A DYNAMIC APPROACH TO DETERMINING THE SURFACE TENSION OF A FLUID

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Abstract — A new formulation has been developed that predicts flow rate of a stream draining from an orifice under the influence of gravity. This model is different from conventional formulations in that it includes the surface tension of the liquid. Results with water and ethylene glycol at various temperatures indicate that it is necessary to account for surface tension under certain conditions including small orifice diameters and operation under low head values. This model is most relevant for liquids of high surface tension including melts such as molten metals, slags and salts. These conditions are accounted for in the Bond number (\( \rho g r h / \sigma \)) which is a dimensionless quantity useful in determining conditions when surface tension is expected to have considerable impact. When an operation is such that the 1/Bo approaches unity, the formulation has the greatest relevance. The formulation provides unique possibilities in measuring surface tension since this property is related to flow rate and head which are two variables that can be experimentally determined. Calibrations of the discharge coefficient, \( C_d \), are required to determine frictional losses in the orifice. The surface tension of water at 321.5 K was calculated to be 0.067 N/m which is 1.75% from the value quoted in the literature. The measurement is highly susceptible to error. A rigorous error analysis was performed on the formulation and it was determined that as 1/Bo approaches unity, accuracy in the surface tension measurement significantly improves. It is expected that melt systems are best suited for such measurements since these liquids often exhibit large values of 1/Bo for a given orifice design.

Résumé — On a développé une nouvelle formule qui prédit le débit d’un écoulement qui se vide par un orifice sous l’influence de la gravité. Ce modèle est différent des formules conventionnelles en ce qu’il inclut la tension superficielle du liquide. Les résultats avec de l’eau et de l’éthylène glycol à des températures variées indiquent qu’il est nécessaire de tenir compte de la tension superficielle dans certaines conditions incluant les orifices à petit diamètre et l’opération sous de faibles valeurs de charge. Ce modèle est des plus pertinents pour les liquides tension de surface élevée incluant les bains de fusion tels que les métaux fondu, le laitier de haut fourneau, les sels, etc. Ces conditions sont prises en compte dans le nombre de Bond (\( \rho g r h / \sigma \)), une quantité adimensionnelle utile dans la détermination des conditions où l’on s’attend à ce que tension de surface ait une répercussion considérable. La formule a sa plus grande pertinence quand l’opération est telle que 1/Bo s’approche de l’unité. La formule offre des possibilités uniques de mesure de tension de surface puisque cette propriété est reliée au débit et à la charge, deux variables qui peuvent être déterminées expérimentalement. Le calibrage du coefficient de débit, \( C_d \), est requis pour déterminer les pertes par frottement à l’orifice. On a calculé que la tension superficielle de l’eau à 321.5 K était de 0.067 N/m, soit 1.75% de la valeur citée dans la littérature. La mesure est extrêmement susceptible à l’erreur. On a exécuté une analyse d’erreur rigoureuse de la formule et on a déterminé que l’exactitude de la mesure de tension de surface s’améliore très distinctement quand 1/Bo s’approche de l’unité. On s’attend à ce que les systèmes de bain de fusion soient les plus appropriés pour de telles mesures puisque ces liquides exhibent souvent de grandes valeurs de 1/Bo pour un concept donné d’orifice.
INTRODUCTION

In the analysis of a liquid draining under the influence of gravity through an orifice, potential, kinetic and viscous forces have conventionally been considered when modeling that dynamic system. The Bernoulli formulation is often used to quantify these forces resulting in a function that relates flow rate, $Q$, with head above the orifice discharge, $h$ (i.e., $Q = \pi r_v^2 \sqrt{2gh}$) [1,2]. This relationship is valid for inviscid flow only. Viscous losses through the orifice are typically characterized by the discharge coefficient, $C_d$, and can be determined through calibration means. This is accomplished by calculating the ratio of experimental flow rate, $Q_{exp}$, and the value provided by the Bernoulli formulation (i.e., $C_d = Q_{exp} / \pi r_v^2 \sqrt{2gh}$). Discrepancies have been observed when such calibrations are performed. This is attributed to the impact that surface tension has on the exiting stream. The purpose of this study is to illustrate these discrepancies and to propose a formulation that includes the surface tension of the liquid. Conditions relevant to the new formulation will also be outlined.

