bo}_d \,\bar{z} - \frac{\sin\phi}{\bar{r}} \tag{3a}$$

$$\frac{\mathrm{d}\bar{r}}{\mathrm{d}\bar{s}} = \cos\phi \tag{3b}$$

$$\frac{\mathrm{d}\bar{z}}{\mathrm{d}\bar{s}} = \sin\phi \tag{3c}$$

where the Bond number associated with the drop Bo_d naturally arises, together with the scaled mean curvature $\bar{H}_0 \equiv a\Delta P_0/2\gamma$. The associated boundary conditions at the particle p and needle n contacts are:

$$p: \bar{s} = 0, \ \bar{r} = \sin \alpha, \ \bar{z} = \cos \alpha, \ \phi = \pi - (\alpha + \theta_p)$$
(4a)

$$n: \bar{s} = \bar{s}_n \ \bar{r} = \bar{r}_n, \ \bar{z} = h, \ \phi = \theta_n.$$
(4b)

Since the particle is stationary, the net force acting on it must be zero. The net force is the sum of three forces:

(i) the interfacial tension $F_{\text{interfacial}}$, acting upwards around the perimeter of the three phase contact,

(ii) the pressure inside the drop $F_{\rm pressure}$ acting downwards on the drop/particle contact area, and

(iii) the weight of the particle F_{weight} acting downwards.

We now calculate each of these components separately, adopting the notation where a force with a positive sign acts in the positive z-direction.

The force arising from the interfacial tension will act around the perimeter of the three phase contact. By symmetry, the resulting force will act only in the z-direction. Taking the vertical component of the interfacial tension and rotating around the perimeter of the three

phase contact line gives

$$F_{\text{interfacial}} = (2\pi a \sin \alpha) (\gamma \sin(\alpha + \theta_p)).$$
(5)

The force due to pressure is a double integral over the particle-drop contact area (denoted 'area'),

$$\mathbf{F}_{\text{pressure}} = -\iint_{\text{area}} \Delta P \, \mathrm{d}\mathbf{S}$$
$$= -\iint_{\text{area}} \Delta P_0 - (\rho_d - \rho) \, g \, z \, \mathrm{d}\mathbf{S}.$$

Although the above expression is a vector quantity, axial symmetry results in a force acting in the z-direction. Changing to spherical coordinates, the signed pressure force is

$$F_{\text{pressure}} = -\int_{0}^{2\pi} \int_{0}^{\alpha} \{ \Delta P_{0} - (\rho_{d} - \rho)g(a\cos\varphi - a\cos\alpha) \}$$
$$a^{2}\sin\varphi\cos\varphi \,\mathrm{d}\varphi \,\mathrm{d}\theta$$
$$= -\pi (a\sin\alpha)^{2} \Delta P_{0} + (\rho_{d} - \rho) g \,v_{\text{cap}}(a,\alpha). \tag{6}$$

The first term above is the Laplace pressure at the particle contact acting on the circular cross section of the particle while the second term represents the force due to the weight of displaced fluid, where $v_{\text{cap}}(a, \alpha)$ is the volume of the displaced fluid, where

$$v_{\rm cap}(a,\alpha) \equiv \frac{\pi a^3}{3} \left(2 - 3\cos\alpha + \cos^3\alpha\right)$$
$$\equiv 2\pi a^3 \nu(\varphi). \tag{7}$$

Finally, the weight of the particle is

$$F_{\text{weight}} = -(\rho_p - \rho)V_p \ g = -(\rho_p - \rho) g v_{\text{cap}}(a, \pi).$$
(8)

Taking the net force on the particle to be zero gives

$$\bar{F}_{\text{net}} = \sin \alpha \sin[\alpha + \theta_p] - \bar{H}_0 \sin^2 \alpha + \operatorname{Bo}_d \nu(\alpha) - \operatorname{Bo}_p \nu(\pi)$$
$$= 0, \tag{9}$$

where we have also introduced the force scale $2\pi a\gamma$, together with the scaled spherical cap volume defined in eq. (7).

Fitting theoretical curves to experimental photographs

In this section we detail the routine developed to fit the theoretical curve to the experimental photograph, thus allowing the Bond numbers, and ultimately the particle density and interfacial tension, to be determined. The routine implemented can be separated into two subroutines: firstly, the compound drop profile is extracted from an experimental photograph via image analysis, and secondly, the theoretical curve is fitted to the extracted experimental drop profile. This is illustrated in Fig. 2.



Figure 2: An example of an experimental photograph that has been fitted with the theoretical solution presented. The compound drop profile is extracted using the Canny edge detection algorithm. This profile is then fitted with the theoretical solution by minimizing the sum of least squares, using the Levenberg–Marquardt algorithm. The three profiles correspond to the experiment Fig. 2 a (v) from the main text.

We now detail each of the subroutines.

Image analysis

For a given experimental photograph, noise is initially reduced using a Gaussian filter. The compound pendant drop profile is then extracted using a Canny edge detection algorithm,¹ returning a list of integer (r, z) coordinates corresponding to pixels of the compound pendant drop profile.

