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Accuracy of Axisymmetric Drop Shape Analysis in Determining Surface and Interfacial Tensions

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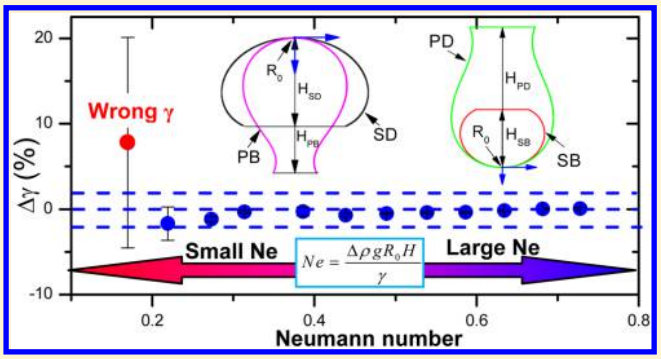
Supporting Information

ABSTRACT: Axisymmetric drop shape analysis (ADSA) has been used in a broad range of applications for determining surface tensions of air−liquid surfaces and interfacial tensions of liquid−liquid interfaces. However, it is well-known that the accuracy of ADSA deteriorates upon the reduction of drop volume. Here, we systematically compared different criteria and parameters in evaluating the accuracy of ADSA upon reducing drop volume. By scrutinizing the dependence of ADSA accuracy on various parameters, including the capillary constant (c), the Bond number (Bo), the Worthington number (Wo), and the shape parameter (P_s), we concluded that the classical Bond number failed to predict the accuracy of drop shape analysis at very small drop volumes. Thus, we proposed a replacement of the classical Bond number, called the Neumann number $Ne \equiv (\Delta\rho g R_0 H)/\gamma$. The design rationale of this new dimensionless number lies in the use of the geometric mean of the radius of curvature at the drop apex (R_0) and the drop height (H) as the new characteristic length (L) to represent the drop size, that is, $L = (R_0 H)^{1/2}$. It is found that the Neumann number is capable of evaluating the accuracy of ADSA. Moreover, we have demonstrated the usefulness of the local Neumann number, $Ne_z \equiv (\Delta\rho g R_0/\gamma)z$, in evaluating the contribution of the local drop profile to the accuracy of ADSA.



INTRODUCTION

Determination of the surface tension of air−liquid surfaces and the interfacial tension of liquid−liquid interfaces plays an important role in a wide range of scientific and industrial fields.[1] Various methods have been developed to measure the surface or interfacial tension, such as the Wilhelmy plate, the drop weight/volume method, and the maximum bubble pressure method.[2] Among these methods, drop shape analysis stands out with a number of advantages.[1,3] First, it only requires a small amount of liquid sample (usually less than 100 μL). Second, it is capable of determining both surface and interfacial tensions. Third, it is capable of measuring dynamic (i.e., time-dependent) and low surface or interfacial tensions (less than 1 mN/m).

Along the lines of early efforts in analyzing liquid−-fluid menisci,[4] Neumann and co-workers developed the numerical algorithm termed Axisymmetric Drop Shape Analysis (ADSA) for determining surface and interfacial tensions from the shape of drops or bubbles.[5−8] To date, ADSA has been widely used in a variety of applications, such as the biophysical study of lung surfactant,[9,10] adsorption of proteins and phospholipids,[11,12] cellular biomechanics,[13,14] and determination of solid surface tensions.[15,16]

Although ADSA has been extensively used in a variety of applications, it is well-known that ADSA only applies to well-deformed drops or bubbles.[8,17,18] Similar to other drop shape analysis methods, the accuracy of ADSA deteriorates given nondeformed nearly spherical drops or bubbles.[19−21] Traditionally, drop deformation is quantified by the Bond number, $Bo = \frac{\Delta\rho g L^2}{\gamma}$,[2,22] where $\Delta\rho$ is the density difference across the surface or interface, g is the gravitational acceleration, γ is the surface or interfacial tension, and L is a characteristic length representing the size of the drop or bubble. When the physicochemical properties of the surface or interface are grouped into a parameter with a length scale called the capillary constant, $c = \sqrt{\frac{\gamma}{\Delta\rho g}}$, the Bond number can be rewritten as $Bo = \left(\frac{L}{c}\right)^2$. The radius of curvature at the drop or bubble apex (R_0) is commonly used as the characteristic length. Hence, the Bond number is generally defined as $Bo = \frac{\Delta\rho g R_0^2}{\gamma} = \left(\frac{R_0}{c}\right)^2$. With this well-accepted definition, a Bo significantly lower than unity indicates a nondeformed nearly spherical drop or bubble where the capillary forces significantly outweigh gravity. In other words, a low Bo means that the size of the drop or bubble is much smaller than the intrinsic capillary constant of the surface or interface. Therefore, the Bo has been commonly used as a criterion for determining the accuracy of ADSA and other drop shape analysis methods.[21,23]

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Despite its wide use, the *Bo*, under certain circumstance, fails to predict the accuracy of drop shape analysis.[19−21] Although multiple variables collectively determine the accuracy of drop shape analysis, it is well accepted that a small drop volume is usually the primary source of errors in many practical applications. To quantify the effect of drop volume on measurement accuracy, Berry et al. defined a new dimensionless group called the Worthington number, $Wo = \frac{V}{V_{max}}$, primarily used for analyzing pendant drops.[21] In this definition, V is the actual drop volume, and V_{max} is the theoretical maximum volume for a pendant drop suspended below a capillary tube with the diameter D_t, that is, $V_{max} = \frac{\pi D_t \gamma}{\Delta\rho g}$. Hence, the *Wo* can be written as $Wo = \frac{\Delta\rho g V}{\gamma\pi D_t}$, which is equivalent to the *Bo* by using $L = \sqrt{\frac{V}{\pi D_t}}$ as the characteristic length. Hence, the *Wo* is intrinsically a variation of the classical *Bo*. However, by redefining and calculating the characteristic length directly from the drop volume, it was found that the *Wo* is more reliable than the *Bo* in predicting the accuracy of pendant drop analysis.[21]

Although plausible for quantifying drop deformation, both *Bo* and *Wo* have limitations since the measured surface or interfacial tension (γ) is required to evaluate both parameters. For nondeformed nearly spherical drops or bubbles, the γ value calculated from drop shape analysis can deviate significantly from the true value and consequently introduce errors to the evaluation of these dimensionless parameters. To overcome this limitation, Neumann and co-workers proposed a purely geometric parameter called the shape parameter (P_s) to predict the accuracy of ADSA calculations.[19,20,24] The P_s measures the extent to which the geometric shape of a drop or bubble deviates from a perfect sphere. The larger the deviation, the larger the deformation, and hence the ADSA calculation is expected to be more accurate. Since the P_s is defined with geometric comparisons, the evaluation of P_s does not require knowledge of physicochemical properties of the surface or interface, that is, the P_s is independent from the capillary constant (c). Therefore, the P_s is capable of predicting the accuracy of ADSA calculation prior to surface or interfacial tension measurement.