There has been an observation in the literature on the effect of surface tension on a stream exiting an orifice. The development of the Saybolt viscometer, first introduced as a standard in 1917, provides a relative viscosity unit. This unit provides a measure of the efflux time that a certain volume of liquid takes to drain through a standard orifice. In calibrating this device, Herschel observed inconsistent behaviour when sucrose solutions were applied instead of alcohol mixtures [3]. Herschel attributed these differences to the absence of surface tension in the formulation; however, no attempts to this date have been made to address this issue [4-17].

Significant implications arise if melts (molten metals and slags) are considered. The surface tension of many melts can be an order of magnitude greater than the surface tension of low temperature liquids (water and organic liquids). For instance, the surface tensions of water, carbon tetrachloride, and benzene at 20 °C are 0.072 N/m, 0.026 N/m, and 0.029 N/m, respectively [18]. The surface tensions of molten magnesium, aluminum and iron at their melting points are 0.577 N/m, 0.871 N/m, and 1.862 N/m, respectively [20]. The impact that surface phenomenon has on metallurgical processes has been extensively discussed in the literature [19-26]. The Marangoni effect (convection induced by gradients in surface tension) is an excellent example of the impact that surface phenomenon has on several metallurgical processes [19]. Processes in which this effect has a significant impact are welding (penetration of liquid phase depending on motion of liquid pool) and corrosion of refractory material at slag-gas and slag-metal interfaces. Atomization and granulation of melts for powder or granule production is also strongly dependent on the surface tension of the melt.

Unfortunately a definitive database of information for the physical properties of melts is missing in the literature. This is attributed to significant challenges in measuring the surface tension, density and viscosity of these systems. Like many metallurgical studies, experimentally studying fluid dynamics is not a trivial matter when high temperatures are required. This paper will first demonstrate that the classical formulation of a stream flowing from an orifice is insufficient to characterize the flow. A revised formulation and validation is then presented. The model is generalized for melts and, in this work, applied to determine the surface tension of water which is compared to the value in the literature.

CLASSICAL FORMULATION

For a vessel having an orifice in the bottom, it is assumed that a free jet will form when the vessel is filled with a liquid and that flow rate is dependent on the liquid head. To predict flow rate, the Bernoulli formulation is used. Refer to Figure 1 for an illustration of unsteady flow through an orifice. The two reference locations under consideration are defined at points 1 and 2. The Bernoulli formulation is applied on a small cylindrical element illustrated in Figure 1.
2. Depicted are the forces acting relative to the direction of a streamline. Newton’s second law \( F = \frac{d}{dt}(m) \) is applied on the cylindrical element as outlined in Daugherty et al. [2]. A formulation applied to a vessel draining under the influence of gravity is outlined in Whitaker [1].

**Bernoulli Derivation: Neglecting Surface Tension**

Daugherty et al. [2] considered the case of unsteady flow (velocity as a function of both position and time; a draining vessel). The following relationship is obtained

\[
-dPdA_c + \rho gdA_c dz = m \left( u \frac{\partial u}{\partial z} + \frac{\partial u}{\partial t} \right) \tag{1}
\]

This force balance accounts for the differential pressure on the fluid element, the weight of the element and the change of its momentum. Equation 1 can be expressed as

\[
-dPdA_c + \rho gdA_c dz = \rho dA_c \left( u \frac{\partial u}{\partial z} + \frac{\partial u}{\partial t} \right) \tag{2}
\]

Dividing Equation 2 by \(-\rho dA_c\), rearranging the terms and integrating between the limits of points 1 and 2 yields

\[
\int \frac{2}{\rho} dP - g \int dz + \int u du = -\left( \frac{\partial u}{\partial t} \right) \int dz \tag{3}
\]

Equation 3 is written as

\[
\frac{(P_2 - P_1)}{\rho} - g(z_2 - z_1) + \frac{1}{2}(u_2^2 - u_1^2) = -(z_2 - z_1) \left( \frac{\partial u}{\partial t} \right) \tag{4}
\]