Next the theoretical curve is fitted to this data.

Levenberg–Marquardt

From the presented theory, a compound pendant drop profile depends on five parameters; the particle radius a and filling angle α , the particle contact angle θ_p , and finally two Bond numbers, Bo_d and Bo_p. From this set of parameters, all other quantities associated with the interface can be determined from eqs. (3), (4) and (9).

For a given experimental photograph, there are three additional parameters; two associated with the position of the axes, (R_0, Z_0) , and finally, a possible small rotation ω associated with a small camera rotation.

The theoretical curve was fitted to the experimental drop profile using a numerical optimization algorithm (Levenberg–Marquardt) similar to those used in current pendant drop tensiometers. We minimize the sum of the distance squared between each data point and the theoretical function, which is a function of the unknown parameters

$$\boldsymbol{\beta} = \{a, \alpha, \theta_p, \operatorname{Bo}_d, \operatorname{Bo}_p, R_0, Z_0, \omega\}.$$

Given a parameter set β , a theoretical profile can be generated. For each data point (r_i, z_i) , the squared residual (the minimal squared distance between the given point and the theoretical curve) can be calculated as follows: the data point is rotated according to the new axes origin (R_0, Z_0) , and axes rotation ω . If the rotated data point is above the particle contact line, $\{(r_i - R_0) \sin \omega + (z_i - Z_0) \cos \omega\} > a \cos \alpha$, the residual is calculated

by finding the minimum distance between the rotated point and the theoretical curve for the drop interface. Thus, the residual e_i can be calculated as

$$e_i^2 = \min_s F_i(s),\tag{10}$$

where $F_i(s)$ is the squared distance between the data point (r_i, z_i) and the theoretical point (r(s), z(s)) at arc length s (see Fig. 3)

$$F_i(s) = e_i^r(s)^2 + e_i^z(s)^2$$
(11)

where

$$e_i^r(s) = |(r_i - R_0)\cos\omega - (z_i - Z_0)\sin\omega| - r(s)$$
 (12)

$$e_i^z(s) = ((r_i - R_0)\sin\omega + (z_i - Z_0)\cos\omega) - z(s)$$
(13)

are the horizontal and vertical distances between the (rotated) experimental data points and the theoretical curve, respectively. In the preceding expression $r = a \bar{r}$ and $z = a \bar{z}$.

If the rotated data point is below the particle contact line, $\{(r_i - R_0) \sin \omega + (z_i - Z_0) \cos \omega\} \le a \cos \alpha$, the residual is calculated by comparing the point to the particle, which gives

$$e_i = \left| \sqrt{(r_i - R_0)^2 + (z_i - Z_0)^2} - a \right|.$$
(14)

The residual e_i is calculated for each experimental data point, thus giving the objective function that we minimize, the sum of squares E, defined

$$E = E(\boldsymbol{\beta}) \equiv \sum_{i=1}^{n} e_i^2.$$
(15)

For a given experimental photograph, this objective function is explicitly a function of the parameters β used in generating a theoretical profile.



Figure 3: The residual e_i for a given data point (r_i, z_i) from the drop interface, found by minimizing the squared distance (the function $F_i(s)$) between the data point and the interface. The axes origin with respect to the experimental photograph (R_0, Z_0) , together with the angular offset ω are also shown.

A robust and efficient iterative procedure to minimize an *m*-dimensional nonlinear function (with m = 8) is the Levenberg–Marquardt optimization routine. To implement the method, the residual vector e (with elements e_i) and the Jacobian matrix **J** are evaluated for each data point, with the Jacobian defined

$$\mathbf{J}_{ij} = \frac{\partial e_i}{\partial \beta_j}.$$
 (16)

The Jacobian can be calculated numerically by individually perturbing each parameter and calculating a numerical derivative, *i.e.* for $h \ll 1$

$$\frac{\partial e_i}{\partial \beta_j} = \frac{e_i(\beta_1, \dots, \beta_j + h, \dots, \beta_m) - e_i(\boldsymbol{\beta})}{h}.$$
(17)

The Levenberg–Marquardt optimization routine iteratively updates the parameter vector $\boldsymbol{\beta}^{(k)}$ according to

$$\boldsymbol{\beta}^{(k+1)} = \boldsymbol{\beta}^{(k)} + \boldsymbol{\delta} \tag{18}$$

where $\boldsymbol{\delta}$ is calculated by solving

$$(\mathbf{J}^{\mathrm{T}}\mathbf{J} + \lambda \operatorname{diag}(\mathbf{J}^{\mathrm{T}}\mathbf{J})) \boldsymbol{\delta} = -\mathbf{J}^{\mathrm{T}}\boldsymbol{e},$$
(19)

where diag($\mathbf{J}^{\mathrm{T}}\mathbf{J}$) is the diagonal matrix with diagonal elements taken from $\mathbf{J}^{\mathrm{T}}\mathbf{J}$, while λ is a parameter which varies at each of the iteration. If the objective function E reduces, the parameter λ is reduced (typically $\lambda = \lambda/10$). Conversely, if the objective function increases in magnitude, the parameter is increased (typically $\lambda = 10\lambda$).