The P_s was first evaluated by calculating the sum of normal distances between the drop or bubble profile and a reference circle with the radius of R_0.[19] The reference was later improved by determining the best-fit circle to all detected points along the drop or bubble profile.[20] In the latest development, it was found that the shape of a drop or bubble can be evaluated by a purely geometric parameter called the total Gaussian curvature, $\kappa = 2\pi(1-\cos\theta)$, where θ is the contact angle of the drop or bubble.[24] Consequently, the P_s can be defined as $P_s = |\kappa - \kappa_s| = 2\pi|\cos\theta - \cos\theta_s|$, where θ_s is the contact angle of a spherical cap sharing the same volume of the drop or bubble. (Derivation of this P_s definition can be found in the Supporting Information.) The P_s has been successfully used to predict the accuracy of ADSA for both pendant drops and sessile drops.[24]

In this paper, we systematically compared different criteria and parameters in evaluating the accuracy of ADSA upon reducing drop volume. We first developed a unified computational scheme that allows the analysis of four commonly used drop or bubble configurations for surface or interfacial tension measurements, that is, pendant drop (PD), sessile drop (SD), pendant bubble (PB), and sessile bubble (SB). Taking advantage of a newly developed versatile experimental apparatus called the constrained drop surfactometer (CDS), we studied the accuracy of PD and SD in determining both surface tension and interfacial tension for a large range of drop volumes. By scrutinizing the dependence of ADSA accuracy on various parameters, including the capillary constant (c), the Bond number (Bo), the Worthington number (Wo), and the shape parameter (P_s), we concluded that the classical Bond number failed to predict the accuracy of drop shape analysis at very low drop volumes. We proposed a replacement of the classical Bond number, called the Neumann number (Ne), which takes account of the effect of the drop height. Although being a simple variation of the classical Bond number, it was found that the Neumann number is capable of evaluating the accuracy of drop shape analysis.

EXPERIMENTAL SECTION

Computational Scheme for a Unified Drop or Bubble Coordinate System. ADSA determines the surface or interfacial tension by numerically fitting the experimental profile to theoretical profiles generated by integrating the Laplace equation of capillarity until the best match is found.[5,7] Figure 1 illustrates a unified coordinate system for the four commonly used axisymmetric drop or bubble configurations, that is, PD, SD, PB, and SB. The origin of the coordinate system is universally defined as the apex of the drop or bubble. The direction of the z-axis is defined as the same direction of the gravitational acceleration (g). Theoretical profiles of these drop or bubble configurations are described by the Bashforth−Adams equation (eq 1), where the tangential angle (φ), radius (x), and height (z) at any point of the drop or bubble profile are expressed as functions of the arc length (s):

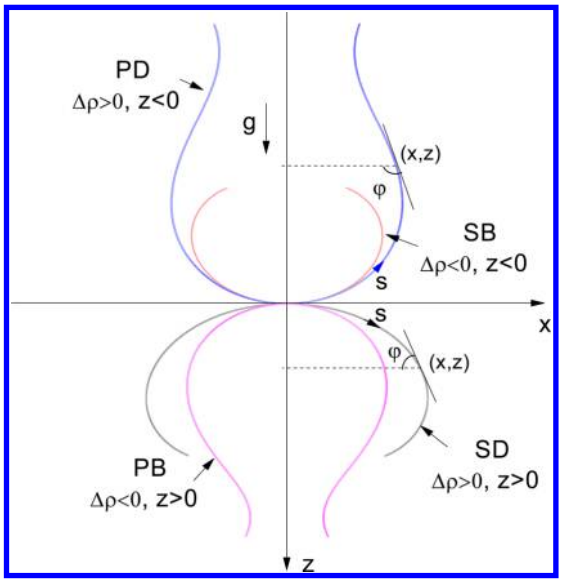

Figure 1. Unified coordinate system for four commonly studied axisymmetric drop or bubble configurations, that is, pendant drop (PD), sessile drop (SD), pendant bubble (PB), and sessile bubble (SB). Four drop or bubble configurations are differentiated by the combination of signs for $\Delta\rho$ and z. $\Delta\rho = \rho_{in} - \rho_{out}$ is the density difference between the fluid inside the discrete drop or bubble and the fluid outside the drop or bubble. $\Delta\rho > 0$ and $z > 0$ defines a sessile drop (SD); $\Delta\rho > 0$ and $z < 0$ defines a pendant drop (PD); $\Delta\rho < 0$ and $z > 0$ defines a pendant bubble (PB); $\Delta\rho < 0$ and $z < 0$ defines a sessile bubble (SB). This coordinate system is applicable to both surface tension and interfacial tension measurements.

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$$\frac{d\varphi}{ds} + \frac{\sin\varphi}{x} = \frac{2}{R_0} + \frac{\Delta\rho g}{\gamma}z$$

$$\frac{dx}{ds} = \cos\varphi$$

$$\begin{cases} \frac{dz}{ds} = \sin\varphi & z > 0 \\ \frac{dz}{ds} = -\sin\varphi & z < 0 \end{cases} \quad (1)$$

Boundary conditions for φ, x, and z are given at the apex of the drop or bubble,

$$\varphi(0) = x(0) = z(0) = 0 \quad (2)$$

In eq 1, R_0 is the radius of curvature at the drop or bubble apex, g is the gravitational acceleration, γ is the surface or interfacial tension, $\Delta\rho \equiv \rho_{in} - \rho_{out}$ is defined as the density difference between the fluid inside the discrete drop or bubble and the immiscible fluid outside the drop or bubble. $\Delta\rho > 0$ defines a "general drop" that includes a liquid drop in air and a liquid drop in another lighter immiscible liquid. $\Delta\rho < 0$ defines a "general bubble" that includes an air bubble in liquid and a liquid drop in another denser immiscible liquid.

The combination of signs for $\Delta\rho$ and z uniquely defines four drop or bubble configurations in the unified coordinate system shown in Figure 1: $\Delta\rho > 0$ and $z > 0$ defines a sessile drop (SD); $\Delta\rho > 0$ and $z < 0$ defines a pendant drop (PD); $\Delta\rho < 0$ and $z > 0$ defines a pendant bubble (PB); $\Delta\rho < 0$ and $z < 0$ defines a sessile bubble (SB).