Note that the formulation has thus far neglected viscosity effects. Equation 4 is therefore considered to be valid for a draining vessel under inviscid flow with negligible surface forces. The term \((z_2 - z_1)\) is the head of fluid just above the exit of the orifice, \(h\), as indicated in Figure 1. By continuity, the velocity at point 1 can be expressed with respect to the velocity at point 2.

\[
u_1 = \frac{r_o^2}{r_e^2} u_2 \tag{5}
\]

Since \(r_o >> r_e\), \(u_1 = 0\). Rearranging Equation 4 in terms of outlet velocity, \(u_2\), yields

\[
u_2 = \sqrt{\frac{2g}{\rho g u}} \left( h - \frac{(P_2 - P_1)}{\rho g} - h \left( \frac{\partial u}{\partial t} \right) \right) \tag{6}
\]

The term \(h \left( \frac{\partial u}{\partial t} \right)\) represents the acceleration of the head term within the vessel [2]. This term is neglected as outlined elsewhere [27]. This quantity is neglected in the analysis since it is a factor equal to \(3.5 \times 10^{-3}\) less than the magnitude of the first term (described by \(h\)) [27]. It is also assumed that there is no pressure difference between points 1 and 2 (atmospheric pressure at the free surface and orifice tip). It will be revealed in subsequent sections that this is a pivotal assumption and must be reconsidered under specific conditions. The following expression is therefore obtained

\[
u_2 = \sqrt{\frac{2gh}{\rho}} \tag{7}
\]

This is the classical expression that relates velocity with head. Since friction is neglected in the formulation, \(u_2\) is considered to be the theoretical maximum velocity at the exit of the orifice. In terms of maximum theoretical volumetric flow rate,

\[Q_{theo} = \pi r_o^2 \sqrt{\frac{2gh}{\rho}} \tag{8}\]

Frictional characteristics must now be determined to accurately relate the true experimental flow rate, \(Q_{exp}\), with

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**Fig. 2.** Control element on streamline neglecting frictional losses.
head, h. The discharge coefficient is used to account for frictional losses in the orifice, and is defined as the ratio between the experimental and theoretical velocity.

\[ C_d = \frac{u_{\text{exp}}}{\sqrt{2gh}} \]  

(9)

In terms of flow rate,

\[ C_d = \frac{Q_{\text{exp}}}{\pi r^2 \sqrt{2gh}} \]  

(10)

The Reynolds number (Re) is used in characterizing the inertial forces relative to viscous losses in the orifice, and is calculated using the following relation

\[ Re_{\text{exp}} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho u_{\text{exp}} 2r_o}{\eta} = \frac{2\rho Q_{\text{exp}}}{\pi r^3 \eta} \]  

(11)

where \( \rho \) and \( \eta \) are the density and viscosity of the fluid, respectively. Plotting \( C_d \), Equation 10, versus Reynolds number, Equation 11, provides a measure of the frictional characteristics of the orifice.

**EXPERIMENTAL**

Equations 10 and 11 clearly show that for a given fluid and a particular orifice radius, the head and flow rate must be measured experimentally. An apparatus was constructed so that head and flow rate, the two experimental variables, could be accurately measured. Small orifice radii (1.5 mm) were used with water and ethylene glycol at various temperatures. This orifice size is just large enough that a stream forms under low head conditions. Refer to Figure 3 for a schematic of the apparatus. A rectangular Pyrex vessel (35 mm x 75 mm x 250 mm) was used to contain the liquid so that visual observations could be made of the fluid head. The scale used for head measurements is accurate to 0.5 mm. The fluid drains through a Teflon orifice plate and is collected in a 1.0 litre beaker that is placed approximately 30 mm below the orifice plate. The orifice is 3 mm in diameter and 17 mm in length with an inlet chamfer of 60°. Teflon is chosen as the material due to its resistance to wetting with water. If wetting is an issue, the liquid may spread along the orifice exit effectively altering the radius of the exiting stream. The collecting beaker is mounted on the load cell that cumulatively measures mass as a function of time. The signal from the loadcell is processed by a data acquisition system. Flow rate is determined by differentiating a 3rd order polynomial function describing the cumulative mass data. By determining the flow rate under variable head conditions, the discharge coefficient can be calculated as head decreases. Further details of the equipment and procedures are outlined elsewhere [27].

