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

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Abstract

A widely used method to determine the interfacial tension between fluids is to quantify the pendant drop shape that is determined by gravity and interfacial tension forces. Failure of this method for small drops or small fluid density differences is a critical limitation in microfluidic applications and when only small fluid samples are available. By adding a small spherical particle to the interface to apply an axisymmetric deformation, both the particle density and the interfacial tension can be simultaneously and precisely determined, providing an accurate and elegant solution to a long-standing problem.

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Introduction: Capillary phenomena have captured the imagination of great minds for centuries, including those of da Vinci, Young, Newton, Laplace and Maxwell among many others.[1] Capillarity also lies at the foundation of modern nanotechnology because it involves interactions that were described by Maxwell as being "sensible only at insensible distances".[1] Tensiometry, the measurement of the interfacial tension between fluid phases, directly probes the competition between intermolecular forces that give rise to interfacial tension, and long-range gravitational or applied forces that deform the fluid interface. By measuring the gravitational deformation of a pendant drop[2–4] and matching that to a solution of the Young-Laplace equation, the interfacial tension can thus be determined. This is one of the most widely used operating principles of current interfacial tension measuring devices.

Bashforth and Adams,[5] equally well-known for developing the robust algorithm for integrating ordinary differential equations, showed that the shape of a pendant drop depends only on a single dimensionless quantity, the Bond number $\mathrm{Bo} \equiv \rho g R^2/\gamma$, that characterizes the ratio of gravitational to interfacial forces in terms of the density ρ, acceleration due to gravity g, drop size R and interfacial tension γ. With advances in numerical computation and image processing, pendant drop tensiometry appears to be a mature technology.[6–9]

However, there are two regimes in which standard pendant drop tensiometry fails. For situations in which the interfacial tension force is too low to sustain a stable hanging drop, corresponding to Bond number $\mathrm{Bo} \gg 1$, the spinning drop method[10] that exploits fluid inertia to deform the drop can be used.

In the opposite regime, $\mathrm{Bo} \to 0$, surface tension dominates and the drop does not deform. To address this problem, a complex experimental apparatus has been developed in which a droplet is formed between two surfaces that are then separated, allowing gravity to act over a larger length scale, providing a quantifiably deformation to the interface.[11–13] A complimentary approach to address this problem is the development of more complex optimization algorithms for image analysis.[14] Although these advances provide some improvements, they cannot circumvent the inherent fundamental physical limitations of the method as $\mathrm{Bo} \to 0$.

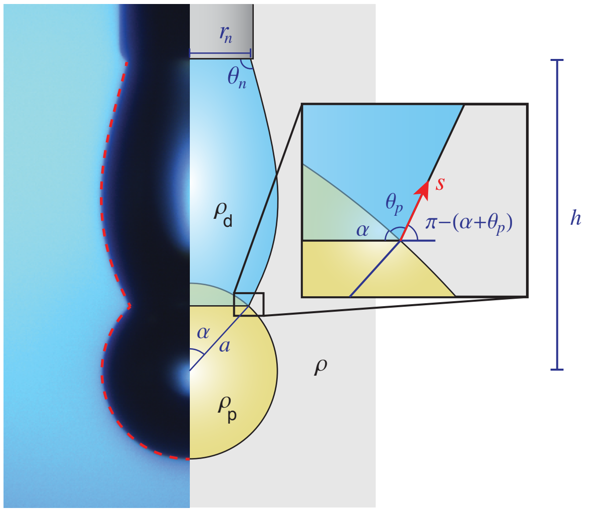
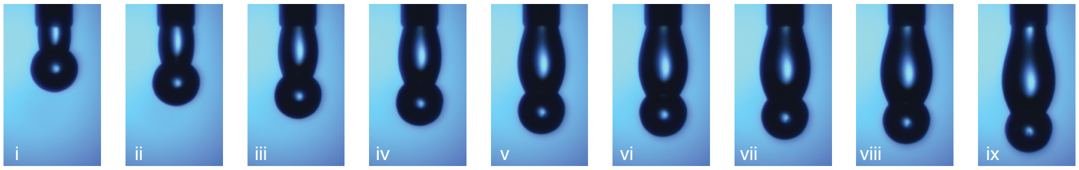
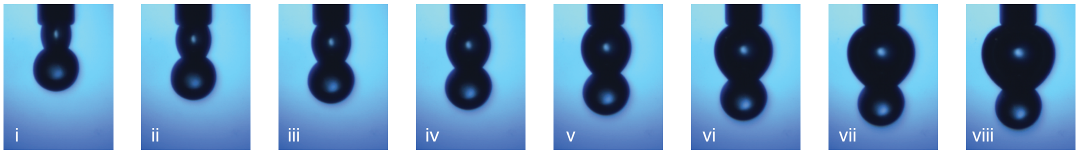