Since growth of the hydrostatic pressure along the drop or bubble profile is determined by $\Delta p = \Delta\rho g z$, given the unified coordinate system defined in Figure 1, it is in agreement that gravity tends to elongate a pendant drop or bubble ($\Delta p < 0$) but flatten a sessile drop or bubble ($\Delta p > 0$).

Test Liquids. Six commonly used solvents, which cover a broad range of surface tensions, were tested for surface and interfacial tension measurements. These were water, formamide, dimethyl sulfoxide (DMSO), 1-octanol, hexadecane, and decane. Physicochemical properties and sources of these liquids are summarized in Table 1.

Table 1. Physicochemical Properties and Sources of the Tested Liquids

liquid	chemical formula	density (g/cm^3)	purity (%)	miscibility with water	supplier
water	H_2O	0.997	99.9		Millipore
formamide	CH_3NO	1.130	99.9	miscible	Fisher scientific
DMSO	$(CH_3)_2SO$	1.096	99.9	miscible	Fisher scientific
1-octanol	$C_8H_{18}O$	0.824	99.0	immiscible	Alfa Aesar
hexadecane	$C_{16}H_{34}$	0.773	99.0	immiscible	Acros Organics
decane	$C_{10}H_{22}$	0.730	99.8	immiscible	Fisher scientific

Both surface tensions of these liquids[25−27] and interfacial tensions of three immiscible solvents with water[28,29] have been well studied. Water, formamide, DMSO, 1-octanol, and decane were used without further purification. Hexadecane was purified with aluminum columns prior to experiments to remove surface active impurities.[29,30]

Experimental Methods. All drop or bubble configurations were studied with a newly developed experimental apparatus called the constrained drop surfactometer (CDS).[31,32] In the CDS, the drop or bubble was formed on a carefully machined pedestal with a sharp edge that prevents the drop or bubble from spreading or detaching, especially at low surface or interfacial tensions. The size of the pedestal was set to a diameter of 3 mm, which is close to the capillary constant of pure water. When measuring the interfacial tension, a drop or bubble of the discrete liquid was contained within another immiscible liquid held in a disposable acrylic cuvette.

We first established the versatility and accuracy of ADSA in determining the surface and interfacial tensions of well studied systems as summarized in Table 1. In these experiments, drop volumes were maintained sufficiently large to ensure accurate surface or interfacial tension measurements. We then scrutinized the applicability and accuracy of ADSA upon reducing the drop volume. The volume of the drop or bubble was carefully controlled using the newly developed closed-loop ADSA (CL-ADSA), which automatically manipulates and controls the drop or bubble parameters using a feedback control system.[33] To determine the accuracy of various configurations, the drop volume was gradually decreased until the measured surface or interfacial tension value deviated from the true value by at least 1%. All measurements were carried out at room temperature (22 ± 1 °C). Every measurement was conducted a minimum of 20 times. Results were shown as mean ± standard deviation.

RESULTS AND DISCUSSION

Surface and Interfacial Tension Measurements with Well-Deformed Drops and Bubbles. We first demonstrate the accuracy of ADSA in determining surface or interfacial tension under normal measurement conditions, that is, using well-deformed drops or bubbles with large enough volumes. Figure 2 shows the surface tension measurements of six commonly studied liquids, including water, formamide, DMSO, 1-octanol, hexadecane, and decane, each obtained through the four drop or bubble configurations, that is, PD, SD, SB, and PB. Volumes of the drop or bubble were maintained at around 15−20 μL to ensure well-deformed shapes (see Figure 2 for sample drop or bubble images). It is found that surface tensions determined with the four configurations are consistent with each other, and have good agreement with literature values.[25−27]

Figure 3 shows the interfacial tension measurements of three oil−water interfaces, that is, hexadecane−water, decane−water, and octanol−water interfaces, each determined with four drop or bubble configurations. Volumes of the drop or bubble were maintained in the range of 50−100 μL to ensure well-deformed shapes (see Figure 3 for sample drop or bubble images). Again, the interfacial tensions determined with these four configurations are consistent with each other. It should be noted that interfacial tension values reported in literature show slight inconsistencies, as summarized in Figure 3. The inconsistencies were most likely caused by the difference in the accuracy of different experimental methods, measurement temperatures,[28,29] and impurities of liquids used.[30] It is found that our measurements are in general agreement with literature values.[28,29]

Accuracy of ADSA Evaluated by the Capillary Constant. After demonstrating the accuracy of ADSA for well-deformed drops or bubbles, we investigated the deterioration of accuracy upon reducing the drop or bubble volume. The accuracy was quantified by the relative error between the measured surface or interfacial tension and the true value determined with well-deformed drops or bubbles (as shown in Figures 2 and 3), that is, $\Delta\gamma = (\gamma_{measured} - \gamma_{true})/\gamma_{true}$. We focused on three representative surface or interfacial systems, that is, the air−decane surface, the air−water surface, and the decane−water interface. The capillary constants (c) of these three representative systems are 1.8, 2.8, and 4.5 mm, respectively. For each of the three systems, we studied the accuracy of two drop configurations, PD and SD. These results are expected to be also applicable to the bubble configurations

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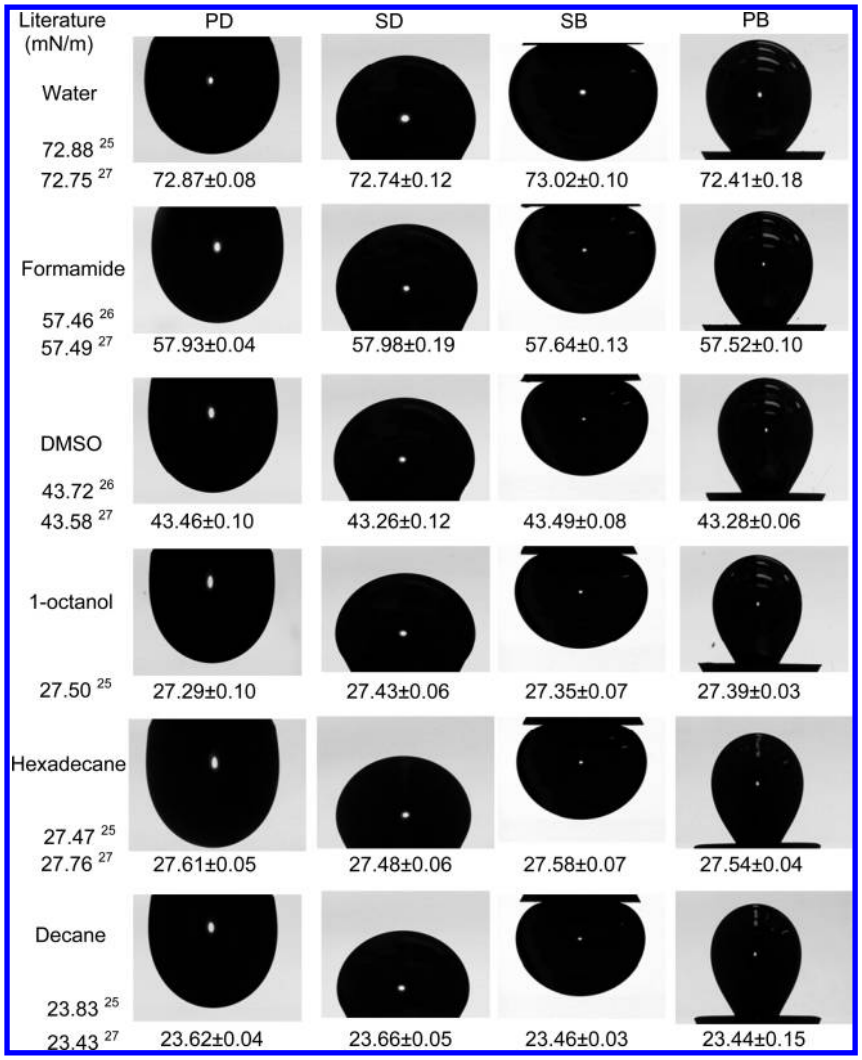