**RESULTS**

Discharge coefficient as a function of Reynolds number was generated for water at 293 K and 321.5 K, and ethylene glycol at 298 K and 333 K. Cumulative mass and head data that was generated for water at 293 K and are illustrated in Figures 4 and 5, respectively.

A 3rd order polynomial used to describe the cumulative mass curve is included in Figure 4. It was determined that a 3rd order polynomial describes the data well and that an increasing polynomial order does not improve accuracy. The function takes the form

\[ C_{m,poly} = 3.442 \times 10^{-8}(t)^3 - 6.315 \times 10^{-5}(t)^2 + 1.113 \times 10^{-2}(t) + 9.842 \times 10^{-3} \]  

(12)

\( \text{kg} \)

Equation 12 is differentiated and divided by the fluid density to yield the volumetric flow rate,

\[ Q_{\text{exp}} = \frac{1}{\rho} \frac{d(C_{m,poly})}{dt} = \frac{1}{\rho} \left[ (3/3.442 \times 10^{-8})(t)^2 - 2(6.315 \times 10^{-5})(t) + 1.113 \times 10^{-2} \right] (m^3/s) \]  

(13)

Similar analyses were performed for water at 321.5 K, and ethylene glycol at 298 K and 333 K. \( C_d \) and Re were calculated by substituting head and flow rate in Equations 10 and 11. Note that the values of fluid density and viscosity at the corresponding fluid temperature were used in the calculation of the respective Reynolds number. Results are presented in Figure 6.
The trends depicted in Figure 6 indicate that when different liquids are used, or when the same fluid is used but at a different temperature, varying frictional characteristics are observed. Note that the effect of temperature on fluid properties was already accounted for in the calculation of the Reynolds number. Thus, testing a fluid with a different temperature is analogous to testing a fluid with different properties. Such results raise concerns either with the discharge coefficient versus Reynolds number analysis or perhaps with key assumptions made in the Bernoulli formulation. A reinvestigation of these assumptions is warranted.

NEW FORMULATION INCLUDING SURFACE TENSION

Recall the assumption that the pressure at reference points 1 and 2 is atmospheric in Figure 1. Considering the principles of interfacial phenomena, it is possible that there may indeed be a pressure induced at the outlet of the orifice if the liquid surface tension is considered. Pressure induced from surface tension occurs at curved interfaces that separate liquid from atmosphere. Such is the case of a cylindrical stream exiting an orifice. The Laplace equation relates the pressure difference across a curved interface to the radii of curvature,

\( \Delta P = 2 \sigma / R \)

where \( \sigma \) is the surface tension and \( R \) is the radius of curvature.

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\[ \Delta P = \sigma \left( \frac{1}{R_a} + \frac{1}{R_b} \right) \]  \hspace{1cm} (14)

\(\Delta P\) is the pressure difference across the liquid/gas interface, and \(R_a\) and \(R_b\) represent the radii of curvature that describe the shape of the surface. If there is a planar surface, \(R \to \infty\), there is no pressure induced as Equation 14 indicates. At reference point 1 (top of the liquid in the vessel), it is assumed that the pressure induced is negligible since the interface is considered to be planar. \(R_a\) and \(R_b\) approach infinity.

Directly below reference point 2 (orifice tip), the stream exiting the orifice is essentially cylindrical with the curvatures illustrated in Figure 7. At a location just below the orifice (where the stream is first in contact with the atmosphere), \(R_a\) is taken to be the radius of the orifice, \(r_o\). The second radius of curvature, \(R_b\), is assumed to be infinity since the stream is assumed to be a perfect cylinder at this location. From the Laplace equation, the pressure induced due to the effects of surface tension directly below the orifice is

\[ \Delta P = \sigma \left( \frac{1}{r_o} \right) \]  \hspace{1cm} (15)