This iterative process is repeated until either:

- i. the objective has converged, $E < tol_1$
- ii. the parameters have converged, $\|\boldsymbol{\beta}^{(k+1)} \boldsymbol{\beta}^{(k)}\| < \mathrm{tol}_2$
- iii. the number of iterations has exceeded a specified threshold, $n_{\text{steps}} > \text{tol}_3$.

The optimized parameter set includes the two Bond numbers, as well as the particle radius. Provided one of these Bond numbers is not zero, this Bond number can be used to express the interfacial tension in terms of the physical quantities associated with the system (from eq. (1)). If both Bond numbers are non-zero, their ratio can be used to express the particle density ρ_p in terms of the two fluid densities,

$$\rho_p = \rho + (\rho_d - \rho) \operatorname{Bo}_p / \operatorname{Bo}_d.$$
⁽²⁰⁾

Experimental details

Water was obtained from a Millipore Direct-Q 5 system (minimum resistivity 18.4 M Ω cm). Toluene and bromodecane were obtained from Sigma (>99%) and used as received. Silica spheres were obtained from Over the Rainbow, Seaford, VIC, Australia. Silica spheres with a radius of ~1 mm were made hydrophobic by sputtering 5 nm of copper onto the spheres, and subsequently soaking in a 1 mM decanethiol solution in absolute ethanol. For each experiment, a pendant drop was formed below the needle, with the particle attached by bringing the drop into contact with the particle.

Experiments were visualized using a CCD camera (Flea3, Point Grey, Richmond, BC, Canada) coupled to a Kozo XJP-300 microscope. The optical system was calibrated using the known needle diameter. Diffuse illumination was provided using a white LED source and a diffuser. A routine developed in Mathematica (Wolfram Research) was used to extract the profile and fit the theoretical solution.

The interfacial tension for the bromodecane/toluene mixture was calcuated from literature values for bromodecane of 44 mN/m,² and toluene of 37 mN/m,³ assuming ideal mixing. The molar ratio used was 1.00:0.97 (bromodecane:toluene) giving a predicted interfacial tension of 40.6 mN/m.



Sensitivity

Figure 4: A comparison between the sensitivity of the compound pendant drop tensiometry method presented here to conventional pendant drop tensiometry. The image on the left shows a bromodecane drop (red), and a compound silica-bromodecane drop (blue). Both drops have the same volume and all other physical quantities are taken from our experiments. Two more simulated plots illustrate a 10% increase in the interfacial tension (dashed purple for the plain drop, dashed green for the compound pendant drop). The figure on the right illustrates the profile change, with the grid lines showing the pixel density of the camera used in this work.

Ultimately the sensitivity of a tensiometer which relies on fitting a theoretical curve to

an experimental drop profile depends on its ability to distinguish between different drop profiles. To illustrate the sensitivity of the method presented in this Letter compared with existing pendant drop tensiometers, we compared theoretical drop profiles formed with the same physical quantities as those in Experiment 3, for a bromodecane drop surrounded by water (*i.e.* the same fluid densities, interfacial tension, needle diameter, particle size and particle density).

Firstly, a theoretical pendant drop profile was formed, which was then compared to a pendant drop of the same volume but with an interfacial tension that differed by 10%. This process was repeated for the compound pendant drop system (with a silica particle attached). The associated Bond number for the system is $Bo_d \sim 0.02$. All four interfaces are shown in Fig. 4. The unperturbed interfaces are shown in blue (compound pendant drop) and red (pendant drop), with the increase in interfacial tension of 10% shown in dashed green and dashed purple, respectively.

An analogy to Hookean springs

We draw an analogy between the system presented and that for a more classical spring scale. A well know method for calculating the mass of an object is to attach it to a spring with a known spring constant k and measure the displacement x. Using Hooke's law for small deformations, the applied force can be calculated and then equated to the gravitational force, *i.e.* F = -kx = mg. To calibrate the spring constant, a precisely known mass is attached to the spring. This analogy illustrates the case where the particle Bond number is appreciable, while the drop Bond number is negligible (Bo_d $\ll 1$, Bo_p ~ 1), where γ takes the role of the spring constant, while the 'displacement' is no longer an easily extracted value, but rather it is related to the deformation profile and can be calculated by fitting the theoretical curve to the experimental data.

The method corresponding to both Bond numbers being appreciable ($Bo_d \sim 1, Bo_p \sim 1$)

is slightly more involved, and can be thought of as a spring with its own mass. Thus, the spring will itself deform due to its own weight. If a mass is added to this new 'heavy' spring, this mass will further deform the spring, however these two deformations will result in fundamentally different deformation profiles. The attached mass deformation will deform the spring constantly throughout, however the spring weight will deform the top of the spring *more* than the bottom. By using knowledge of the spring mass will then enable the spring constant to be calculated, which in turn can be used to calculate the weight of the added mass. Similarly, if a pendant drop is deformed with both the drop and particle Bond numbers being appreciable, it is possible to calculate both the interfacial tension and the particle density simultaneously.

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