Figure 2. Surface tensions (in mN/m) of six test liquids, that is, water, formamide, DMSO, 1-octanol, hexadecane, and decane, each determined with four drop or bubble configurations, that is, PD, SD, SB, and PB, at room temperature (22 ± 1 °C). All measurements are shown in mean ± standard deviation (n = 20). Literature values are listed in the first column as a reference. It is demonstrated that surface tensions of the same liquid determined with different drop or bubble configurations are consistent with each other and are in good agreement with the literature value.

since the PB and SB can be considered as the geometric inversion of corresponding drop configurations. Representative experimental results for air−decane, air−water, and decane−water systems can be found in Figures S1−S3 of the Supporting Information (SI).

Figure 4 summarizes the measurement results of $\Delta\gamma$ for decane, water, and decane−water surface or interfacial tension upon reducing drop volume, using both PD and SD (reproducibility of these results can be found in Figure S4 of the SI). It is clear that the measured surface or interfacial tension with both PD and SD configurations are consistent and accurate ($\Delta\gamma$ < 1%) with a sufficiently large drop volume. However, the results become inaccurate when the drop volume is smaller than a critical value at which $\Delta\gamma$ > 1%. As shown in the inset, the critical volume (V_{crit}) for both PD and SD increases with an increasing capillary constant of the surface or interface. For example, the air−water surface has a capillary constant of 2.8 mm, which requires a drop volume of at least 7.04 μL for the PD or 7.58 μL for the SD to ensure an accurate surface tension measurement ($\Delta\gamma$ < 1%). Although the differences in V_{crit} for PD and SD are only moderate for surfaces or interfaces with small capillary constant, the differences increase with increasing capillary constant. For the decane−water interface whose capillary constant is 4.5 mm, the V_{crit} for PD and SD become 17.58 and 18.98 μL, respectively. In general, these results indicate that the PD method has a larger volume range of applicability than the SD method, especially for the measurement of interfacial tensions.

Accuracy of ADSA Evaluated by the Bond Number (*Bo*). Figure 5a shows the results of $\Delta\gamma$ against the *Bo* for decane, water, and decane−water surface or interfacial tension measurements using both PD and SD. It is found that except for the decane−water measurements, $\Delta\gamma$ randomly scatters in the entire range of the *Bo* obtained in experiments (from 0.1 to 1.6). No clear correlations between the *Bo* and the accuracy of surface or interfacial tensions ($\Delta\gamma$) can be found, which indicates that the *Bo* fails to predict the accuracy of ADSA as a general criterion for PD and SD, similar to what has been previously observed by others.[19,21]

To explain the failure of the *Bo* in predicting ADSA accuracy, Figure 5b shows the dependence of the *Bo* on the drop volume. It is clear that the *Bo* is not a monotonic function of the drop volume for surface tension measurements. The *Bo* only decreases with decreasing drop volume when the droplet is

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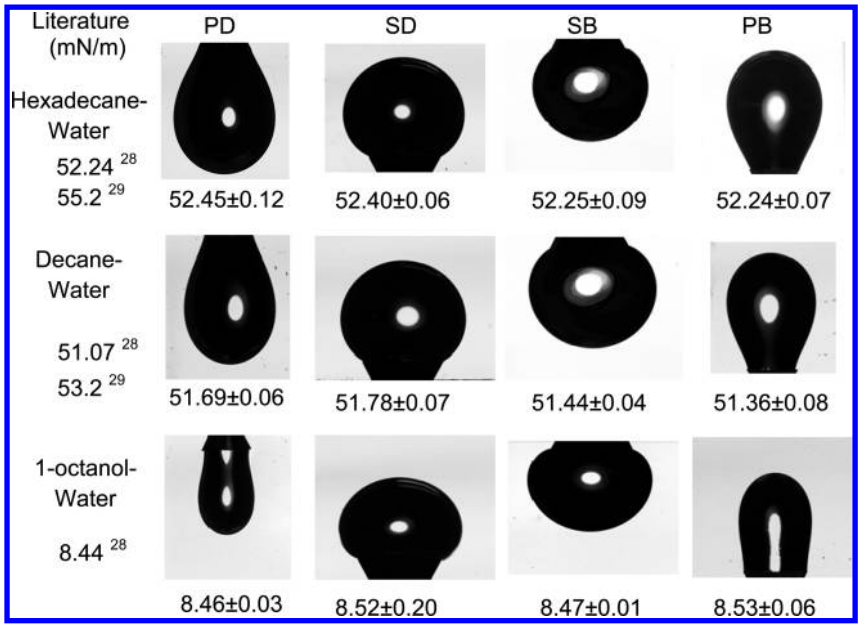

Figure 3. Interfacial tensions (in mN/m) of three oil−water systems, that is, hexadecane−water, decane−water, and 1-octanol−water, each determined with four drop or bubble configurations, that is, PD, SD, SB, and PB, at room temperature (22 ± 1 °C). All measurements are shown in mean ± standard deviation (n = 20). Literature values are listed in the first column as a reference. It is demonstrated that interfacial tensions of the same oil−water interface determined with different drop or bubble configurations are consistent with each other and in general agree with the literature value.