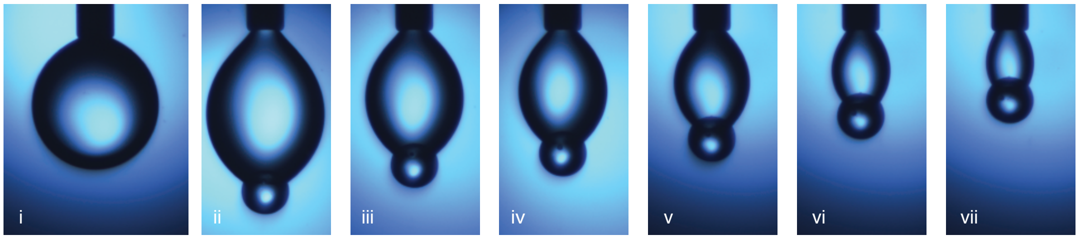
Figure 1: Gravitational forces on both the particle and the liquid drop result in coupled drop deformations of a compound pendant drop. Right side: A schematic representation of a spherical particle attached to the interface of an axisymmetric pendant drop emerging from a needle into a bulk fluid phase. Left side: An image of a compound pendant drop from Fig. 2 a (v) with the drop shape (red dashed line) found by solving the Young-Laplace equation to determine the drop and particle Bond numbers.

Theory and experimental: In this Letter, we adopt a different strategy by implementing a compound pendant drop technique, achieved simply by adding a spherical particle of known size to the pendant drop. The pendant drop becomes deformed axisymmetrically by the weight and natural positioning of the particle. A significant advantage of this approach is that it does not require new instrumentation, and with the theoretical framework presented here, allows accurate simultaneous determination of the interfacial tension and the particle density. We further demonstrate that the interfacial tension between two fluids that are density matched can be accurately determined, even though the Bond number is zero. The method can also be used to determine the surface tension of pure liquids for which the Bond number is negative.

Consider a pendant drop of density ρ_d emerging from a blunt needle that is used to dispense the drop of varying volume into a bulk external fluid of density ρ. A particle of radius a and density ρ_p is attached to the drop, with gravity naturally positioning it at the bottom of the axisymmetric drop,[15] as illustrated in Fig. 1.