Considering Equation 6 and assuming quasi-steady state conditions, an added pressure at reference point 2 is included in the formulation that corresponds to a magnitude of \(\sigma/r_o\).

\[ u_2 = \sqrt{2g \left( h - \frac{(P_2 - P_1)}{\rho g} \right)} = \sqrt{2g \left( h - \frac{(\sigma/r_o + P_{atm} - P_{atm})}{\rho g} \right)} = \sqrt{2g \left( h - \frac{\sigma}{\rho g r_o} \right)} \]  \hspace{1cm} (16)

\(P_1\) is taken to be atmospheric pressure only because the free surface is considered to be planar which indicates no effects from due to the surface tension of the liquid. Equation 16 is considered to represent the theoretical maximum velocity since frictional losses are not considered at this point. In terms of maximum theoretical flow rate:

\[ Q_{theo} = \pi r_o^2 \sqrt{2gh \left( h - \frac{\sigma}{\rho g r_o} \right)} \]  \hspace{1cm} (17)

Calculating discharge coefficient using Equation 17 instead of Equation 10:

\[ C_d = \frac{Q_{exp}}{\pi r_o^2 \sqrt{2gh \left( h - \frac{\sigma}{\rho g r_o} \right)}} \]  \hspace{1cm} (18)

\[ Fr + \frac{1}{Bo} = 1 \]  \hspace{1cm} (21)

where the Bond number is defined as

\[ Bo = \frac{\text{potential forces}}{\text{surface forces}} = \frac{\rho gh h}{\sigma} \]  \hspace{1cm} (22)

and the Froude number is defined as

\[ Fr = \frac{\text{inertial forces}}{\text{potential forces}} = \frac{u_{theo}^2}{2gh} = \frac{\left( \frac{Q_{exp}}{C_d \pi r_o^2} \right)^2}{2gh} \]  \hspace{1cm} (23)

The experimental results collected for head and volumetric flow rate for water and ethylene glycol at different temperatures were used to calculate the \(C_d\) versus Re relationship based on Equations 11 and 18. As was done previously, the fluid properties at the experimental temperature were used for the calculation of the Reynolds number. The results presented in Figure 8 clearly indicate that surface tension does indeed impact the analysis and should be considered under these experimental conditions.

RESULTS

The experimental results collected for head and volumetric flow rate for water and ethylene glycol at different temperatures were used to calculate the \(C_d\) versus Re relationship based on Equations 11 and 18. As was done previously, the fluid properties at the experimental temperature were used for the calculation of the Reynolds number. The results presented in Figure 8 clearly indicate that surface tension does indeed impact the analysis and should be considered under these experimental conditions.

DIMENSIONLESS FORMULATION

To generalize the results of the new formulation, Equation 18 may be written in dimensionless form as

\[ \left( \frac{Q_{exp}/C_d \pi r_o^2}{2gh} \right)^2 = 1 - \frac{\sigma}{\rho g r_o h} \]  \hspace{1cm} (19)

or

\[ \frac{u_{theo}^2}{2gh} = 1 - \frac{\sigma}{\rho g r_o h} \]  \hspace{1cm} (20)

or

\[ Fr + \frac{1}{Bo} = 1 \]  \hspace{1cm} (21)

where the Bond number is defined as

\[ Bo = \frac{\text{potential forces}}{\text{surface forces}} = \frac{\rho gh h}{\sigma} \]  \hspace{1cm} (22)

and the Froude number is defined as

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Inspection of Equation 21 indicates that as the reciprocal of the Bond number increases, the Froude number must
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decrease since the sum of these numbers must equal unity. A small Bond number is indicative of a system where surface tension is playing a significant role. Note that when the surface tension force is negligible, Equation 21 reduces to:

\[ Fr = 1 \] (24)

This is the classical formulation of the quasi-steady state flow of a stream falling under gravity through an orifice. Also note that as \( 1/Bo \rightarrow 1 \), then \( Fr \rightarrow 0 \). Hence, as the head decreases, surface tension plays an increasingly important role in governing the flow rate of fluid. Finally, when \( 1/Bo > 1 \), \( Fr < 0 \) (\( u_{theo} < 0 \)) meaning that continuous flow has stopped and a different formulation is required to describe throughput (dripping supplied by capillary action).