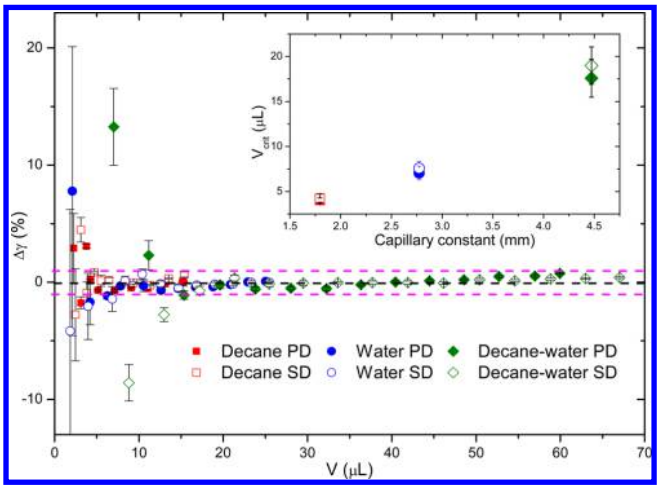

Figure 4. Relative errors of measured surface and interfacial tensions ($\Delta\gamma$) for decane, water, and decane−water systems upon reducing drop volume, using both PD and SD. The measurements become inaccurate ($\Delta\gamma$ > 1%) when the drop volume is smaller than a critical value (V_{crit}). Inset shows the V_{crit} for both PD and SD as a function of the capillary constant of the surface or interface.

sufficiently large. However, for very small droplets, that is, when the drop volume is close to the V_{crit} shown in the inset of Figure 4, further reduction in the drop volume increases the *Bo*. The nonmonotonic correlation between the *Bo* and the drop volume is due to the characteristic length scale used in defining the classical *Bo* number, R_0. Inset in Figure 5B shows that the point inflection in R_0 (i.e., the point inflection in the *Bo*) is associated with the transition of contact angle (θ) across 90°. Consequently, the same *Bo* represents two drop volumes, a larger volume with θ > 90° and a smaller volume with θ < 90°. It is also found that the nonmonotonic nature of the *Bo* is only predominant for surface tension measurement rather than interfacial tension measurement. Hence, although the *Bo* fails to predict the accuracy of ADSA in surface tensions measurements, it seems to be still a valid criterion for evaluating interfacial tension measurements.

Accuracy of ADSA Evaluated by the Worthington Number (*Wo*). Figure 6a shows the results of $\Delta\gamma$ against the *Wo* for decane, water, and decane−water surface or interfacial measurements using both PD and SD. Differing from the random dependence of $\Delta\gamma$ on the *Bo* shown in Figure 5a, the accuracy of surface or interfacial tension measurements only deteriorates ($\Delta\gamma$ > 1%) for low *Wo*. The lower the *Wo*, the worse is the accuracy of ADSA. The critical *Wo* (Wo_{crit}) for decane, water, and decane−water systems was found to be 0.13, 0.10, and 0.10, respectively, for the PD and 0.14, 0.11, and 0.10, respectively, for the SD (shown in the inset). Despite the capillary constant varying from 1.8 to 4.5 mm, the change in the Wo_{crit} is limited to between 0.14 and 0.10.

Figure 6b shows the dependence of the *Wo* on the drop volume. It is seen that the *Wo* and the drop volume are linearly correlated. The slope of the linear curve is inversely correlated with the capillary constant. For the same surface or interface (i.e., a certain capillary constant), the slopes of PD and SD are identical (see inset in Figure 6b). These correlations can be explained by the definition of the *Wo*. Slope of the *Wo* vs *V* curve is calculated as $\frac{1}{V_{max}} = \frac{\Delta\rho g}{\pi D_t \gamma} = \frac{1}{\pi D_t c^2}$, which is a function of only the capillary constant and the size of the capillary tube. In our experiments with the CDS, we used a 3 mm drop pedestal to replace the capillary tube. Hence, the definition of the *Wo* ensures that it is linearly correlated with the drop volume, and the slope of the linear curve only depends on the capillary constant of the system rather than the specific drop configuration used in measurements. It should also be noted that the *Wo* was developed primarily for analyzing PD as it requires the evaluation of the V_{max} defined only for the PD. Hence, the analysis of SD with the *Wo* shown in Figure 6 can be only indicative.

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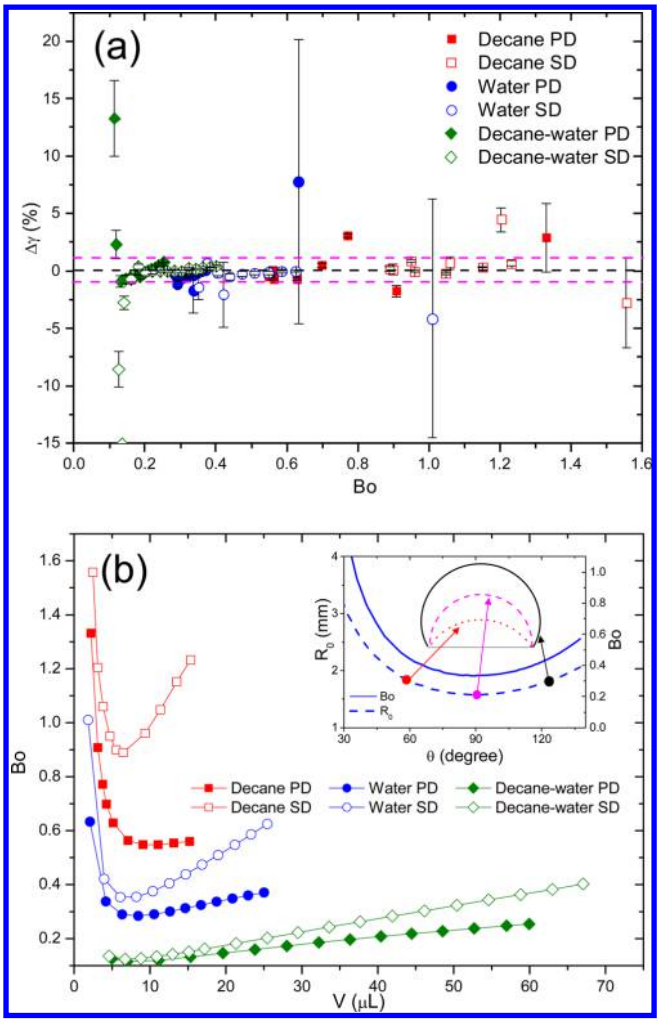

Figure 5. (a) Relative errors of measured surface or interfacial tensions ($\Delta\gamma$) for decane, water, and decane−water systems as a function of the Bond number (Bo), using both PD and SD. It is found that $\Delta\gamma$ randomly scatters in the entire range of the Bo obtained in experiments (from 0.1 to 1.6) except for the decane−water measurements; that is, no clear correlations between the Bo and the accuracy of ADSA can be established. (b) The Bo as a function of the drop volume (V). It is found that the Bo is not a monotonic function of V. The inset shows that the point inflection in the R_0 (as well as the Bo) is associated with the transition in contact angle (θ) across 90°.