(a) Silica particle below water drop in air


(b) Silica particle below air bubble in water


(c) Silica particle below bromodecane drop in water

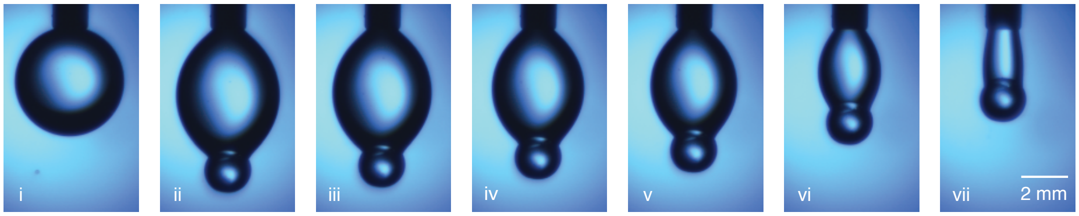

(d) Silica particle below bromodecane-toluene drop in water

Figure 2: (a) A silica particle attached to a pendant water drop in air: (i)-(ix) Gravitational force on the drop and particle elongates the drop as the drop volume increases. (b) A silica particle attached to a pendant air bubble in water: (i)-(viii) Variation of the bubble shape as the volume is increased by injecting air via the needle. The drop Bond number $\mathrm{Bo}_d \sim -1$, so the buoyancy forces on the bubble and the particle act in opposite directions. (c) Bromodecane pendant drop in water with drop Bond number $\mathrm{Bo}_d \sim 0.005$: (i) a near spherical drop shape prior to particle attachment, (ii)-(vii) drop shape after attachment of a silica particle at decreasing drop volume. (d) Density matched bromodecane-toluene pendant drop in water with zero drop Bond number $\mathrm{Bo}_d = 0$: (i) a spherical drop prior to particle attachment, (ii)-(vii) drop shape after attachment of a silica particle at decreasing drop volume. The scale bar shown applies to all images.

This system is characterized by a drop Bond number, Bo_d, and a particle Bond number, Bo_p, defined by

$$\mathrm{Bo}_d \equiv (\rho_d - \rho)\, ga^2/\gamma, \qquad \mathrm{Bo}_p \equiv (\rho_p - \rho)\, ga^2/\gamma. \tag{1}$$

Here, Bond numbers are directional, as defined by the sign of the density difference. The pendant drop shape is described by the axisymmetric Young–Laplace equation, that can be written as a system of first order differential equations for the cylindrical coordinates r and z of the drop interface, together with the tangent angle ϕ, in terms of the arc length s, measured from the three phase contact at the particle.[5,15] These quantities are defined in Fig. 1.

With length variables scaled by the particle radius a (as indicated by the overbar), the Young-Laplace equation can be written as a set of coupled ordinary differential equations:

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

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

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

where $\bar{H}_0 \equiv a\Delta P_0/2\gamma$ is the scaled mean curvature at the point of contact with the particle at $\bar{s} = 0$. ΔP_0 is the pressure difference between the outside and inside of the drop and may be regarded as the Lagrange multiplier that is determined by the volume of the drop.

The boundary conditions at contact with the particle, p, at $\bar{s} = 0$ and with the needle, n, at $\bar{s} = \bar{s}_n$ are:

$$p : \bar{s} = 0,\ \bar{r} = \sin\alpha,\ \bar{z} = \cos\alpha,\ \phi = \pi - (\alpha + \theta_p) \tag{3a}$$

$$n : \bar{s} = \bar{s}_n\ \bar{r} = \bar{r}_n,\ \bar{z} = \bar{h},\ \phi = \theta_n. \tag{3b}$$

The equilibrium position of the particle is determined by the balance of three forces: (i) the interfacial tension acting around the three phase contact line at the particle, (ii) the pressure difference on different parts of the particle within the drop phase and the bulk fluid phase, and (iii) the gravitational force on the particle. Equating these three contributions gives the the final equation that completes the specification of the problem

$$\sin\alpha\sin(\alpha+\theta_p)-\bar{H}_0\sin^2\alpha+\mathrm{Bo}_d\,\nu(\alpha)-\mathrm{Bo}_p\,\nu(\pi)=0 \tag{4}$$

where $2\pi a^3\nu(\alpha)\equiv\pi a^3(2-3\cos\alpha+\cos^3\alpha)/3$ is the volume of a spherical cap subtending an angle α (see Fig. 1).

The pendant drop profile is characterized by the drop Bond number, Bo_d, and the particle Bond number, Bo_p, defined in eq. (1). We will focus on results specific to compound pendant drop tensiometry that corresponds to $\mathrm{Bo}_p\sim 1$ and arbitrary values of Bo_d. The limit $\mathrm{Bo}_p\to 0$ corresponds to standard pendant drop tensiometry and will therefore not be considered further.

We now present four experimental cases to illustrate the key features and capabilities of compound pendant drop tensiometry:

Case 1. $\mathrm{Bo}_d\sim 1$, $\mathrm{Bo}_p\sim 1$: The drop is deformed by the combined weight of the particle and the fluid.[11,13] These two contributions to interfacial deformation can be decomposed and allows simultaneous measurement of the interfacial tension and the particle weight or the particle density. The experimental system is a silica particle in a water pendant drop in air.

