An absolute method for the determination of surface tension of liquids using pendent drop profiles

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Abstract. Drop formation at conical tips which is of relevance to metallurgists is investigated based on the principle of minimization of free energy using the variational approach. The dimensionless governing equations for drop profiles are computer solved using the fourth order Runge-Kutta method. For different cone angles, the theoretical plots of X_T and Z_T vs their ratio, are statistically analyzed, where X_T and Z_T are the dimensionless x and z coordinates of the drop profile at a plane at the conical tip, perpendicular to the axis of symmetry. Based on the mathematical description of these curves, an absolute method has been proposed for the determination of surface tension of liquids, which is shown to be preferable in comparison with the earlier pendent-drop profile methods.

Keywords. Surface tension; drop profiles; regression analysis; Runge-Kutta method

1. Introduction

The importance of the understanding of interfacial phenomena in many metallurgical processes has been rightly recognized (Richardson 1973, 1974; Szekeley 1979). For any study pertaining to interfacial phenomena, a good knowledge of the interfacial tension/surface tension of liquids is indispensable. Therefore, the methods available for the determination of this important physical property warrant considerable attention. While there are a number of methods available for this purpose (Padday 1969), very few methods are applicable for the determination of surface tension of liquid metals. Among these, White (1962) recommends the pendent drop profile method as most suitable. Again, among the various versions of the pendent drop profile methods (Hartland and Hartley 1976), the method proposed originally by Andreas *et al* (1938) which has subsequently been refined, particularly with the advent of modern fast and reliable computing facilities (Stauffer 1965; Winkel 1965), is recommended for accurate work. While the pendent drops at capillary tips have been investigated since the time of Rayleigh, excepting a simple dimensional analysis by Brown and McCormick (1948) that lead to a comparative method for the surface tension determination, no other significant work on drop formation at conical tips has appeared in literature. It may be mentioned that the drop formation studies at conical tips can also lead to an understanding of drop formation at the tip of melting rods, which will be of relevance to metallurgists as in the area of ESR process. The computer-aided analysis of drop formation at conical tips leading to an absolute method for the determination of surface tension of liquids using pendent drop profiles, is discussed in this paper.

2. Model

The principle of minimization of free energy has been used to develop a model to predict the pendent drop profiles at conical tips (see figure 1) using the 'variational approach' (Ramesh Babu 1985a). The governing equations, in dimensionless form are given by

$$d\theta/dS = (2/B) - (\sin\theta/X) - Z, \quad (1)$$

$$dX/dS = \cos\theta, \quad (2)$$

$$dZ/dS = \sin\theta, \quad (3)$$

$$dV/dS = \pi X^2 \sin\theta. \quad (4)$$

With the following boundary conditions

$$\text{at } Z = 0, X = 0; dX/dZ = \infty \text{ and } V = 0, \quad (5)$$

$$\text{at } Z = Z_0, dX/dZ = \tan\beta, \quad (6)$$

where, $X = x C^{1/2}$; $Z = z C^{1/2}$; $S = s C^{1/2}$; $V = v C^{1/2}$; $B = b C^{1/2}$; $C = g(\rho_d - \rho_L)/\gamma$; b = radius of curvature at the drop apex, s = arc length, ρ_d = density of the drop, and ρ_L = density of the surrounding fluid, γ = interfacial tension at the drop-fluid interface and v = drop volume.

The same governing equations have also been shown to be deducible by an alternate approach using the concept of double buoyancy effect (Ramesh Babu 1984). Choosing a particular value of B , equations (1) to (4), together with the boundary conditions, equations (5) to (6), were solved simultaneously by the 'fourth order Runge-Kutta procedure', for which a computer program was developed ensuring an accuracy better than a part per million in the computed values (Ramesh Babu 1985b). The method of 'Regula-Falsi' was also incorporated in the program for calculating the interpolated values of interest. The flow chart highlighting the programme logic is given in figure 2.

Figure 1. Axisymmetric pendent liquid drop at an infinite conical tip.

Figure 2. Flow chart highlighting the programme logic for generating pendent drop profiles at conical tips.