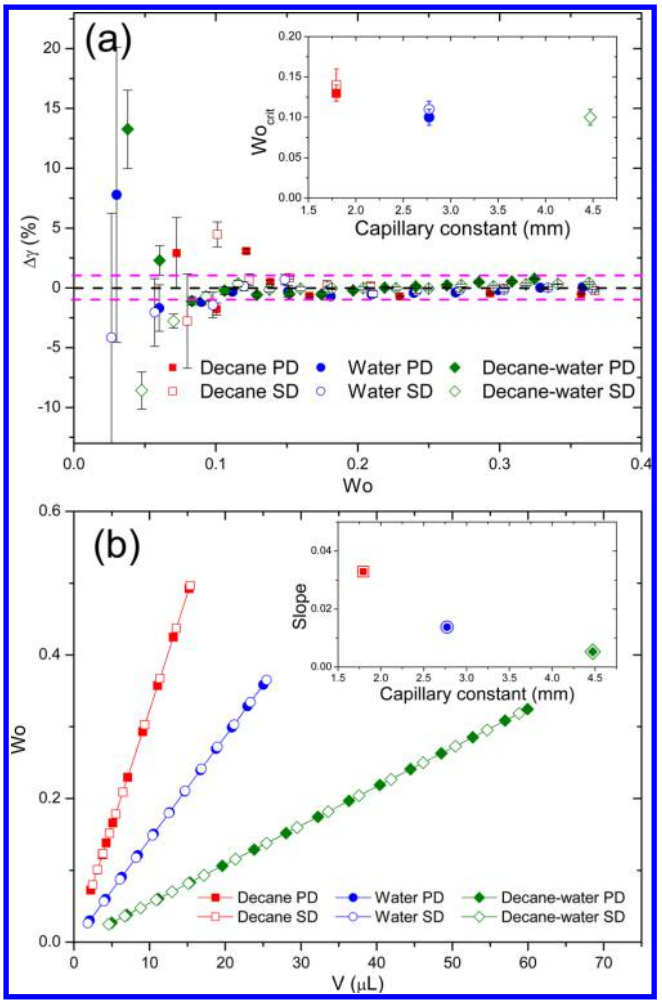

Figure 6. (a) Relative errors of measured surface or interfacial tensions ($\Delta\gamma$) for decane, water, and decane−water systems as a function of the Worthington number (Wo), using both PD and SD. It is found that the accuracy of ADSA deteriorates ($\Delta\gamma$ > 1%) upon reducing the Wo. The inset shows the critical Wo (Wo_{crit}) as a function of the capillary constant. (b) The Wo as a function of the drop volume (V). It is found that the Wo and V are linearly correlated, with the slope inversely dependent on the capillary constant (as shown in the inset).

Accuracy of ADSA Evaluated by the Neumann Number (*Ne*). To investigate the validity of the Bo in evaluating the accuracy of drop shape analysis, we non-dimensionalized eq 1 as follows,

$$\frac{d\varphi}{d\bar{s}} + \frac{\sin\varphi}{d\bar{x}} = 2 + \frac{\Delta\rho g}{\gamma} zR_0 \tag{3}$$

Equation 3 indicates that the shape of a drop or bubble is ultimately controlled by the dimensionless group on the right-hand side of the equation. We therefore define this dimensionless group to be a new parameter called the Neumann number (in honor of A. Wilhelm Neumann for his contribution to drop shape analysis), $Ne \equiv \frac{\Delta\rho g}{\gamma} R_0 H = \frac{R_0 H}{c^2}$, where H is the height of the drop or bubble. The Neumann number (Ne) can be considered as a modified Bond number $Bo = \left(\frac{L}{c}\right)^2$, where the characteristic length of the drop or bubble is defined as $L = \sqrt{R_0 H}$, which is the geometric mean of the radius of curvature at the drop apex (R_0) and the drop height (H).

Figure 7a shows the results of $\Delta\gamma$ against the Ne for decane, water, and decane−water surface or interfacial tension measurements using both PD and SD. Differing from the classical Bo, the Ne is capable of predicting the accuracy of ADSA for both PD and SD. The smaller the Ne, the larger is the $\Delta\gamma$. In general, a Ne larger than 0.5 is required for accurate surface tension measurements with both PD and SD. As shown in the inset of Figure 7a, the critical Ne (Ne_{crit}) decreases with an increasing capillary constant. For the same capillary constant, the Ne_{crit} of PD is always slightly lower than that of the SD, indicating that the PD method has a larger volume range of applicability compared to the SD. These conclusions drawn from the Ne are all consistent with the prediction by the capillary constant (Figure 4) and the Wo (Figure 6). However, the Ne_{crit} changes from 0.45 to 0.25 while the capillary constant varies from 1.8 to 4.5 mm, indicating a higher measurement sensitivity than the Wo.

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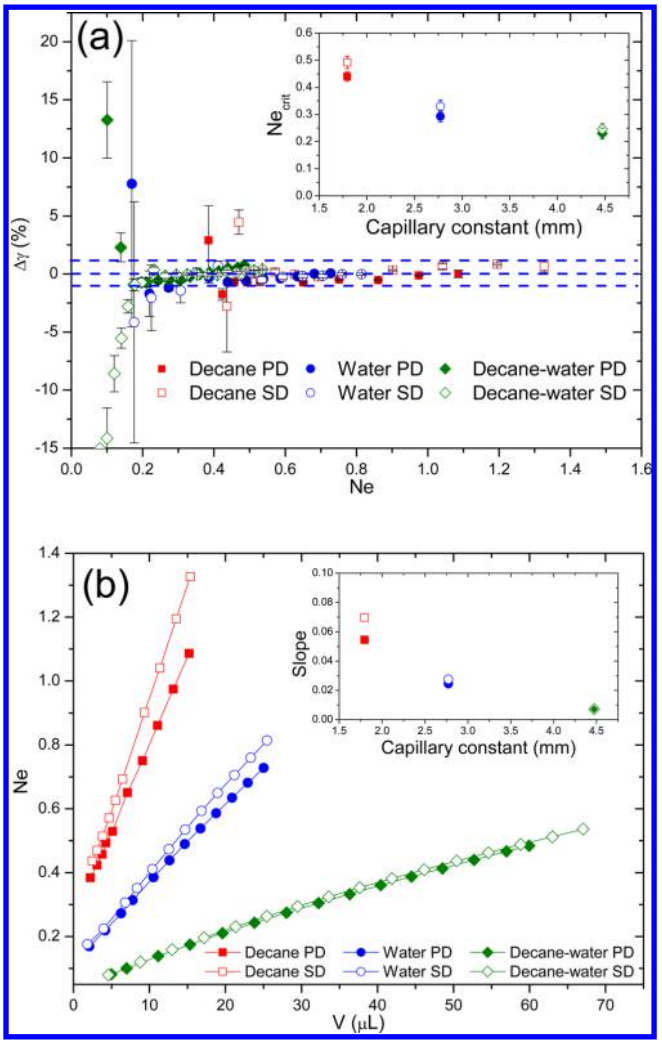