Case 2. $\mathrm{Bo}_d<0$, $\mathrm{Bo}_p\sim 1$: As the Bond numbers have opposite signs, gravitational forces on the drop and the particle act in opposite directions. If the drop is a "bubble", this is a way to use compound pendant drop tensiometry to measure the surface tension of a bulk liquid-vapor interface. The experimental system is a silica particle in a pendant gas bubble in water.

Case 3. $\mathrm{Bo}_d\ll 1$, $\mathrm{Bo}_p\sim 1$: The drop is mainly deformed by the particle weight, the effect of the drop weight is small. The experimental system is a silica particle in a bromodecane pendant drop in water.

Case 4. $\mathrm{Bo}_d = 0$, $\mathrm{Bo}_p \sim 1$: The interface is only deformed by the weight of the particle. The experimental system is a silica particle in a bromodecane-toluene pendant drop in water. The composition of the miscible bromodecane-toluene mixture is density matched to water to give $\mathrm{Bo}_d = 0$.

Results and discussion: Photographs of these four experimental systems are shown in Fig. 2 for varying drop volumes. For each photograph the theoretical compound pendant drop profile is fitted to the experimental profile (see Fig. 1), determining the Bond numbers, Bo_d and Bo_p, together with the particle radius a. The interfacial tension can be calculated from eq. (1), while the ratio of Bond numbers

$$\mathrm{Bo}_p/\mathrm{Bo}_d = (\rho_p - \rho)/(\rho_d - \rho), \tag{5}$$

determines the particle density, ρ_p. The compound pendant drop profile is extracted from a photo image using a Canny edge detection algorithm[16] after checking that there is no anisotropy in the optical system. Optimal values of the particle radius, a, the filling angle, α, the particle contact angle, θ_p, and the Bond number, Bo_d and Bo_p, are determined by the Levenberg-Marquardt method[17,18] (see Supporting Information for details).

In Fig. 2a, for **Case 1**: $\mathrm{Bo}_d \sim 1$, $\mathrm{Bo}_p \sim 1$, we show a sequence of pendant water drop shapes in air with an attached silica particle and in Fig. 2b, corresponding to **Case 2**: $\mathrm{Bo}_d < 0$, $\mathrm{Bo}_p \sim 1$, we show a sequence of pendant bubble shapes in water with an attached silica particle. The particle density found by analyzing the variations of drop shape with drop volume is shown in Fig. 3. Also shown for comparison is the mean density calculated by weighing the particles independently with a microbalance. The accuracy of the results for the particle density improves with increasing drop volume because larger and more complex drop shapes provide more varied data points to facilitate accurate image analysis. The agreement between the three methods of determining the particle density is very good.

The air/water surface tension, $\gamma_{A/W}$, determined by this method is shown in Fig. 4 and compares favorably with the literature value of 72 mN/m.

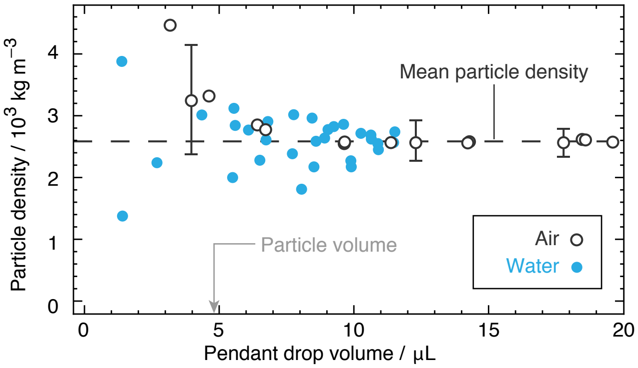


Figure 3: The density of the silica particle deduced from the compound pendant water drop in air (filled blue circles) and the compound pendant bubble in water (open white circles) experiments. The mean density calculated by independently weighing the particles with a microbalance is shown as the dashed line. Representative experimental uncertainties are included.