This has significant implications if melt systems are considered. Referring to Equations 20 and 21, fluids with a relatively high surface tension to density ratio exhibit fluid dynamic behaviour in which surface forces are considerable. Recall that the surface tensions of melts are much higher in comparison to water and other organic liquids.

Figure 9 is a plot of Equation 21 and illustrates the magnitude of the Bond number for a variety of fluids subjected to a head of 10 mm and an orifice radius of 4 mm. Mercury and lead are the only metals on this chart that are within the same range as water and other organic fluids. Note that for other values of head and orifice radius, only the magnitude of \( Fr \) and \( Bo \) will vary along the same unique line shown in Figure 9 and given by Equation 21.

Surface tension is expected to exhibit greater influence when a relatively small orifice is used, as indicated by Equations 20 and 21. This is illustrated in Figure 10 for water at 293 K with a head of 10 mm.

Head is also an important variable in determining the magnitude of surface forces. During the course of an experiment, head conditions are lowered as the vessel drains and surface forces increase. The Froude-Bond relationship for water at 293 K draining under variable head is illustrated in Figure 11.

**DETERMINING SURFACE TENSION**

An important consequence of the new formulation, Equation 21, is that the surface tension, \( \sigma \), may be deter-
determined from the experimental measurement of \( h \) and \( Q_{exp} \) using a calibrated orifice. The calibration is performed to determine the discharge coefficient, \( C_d \) versus \( Re \) relationship. Liquids of known physical properties (density and viscosity) must be used to do this. Rewriting Equation 20 in terms of surface tension,

\[
\sigma = \rho g r_o \left( h - \left( \frac{Q_{exp}}{C_d r_o^2} \right)^2 \right)
\]

Tests with water at 321.5 K were conducted to assess the feasibility in making such a measurement. The 1.5 mm radius orifice used in the previous section was also used in this study. Four independent calibrations were conducted. Water at room temperature was used as the calibration liquid. The density and viscosity of water at 298 K are 998 kg/m\(^3\) and 1.002 \( \times \) \( 10^{-3} \) Ns/m\(^2\), respectively [18]. At an elevated temperature of 321.5 K, the density is 988 kg/m\(^3\) and the viscosity is significantly less at 5.86 \( \times \) \( 10^{-4} \) Ns/m\(^2\) [18]. For calibration purposes, these differences in property values reflect two distinct liquids. Refer to Figure 12 for four independent calibrations performed at 293 K.

A 3\(^{rd}\) degree polynomial curve was fit on all four calibrations together, as indicated in Figure 12. Higher order polynomial curves were implemented; however, precision was not improved. A polynomial fit was also made on each calibration independently. The polynomial constants are listed in Table I. Substituting the 3\(^{rd}\) degree polynomial into Equation 24 yields:

\[
\sigma = \rho g r_o \left[ h - \frac{1}{2 g} \left( \frac{Q_{exp}}{a \times Re^3 + b \times Re^2 + c \times Re + d} \right) r_o^2 \right]^2
\]

The detailed data collected for water at 321.5 K are available elsewhere [27]; however, head and flow rate are measured using the same methods described in the experimental section. Figure 13 illustrates results for the surface tension of water at 321.5 K as a function of head using each of the four independent calibrations. It is immediately evident from each of the curves that surface tension value depends on the calibration as well as head.

Figure 14 illustrates results for the polynomial fit using an average of the four calibrations. The average surface tension indicated in Figure 14 is presented in Table II with the quoted value in the literature. Since all four calibrations are considered, results presented in Figure 14 are more statistically relevant than values presented in Figure 13.