The maximum drop volume was obtained numerically. The significance of the numerical results obtained for various cone angles is discussed elsewhere (Ramesh Babu 1985a). The model permits the calculation of drop volume as well as to follow the changing sequence of drop profiles until the onset of instability. The sequence of drop growth at different conical tips is illustrated in figure 3.

3. Determination of surface tension

Considering the equilibrium situation of a pendent liquid drop at a conical tip as shown in figure 1, for a specified cone angle, it is possible to theoretically calculate the values of X_T corresponding to Z_T , and hence their ratio, during the drop formation until it enters the instability stage, where,

$$X_T = x_T \left(\frac{(\rho_d - \rho_L)g}{\gamma} \right)^{1/2}, \quad (7)$$

and

$$Z_T = z_T \left(\frac{(\rho_d - \rho_L)g}{\gamma} \right)^{1/2}. \quad (8)$$

Figure 3. Sequence of drop growth at conical tips.

Dividing (8) by (7), we get

$$Z_T/X_T = z_T/x_T. \quad (9)$$

Therefore, by photographically measuring the values of x_T and z_T , in view of (9) the corresponding X_T and Z_T can be calculated. The interfacial tension can be calculated using (7) or (8).

4. Regression analysis

To facilitate quick computation of γ , it is desirable to have a relation between X_T and Z_T and their ratios. Figures 4–7 illustrate the variation of both X_T and Z_T with X_T/Z_T and Z_T/X_T in the range $0 \leq Z_T \leq Z_T^{\max}$, where, $Z_T^{\max}$ corresponds to the critical profile enclosing the maximum drop volume, for each of the cone angles 60°, 90°, 120° and 150°. Each of these plots was statistically analyzed using a computer algorithm that has been shown to be superior even to Gauss elimination technique upto fifth order polynomial (Ramesh Babu 1985c). The coefficient of variation defined below was used as the criterion for choosing the best fit polynomial.

$$CV = \frac{SD}{\bar{y}} \times 100; \quad SD = \left(\frac{\sum_{i=1}^n (y_{LF} - y_i)^2}{n - (K + 1)} \right)^{1/2}, \quad (10)$$

where, SD is the standard deviation, y_{LF} is the least square fitted value of y_i , $\bar{y}$ is the average of y_i and K is the degree of the polynomial fitted onto n data points.

Table 1. Summary of the regression analysis of the curves X_T vs X_T/Z_T and Z_T vs X_T/Z_T

Curve investigated			X_T vs X_T/Z_T			Z_T vs X_T/Z_T		
Cone angle	Range of X_T/Z_T	n	K	PEM (%)	CV (%)	K	PEM (%)	CV (%)
60°	1.34-6.60	16	2	4.52	1.03	2	87.34	11.992
	1.34-2.88	12	5	0.32	0.239	2	3.59	1.456
90°	0.97-3.48	22	1	2.66	1.387	2	25.31	4.059
	0.97-3.14	21	2	2.48	1.223	2	15.96	3.011
120°	0.90-18.39	27	2	44.91	6.076	2	2402.30	41.84
	1.11-3.61	19	2	2.03	1.046	2	16.79	3.172
150°	0.95-23.16	24	2	30.68	5.575	2	2355.5	49.87
	1.08-5.21	17	2	3.44	2.003	2	41.56	7.52

Table 2. Summary of the regression analysis of the curves X_T vs Z_T/X_T and Z_T vs Z_T/X_T

Curve investigated			X_T vs Z_T/X_T			Z_T vs Z_T/X_T		
Cone angle	Range of Z_T/X_T	n	K	PEM (%)	CV (%)	K	PEM (%)	CV (%)
60°	0.15-0.75	16	2	0.27	0.175	2	26.78	1.782
	0.35-0.75	12	2	0.19	0.114	2	1.17	0.371
90°	0.28-1.03	22	2	2.22	0.823	5	6.88	0.785
	0.32-1.03	21	2	1.84	0.727	5	4.11	0.558
120°	0.05-1.12	27	2	26.16	3.567	1	706.65	5.291
	0.28-0.90	19	2	1.80	0.705	5	3.90	0.518
150°	0.04-1.05	24	2	47.58	6.365	5	599.96	5.399
	0.19-0.93	17	2	4.64	1.887	5	5.31	0.668

Since the analysis showed too large values of CV, the analysis was repeated by reducing the range. The results are summarized in tables 1 and 2. The significant improvement in the CV value upon reducing the range is obvious. It could also be seen that the descriptions of the plots X_T vs Z_T/X_T and Z_T vs Z_T/X_T are far more desirable than the other two. The coefficients of the best fit polynomial to these curves are tabulated in tables 3 and 4. Utilizing these results, tables have been prepared in intervals of 0.001 of Z_T/X_T over a sufficiently wide range of practical utility for each of the 4 cone angles.