In Fig. 2c, for **Case 3**: $\mathrm{Bo}_d \ll 1$, $\mathrm{Bo}_p \sim 1$, we show a sequence of pendant bromodecane drop shapes in water with an attached silica particle and in Fig. 2d, corresponding to **Case 4**: $\mathrm{Bo}_d = 0$, $\mathrm{Bo}_p \sim 1$, we show a sequence of pendant bromodecane-toluene drop shapes in water with an attached silica particle. The composition of the bromodecane-toluene mixture is adjusted to match the density of water thereby giving a zero drop Bond number, $\mathrm{Bo}_d = 0$. From photos (i) of Fig. 2c where $\mathrm{Bo}_d \sim 0.005$ and of Fig. 2d where $\mathrm{Bo}_d = 0$, we see that the drop shape is spherical so no information can be deduced about the interfacial tension. The drop shapes at different drop volumes with the silica particle attached is shown in photos (ii)-(vii) in each case.

From such images, variations of the extracted bromodecane/water, $\gamma_{BD/W}$ and bromodecane-toluene/water interfacial tensions with drop volume are shown in Fig. 4. The results for bromodecane/water interfacial tension agree very well with the literature value of 44 mN/m for almost all drop volumes.[19] The expected interfacial tension for the bromodecane-toluene system is calculated from the pure components as 40.6 mN/m as described in the Supporting Information,

Conclusion: In conventional pendant drop tensiometry, the zero Bond number limit is a

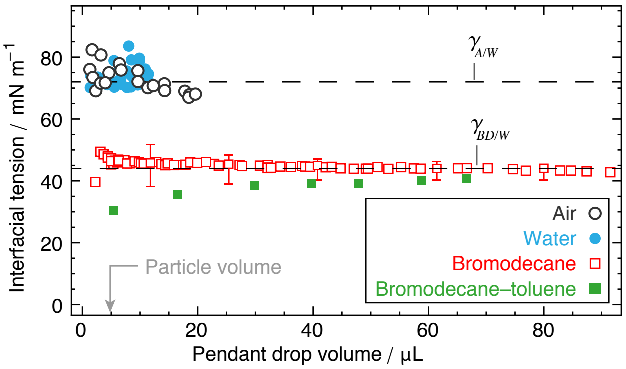


Figure 4: The interfacial tension for each of the four particle-drop systems deduced by compound pendant drop tensiometry shown in Fig. 2: the air-water interfacial tension calculated from a water drop in air (filled blue circles) and from an air bubble in water (open white circles); a bromodecane drop in water (open red squares) and a bromodecane-toluene drop density matched to water (solid green squares) demonstrates the applicability of the method even at zero Bond number.

physical constraint that cannot be overcome by improving the measurement precision. The attachment of a particle to a pendant drop to create a compound pendant drop tensiometer, that, together with appropriate theoretical modeling provides a simple and accurate route to measure key physical and thermodynamic parameters at low and zero Bond numbers. From a single drop profile acquisition, the interfacial tension, liquid/solid contact angle and particle density can be obtained. As well as circumventing the limits of conventional pendant drop tensiometry, the present approach can possibly be improved with more sophisticated image analysis methods. In any case, the compound pendant drop method facilitates access to surface and interfacial tensions with much smaller liquid sample sizes, which is of particular interest when dealing with valuable or scarce biological samples. It additionally provides new opportunities for the study of interfacial dynamics by offering simultaneous acquisition of interfacial tension and contact angle, pertinent to inkjet and 3D printing as well as formulation of smart coatings.

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Supporting Information Available

A derivation of the theory, experimental and optimization details, a comparison between the sensitivity for the method presented compared with existing pendant drop tensiometry, and an analogy with classical Hookean springs.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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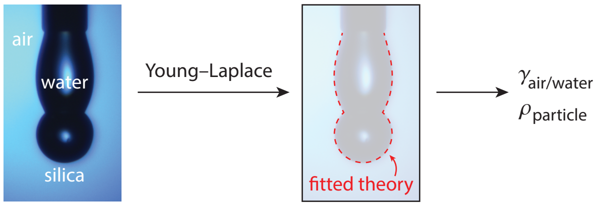
Graphical TOC Entry



Adding a small, spherical particle to a drop allows measurement of interfacial tension, contact angle and particle mass, even at zero Bond number.