<table>
<thead>
<tr>
<th>Calibration</th>
<th>a ( \times ) ( 10^{-12} )</th>
<th>b ( \times ) ( 10^{-8} )</th>
<th>c ( \times ) ( 10^{-4} )</th>
<th>d ( \times ) ( 10^{1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>3.38</td>
<td>-3.80</td>
<td>1.52</td>
<td>5.83</td>
</tr>
<tr>
<td>#2</td>
<td>2.92</td>
<td>-3.71</td>
<td>1.61</td>
<td>5.60</td>
</tr>
<tr>
<td>#3</td>
<td>2.53</td>
<td>-2.84</td>
<td>1.81</td>
<td>6.18</td>
</tr>
<tr>
<td>#4</td>
<td>4.64</td>
<td>-4.84</td>
<td>1.76</td>
<td>5.61</td>
</tr>
<tr>
<td>Combination</td>
<td>2.587 ( \times ) ( 10^{-12} )</td>
<td>-3.11 ( \times ) ( 10^{-8} )</td>
<td>1.326 ( \times ) ( 10^{-4} )</td>
<td>5.965 ( \times ) ( 10^{-1} )</td>
</tr>
</tbody>
</table>

Table I – Polynomial constants that describe the calibration curve.
A rigorous error analysis can be used to describe the deviations illustrated in Figure 13. This exercise provides a quantitative method that outlines conditions for reliable surface tension measurements.

**Error Analysis**

Figure 13 indicates that errors in the discharge coefficient calibration result in significant deviations in surface tension under high head conditions. However, it is possible that error in head and flow rate may also contribute to the overall error of the calculation. So that a complete analysis is provided, all three variables will be considered. These deviations can be explained through implementation of the propagation of errors analysis [28]. This method allows for the error in surface tension to be predicted if errors in each measurements are known. This is performed as follows

$$
\delta \sigma = \sqrt{ \left( \frac{\partial \sigma}{\partial h} \right)^2 \delta h^2 + \left( \frac{\partial \sigma}{\partial Q_{exp}} \right)^2 \delta Q_{exp}^2 + \left( \frac{\partial \sigma}{\partial C_d} \right)^2 \delta C_d^2 } \quad (26)
$$

The value $\delta \sigma$ is the expected deviation in surface tension. Quantities, $\delta h$, $\delta Q_{exp}$, and $\delta C_d$ represent the standard deviations of head, flow rate and discharge coefficient, respectively.

The differentials in Equation 26 are determined by taking the derivative of Equation 24 with respect to $h$, $Q_{exp}$, and $C_d$. These relationships are represented in Equations 27 to 29:

$$
\frac{\partial \sigma}{\partial h} = \rho g r_o \quad (27)
$$

$$
\frac{\partial \sigma}{\partial Q_{exp}} = -\frac{\rho g^2 h (1 - \frac{1}{Bo})}{C_d \sigma_o} \quad (28)
$$

and

$$
\frac{\partial \sigma}{\partial C_d} = \frac{\rho r_o \mu_{ave}}{C_d} \quad (29)
$$

Substituting Equations 21 and 24 into Equation 29 yields

$$
\frac{\partial \sigma}{\partial C_d} = \frac{2 \rho g r_o h (1 - \frac{1}{Bo})}{C_d} \quad (30)
$$

Table II – Comparison between experimental surface tension and literature value for water at 321.5 K.

<table>
<thead>
<tr>
<th>Average experimental surface tension (N/m)</th>
<th>CRC handbook of chemistry and physics [18] (N/m)</th>
<th>Percentage difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0670±0.002</td>
<td>0.0682</td>
<td>1.75</td>
</tr>
</tbody>
</table>

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Fig. 13. Surface tension of water measured at 293 K using four independent calibrations.

Fig. 14. Surface tension of water measured at 321.5 K using four independent calibrations.
Errors in Head

Referring to Equations 26 and 27, uncertainties in head will produce a deviation in surface tension proportional to the product of \( p, g \) and \( r_o \). This indicates that low density fluids and small orifice sizes are favourable in terms of the accuracy of the surface tension calculation. The derivative is independent of processing variables \( h \), \( Q_{exp} \), and \( C_d \) and indicates the errors in the measurement are constant for any orifice regardless of the conditions.

Errors in Flow Rate

In the presence of errors in flow rate, Equation 28 indicates that large values of \( 1/Bo \) will result in decreasing error in the calculation for surface tension. Liquids with high surface tension to density ratios, high head conditions, and small orifice radii are desirable for calculating surface tension. This is particularly relevant for many melt systems as indicated in Figure 9.