Figure 7. (a) Relative errors of measured surface or interfacial tensions ($\Delta\gamma$) for decane, water, and decane−water systems as a function of the *N*eumann number (*Ne*), using both PD and SD. It is found that the *Ne* is capable of predicting the accuracy of ADSA for both PD and SD. The inset shows the critical *Ne* (Ne_{crit}) as a function of the capillary constant. (b) The *Ne* as a function of the drop volume (V). It shows that the *Ne* is a monotonically near-linear function of V, with the slope inversely dependent on the capillary constant (as shown in the inset).

Figure 7b shows the dependence of the *Ne* on the drop volume. It is clear that different from the classical *Bo*, the *Ne* is a monotonic function of the drop volume. With decreasing drop volume, the *Ne* decreases near-linearly. As shown in the inset, similar to the *Wo*, the slope of the linear curve decreases with an increasing capillary constant. However, different from the *Wo*, curves of the same capillary constant for PD and SD do not overlap each other. There is a slightly higher slope for the SD than the PD, indicating that the SD has a faster decay in drop deformation than the PD upon volume reduction.

Table 2 summarizes the different variations of the Bond number. Compared to the *Wo*, the *Ne* is not only applicable to PD but also to SD. Most importantly, it is clear that the design rationale of this new dimensionless number lies in the use of the geometric mean of the radius of curvature at the drop apex (R_0) and the drop height (H) as the new characteristic length to represent the drop size, that is, $L = \sqrt{R_0 H}$. While it is well accepted that the R_0 can be used as an accessible approximation

Table 2. Various Definitions of the Bond Number $Bo = \left(\frac{L}{c}\right)^2$ for Evaluating the Accuracy of Drop Shape Analysis[a]

definition	symbol	characteristic length (L)	formula	ref
classical Bond number	*Bo*	R_0	$Bo = \frac{\Delta\rho g {R_0}^2}{\gamma}$	22
Worthington number	*Wo*	$\sqrt{\frac{V}{\pi D_t}}$	$Wo = \frac{\Delta\rho g V}{\gamma \pi D_t}$	21
Neumann number	*Ne*	$\sqrt{R_0 H}$	$Ne = \frac{\Delta\rho g R_0 H}{\gamma}$	this work

[a] L is the characteristic length; c is the capillary constant, $c = \sqrt{\frac{\gamma}{\Delta\rho g}}$.

of the drop size, the effect of H on the accuracy of drop shape analysis was largely ignored in previous studies. Nevertheless, it has long been known that the surface or interfacial tension of a SD or SB is a function of the ratio between drop diameter and drop height.[34,35] Recent experimental studies by Neumann and co-workers concluded that compared to other factors, such as the drop volume and the size of the capillary tube, the drop height plays a predominant role in the accuracy of ADSA.[36] The definition of the Neumann number therefore suggests that it is neither R_0 nor H but their geometric mean $\sqrt{R_0 H}$ that better represents the drop size in determining the accuracy of surface or interfacial tension measurements.

Accuracy of ADSA Evaluated by the Shape Parameter (P_s). Figure 8a shows the results of $\Delta\gamma$ against the P_s for decane, water, and decane−water surface or interfacial measurements using both PD and SD. Similar to the *Wo* and *Ne*, the accuracy of surface or interfacial tension measurements only deteriorates ($\Delta\gamma$ > 1%) for low P_s. The lower the P_s, the worse is the accuracy of ADSA. As shown in the inset, the critical P_s ($P_{s,crit}$) for decane, water, and decane−water systems with both PD and SD is identical. This result is not unexpected because the P_s is designed to take account of the geometric deformation of the drop or bubble in order to circumvent the dependence on capillary constant.

Figure 8b shows the dependence of the P_s on the drop volume. Similar to the *Wo* and *Ne*, the slope of the P_s vs V curve decreases with an increasing capillary constant. For the same capillary constant, with increasing drop volume, the slope for PD is increasingly larger than SD. This is particularly obvious for the decane−water interfacial tension measurement. It means that to achieve the same level of drop deformation, the SD needs a larger volume than the PD. Hence, the PD is more suitable than the SD for measuring interfacial tensions. However, at very low drop volumes, both PD and SD become inaccurate.

It can be seen that both the *Ne* and the P_s are capable of predicting the accuracy of ADSA. For both parameters, there exists an experimentally determined critical value below which the ADSA measurements become erroneous. In addition to common factors that influence the accuracy of drop shape analysis, such as the quality of image acquisition and image analysis and the size of the drop or bubble support (capillary tubing or drop pedestal), the critical *Ne* is also dependent on the specific drop shape (PD or SD) and the capillary constant of the system (inset in Figure 7a). Nevertheless, the critical P_s is independent from the specific drop shape and the capillary constant (inset in Figure 8a). This difference in dependence is caused by the intrinsic differences between these two

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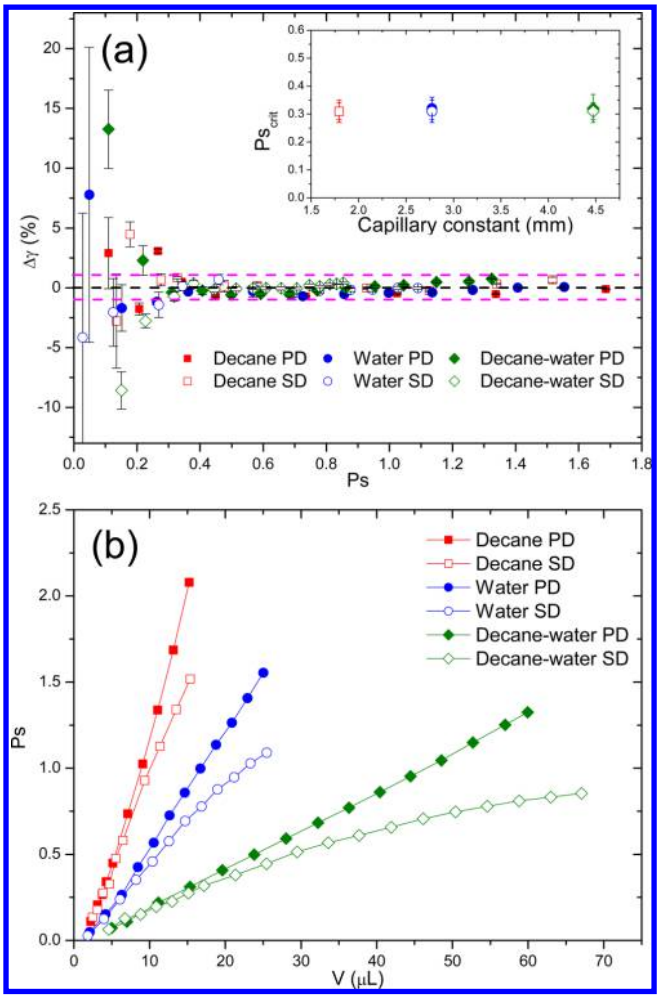