5. Results and discussion

A common feature of all the curves (see figures 4-7) is that the slope of the curve increases with cone angle, which suggests that a 60° cone is preferable. While the plots of Z_T vs Z_T/X_T show a uniform gradient throughout, the plots of Z_T vs X_T/Z_T show steep gradients in the range of practical interest. The plots of X_T vs Z_T/X_T indicate that

Table 3. Coefficients of the best fit polynomial to the curve X_T vs Z_T/X_T

Cone angle	Range of Z_T/X_T	CV (%)	$X_T = A_1 + A_2(Z_T/X_T) + A_3(Z_T/X_T)^2$		
			A_1	A_2	A_3
60°	0.35–0.75	0.114	–0.00054	1.91325	–1.11559
90°	0.32–1.03	0.727	0.11320	2.01519	–1.10914
120°	0.28–0.90	0.705	0.17625	2.73173	–1.67780
150°	0.19–0.93	1.887	0.48231	3.59968	–2.49335

Table 4. Coefficients of the best fit polynomial to the curve Z_T vs Z_T/X_T

Cone angle	Range of Z_T/X_T	CV (%)	$Z_T = A_1 + A_2(Z_T/X_T) + A_3(Z_T/X_T)^2 + A_4(Z_T/X_T)^3 + A_5(Z_T/X_T)^4 + A_6(Z_T/X_T)^5$					
			A_1	A_2	A_3	A_4	A_5	A_6
60°	0.35–0.75	0.371	–0.16413	0.96421	0.08756	—	—	—
90°	0.32–1.03	0.558	–0.22483	1.31150	–0.00061	–0.00056	–0.00003	–0.05832
120°	0.28–0.90	0.518	–0.23624	1.61267	–0.00063	–0.00068	–0.00006	–0.09064
150°	0.19–0.93	0.668	–0.21477	2.09723	0.00012	–0.00129	–0.00045	–0.19713

over a wide range of Z_T/X_T the curves are almost parallel to the x-axis, hence errors in the measured Z_T/X_T will not significantly affect the accuracy of the corresponding X_T value.

The proposed method has several distinct advantages over the other methods employing the pendent drop profiles at capillary tips (Padday 1969):

- (i) The method is free from empiricism, as it is based on a sound theory;
- (ii) The well-defined conical tip inside the drop enables accurate measurements of x_T and z_T ;
- (iii) The measurement of the linear dimensions being independent of each other, the undesirable cascading error in the method of selected planes (Andreas *et al* 1938) is obviated;
- (iv) A single cone is sufficient to form drops of desirable shapes. This is in sharp contrast to the extra care required in selecting a suitable capillary to obtain a desired drop shape, in all the earlier methods.
- (v) Since different drop shapes could be obtained from a single cone, a number of measurements of x_T and z_T could be made, providing as many cross checks for γ as required. In addition, each set of x_T and z_T values permits the calculation of γ by two independent methods vide (7) and (8).
- (vi) Formation of drops at conical tips is much simpler and easier compared to any other method of drop formation reported in literature.

Figures 4-7. 4. Variation of Z_T with X_T/Z_T . 5. Variation of X_T with X_T/Z_T . 6. Variation of Z_T with Z_T/X_T . 7. Variation of X_T with Z_T/X_T .

The design of a simple experimental set-up to form drops at conical tips under desired controlled flow rates has been described elsewhere (Ramesh Babu 1985b). Drops could also be formed at conical tips by immersing a metal cone in the liquid bath and gradually moving it away from the liquid surface or vice versa. This method of drop formation is particularly suited for liquid metals. In view of the several advantages of the proposed method, application to liquid metals deserves considerable attention.

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