Errors in Discharge Coefficient

Similar to errors in flow rate, large values of \( 1/Bo \) are desirable. It is therefore expected that melt systems, especially light metals, are less susceptible to this form of error. The standard deviation in \( C_d \) was calculated by quantifying the variability between the four calibrations illustrated in Figure 12. This was done by considering the difference between each data point in Figure 13 and the discharge coefficient described by the combination polynomial presented in Table I.

\[
\delta C_d = \sqrt{\frac{\sum (C_{d, poly} - C_{d, exp})^2}{n - 4}} = 0.0035 \quad (31)
\]

The solid lines depicted in Figure 13 represent the expected deviations predicted by propagation of errors analysis. This was done by substituting Equations 30 and 31 into Equation 26. Errors in head and flow rate were not considered. The lines successfully predict that as head increases, the precision in surface tension measurement decreases.

This analysis is important in experimental design. For example, by rearranging Equation 29, a range in head can be outlined so that error in surface tension can be maintained within a set limit

\[
h < \left( \frac{\partial \sigma}{\partial C_d} \right) \frac{C_d}{2 \rho g r_o (1 - 1/Bo)} \quad (32)
\]

Figure 15 illustrates the expected deviations in surface tension as head increases. The quantity \( 1/Bo \) is also indicated and may provide an indication of desirable conditions that would improve accuracy.

CONCLUSIONS

Experiments performed in this study have focused on an experimental system that has traditionally neglected surface tension. Using the analysis of a draining vessel through a small orifice (1.5 mm radius), it has been confirmed experimentally that surface tension plays a fundamental role under certain circumstances. The Bernoulli formulation is insufficient in characterizing frictional losses under certain processing conditions. The new model developed in this study is an extension of the traditional Bernoulli formulation; however, it includes a surface tension term. The following conclusions have been made from experimental results:

1. The new formulation is relevant for low density liquids with high surface tensions compared with high density and low surface tension liquids.
2. The new formulation is relevant, from the perspective of design and operation, for small orifice radii operating under low head conditions.

3. High values of $1/Bo$ are an indication of conditions where the new formulation is most relevant (i.e. $1/Bo = \frac{\sigma}{\rho grh \sigma}$).

4. Melts should be considered in the new formulation more often than low temperature fluids because of the high surface tension/density ratios indicative to many of these liquids (large $1/Bo$).

These conclusions are also important if the formulation is to be used for measuring surface tension. Propagation of errors analysis indicates that precision is improved under low head conditions for liquids with high surface tension/density ratios. A subsequent paper will outline experiments with molten aluminum. Density and viscosity will also be evaluated since a large amount of data is collected during the course of one experiment.

**NOMENCLATURE**

- $A_c$: Cross-sectional area for Bernoulli formulation (m$^2$).
- $Bo$: Bond number = $\frac{\rho grh}{\sigma}$ (no units).
- $C_d$: Discharge coefficient (no units).
- $C_m$: Cumulative mass (kg).
- $Fr$: Froude number = $u_{theo}^2/(2gh)$ (no units).
- $g$: Gravitational constant (m/s$^2$).
- $h$: Liquid head above a point of reference (m).
- $m$: Mass (kg).
- $P$: Pressure (Pa).
- $Q$: Flow rate (m$^3$/s).
- $R$: Radius of curvature (m).
- $Re$: Reynolds number = $\frac{\rho 2r u}{\eta}$ (no units).
- $r$: radius (m).
- $T$: Temperature (K).
- $t$: Time (s).
- $u$: Velocity (m/s).
- $z$: Distance on z-axis (m).
- $\eta$: Viscosity (Nsm$^{-2}$).
- $\rho$: Density (kg/m$^3$).
- $\sigma$: Surface tension of liquid (N/m).

**Subscripts**

- $a$: Location described by radius of curvature.
- $b$: Location described by radius of curvature.
- $exp$: Experimental.
- $o$: Orifice.
- $Poly$: Polynomial.
- $v$: Vessel.

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**REFERENCES**