Figure 8. (a) Relative errors of measured surface or interfacial tensions ($\Delta\gamma$) for decane, water, and decane–water systems as a function of the shape parameter (P_s), using both PD and SD. It is found that the accuracy of surface or interfacial tension measurements deteriorates ($\Delta\gamma$ > 1%) upon reducing the P_s. As shown in the inset, the critical P_s ($P_{s,crit}$) is independent from the capillary constant. (b) The P_s as a function of the drop volume (V).

definitions. While the P_s is defined as a geometric measurement of the drop shape, the definition of the *Ne* is along the lines of the classical *Bo*, which measures the relative importance of the gravitational forces over the capillary forces (Table 2). A drop or bubble with a low *Ne* means the capillary forces outweigh gravity, thus resulting in a nondeformed nearly spherical drop or bubble and leading to erroneous surface or interfacial tension measurements.

Another advantage of the *Ne* over the P_s lies in its simplicity. Compared to the intricacies in applied mathematics used in evaluating the P_s, the *Ne* is much simpler in format and more straightforward in physical meaning. Definition of the *Ne* clearly establishes the importance of drop height in evaluating the accuracy of drop shape analysis.

Implications of the Local Neumann Number (Ne_z). We have demonstrated the usefulness of the Neumann number in determining the accuracy of the drop shape analysis (Figure 8). Here we show that the Neumann number can be used as a localized parameter to measure the contribution of points along the drop profile to the overall accuracy of the drop shape analysis. Complementary to the global Neumann number (*Ne*), we define a local Neumann number, $Ne_z \equiv \frac{\Delta\rho g R_0}{\gamma} z$, where z is the height of any point along the drop profile (see Figure 1).

Figure 9 shows the theoretical calculation of the Ne_z along the normalized arc length from the drop apex to the three-phase contact line, for PD and SD of water with three representative volumes of 3, 7, and 15 μL, respectively. These three volumes were selected to represent drop volumes less than, close to, and larger than the critical volume for water ($V_{crit} \approx 7$ μL), based on results shown in Figures 4 and 7. (More theoretical analyses for the air–decane surface and the decane–water interface can be found in Figure S5 of SI.) It can be seen that the Ne_z increases from the drop apex to the maximum along the drop profile. However, the increase in Ne_z is nonlinear, with a relatively slower increase close to the drop apex but faster increase close to the three-phase contact line. This indicates that the drop profile close to the apex is insensitive to a change in surface tension; while the drop profile close to the three-phase contact line contributes the most to a change in surface tensions.[6] It is also found that although the Ne_z curves for PD and SD overlap for points close to the drop apex, the SD curve increases more quickly than the PD curve when approaching the three-phase contact line, thus indicating that the accuracy of the SD is more dependent on the points close to the three-phase contact line than the PD. This theoretical analysis is consistent with the general experimental observation that the PD is more accessible than the SD in accurate surface tension measurements.

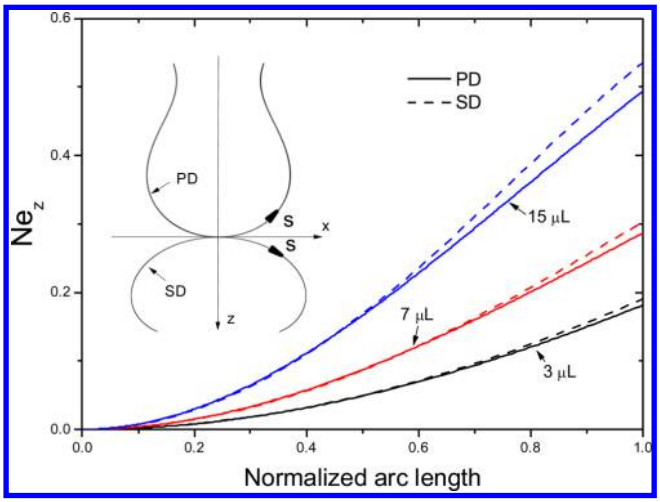

Figure 9. Theoretical calculation of the local Neumann number (Ne_z) along the normalized arc length from the drop apex to the three-phase contact line, for PD and SD of water with the volume of 3, 7, and 15 μL, respectively. These three volumes were selected to represent drop volumes less than, close to, and larger than the critical volume for water ($V_{crit} \approx 7$ μL), based on results shown in Figures 4 and 7. It shows that the Ne_z can be used to evaluate the relative importance of the local drop profile on the accuracy of ADSA.

CONCLUSIONS

We studied different criteria and parameters in evaluating the accuracy of drop shape analysis upon drop volume reduction. By scrutinizing the dependence of ADSA accuracy on the *Bo*, *Wo*, and P_s, for three representative systems with various capillary constants, we concluded that the classical *Bo* failed to predict the accuracy of drop shape analysis at very low drop

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volumes. Consequently, we proposed a replacement of the classical Bond number, called the Neumann number, $Ne \equiv \frac{\Delta\rho g R_0 H}{\gamma}$. The design rationale of this new dimensionless number lies in the use of the geometric mean of the radius of curvature at the drop apex (R_0) and the drop height (H) as the new characteristic length to represent the drop size, that is, $L = \sqrt{R_0 H}$. It is found that the Neumann number is capable of evaluating the accuracy of drop shape analysis. We have also demonstrated the usefulness of the local Neumann number, $Ne_z \equiv \frac{\Delta\rho g R_0}{\gamma} z$, in evaluating the contribution of the local drop profile to the surface tension measurement.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01778.

Derivation of the shape parameter from the total Gaussian curvature, additional figures that show typical results of surface tension, drop volume, contact angle, and curvature as a function of time, reproducibility of experiments, and theoretical analysis of the Ne_z (PDF)

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Notes

The authors declare no competing financial interest.

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