Some Mathematical Characteristics of Menisci and Their Use in Determination of Surface Tension

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By expressing the meniscus height and the sine of the angle between the horizontal and a tangent to the meniscus curve as simple exponential functions of radial position, a new calculational procedure for determining surface tensions from menisci has been developed. These simple functions, when combined with the Laplace-Young equation, generated three useful equations for calculating surface tensions as a function of radial positions. The overall procedure by using the three equations and five smoothing methods was tested on both experimental and calculated menisci. The results from the procedure for the calculated menisci agreed within 1.5% with the original surface tensions used to generate the meniscus. The agreement of values generated with the method and the comparison method previously reported for experimental menisci was within ±8% in general and within ±2% for the best formed menisci.

Previous work (*1, 2*) has shown that surface tensions can be determined from liquid menisci as formed in cylindrical tubes. In that work, the surface tensions were obtained by comparing computed menisci with the experimental meniscus. The correct surface tension was indicated when a minimum in the sum of squares of the differences in meniscus heights was obtained as surface tension and the contact angles were varied. This procedure gave excellent results but required quite lengthy computer computations.

The work reported here was initiated in an attempt to produce a more rapid procedure for determining surface tensions from menisci. Instead of comparing computed and experimental menisci, it was hoped that surface tensions could be calculated directly from mathematical properties of the meniscus itself.

From many computed menisci, the following interesting mathematical characteristics were empirically observed. Both the $\sin\theta$, sine of the angle between the meniscus tangent and the horizontal, and ζ', the height of the meniscus at radial position ξ, could be expressed as exponential functions of ξ with the exponent relatively constant in local regions of the meniscus. (See Figure 1 for a display of the variables used to describe the meniscus.) When the exponents did vary, they monotonically increased in size as ξ was increased. For menisci formed in capillary tubes with the capillary rise heights ten to one hundred times larger than the maximum meniscus height, the exponents for the $\sin\theta$ and ζ' functions were nearly constant with values of 1 and 2, respectively.

The mathematical procedure described below followed naturally from these observations by assuming that the curve in a local region about a given radial position could be expressed by $\zeta' = \zeta'_M \xi^n$ and $\sin\theta = S_M \xi^m$. The surface tension for the local region was then generated by introducing these functions into the Laplace-Young equation.

MATHEMATICAL DEVELOPMENT

The meniscus height above the datum plane, a surface with no curvature formed by a reservoir of the fluid below the meniscus, is assumed to be expressed by Equation (1).

$$\zeta = \zeta_0 + \zeta'_M \xi^n \tag{1}$$

ζ'_M and n are slowly changing functions of ξ, but for a local region they are assumed to be constant. Thus, when derivatives of ζ are taken, ζ_0, n, and ζ'_M are considered to be constants.

Equation (1) is then combined with the Laplace-Young equation as modified in the previous publications (*1, 2*) to generate a function for $\sin\theta$. The Laplace-Young equation in dimensionless form is given as Equation (2):

$$\zeta = \frac{\Gamma}{\xi}\frac{d}{d\xi}(\xi \sin\theta) \tag{2}$$

Γ is the dimensionless surface tension and is equal to $\gamma/[r_0^2 g(\rho_1 - \rho_2)]$. When Equations (1) and (2) are combined and the result is integrated, Equation (3) results:

$$\sin\theta = \left(\frac{\zeta_0}{2\Gamma}\right)\xi + \left[\frac{\zeta'_M}{\Gamma(n+2)}\right]\xi^{n+1} \tag{3}$$

The derivatives of the above equation are also useful and are given as Equations (4) and (5):

$$\sin'\theta = \frac{\zeta_0}{2\Gamma} + \left[\frac{\zeta'_M(n+1)}{\Gamma(n+2)}\right]\xi^n \tag{4}$$

$$\sin''\theta = \left[\frac{\zeta'_M(n+1)(n)}{\Gamma(n+2)}\right]\xi^{n-1} \tag{5}$$

Empirically, $\sin\theta$ was observed also to behave exponentially. Therefore, a second mathematical procedure was developed by starting with the assumption that $\sin\theta$ could be approximated by Equation (6):

$$\sin\theta = S_M\,\xi^m \tag{6}$$

Again, S_M and m are considered to be constant in a local region of ξ, even though they do slowly change with ξ.

By substituting Equation (6) in Equation (2) and by performing the differentiation, an expression for ζ is obtained and is given in Equation (7):

$$\zeta = \Gamma(m+1)\xi^{m-1}\,S_M \tag{7}$$

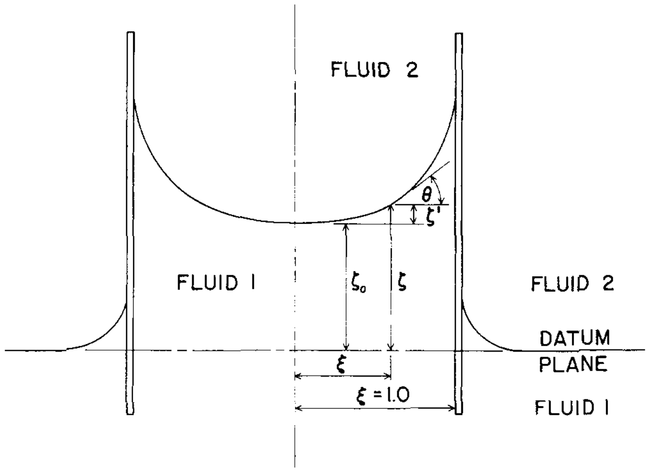

Fig. 1. Pictorial representation of meniscus and its variables.

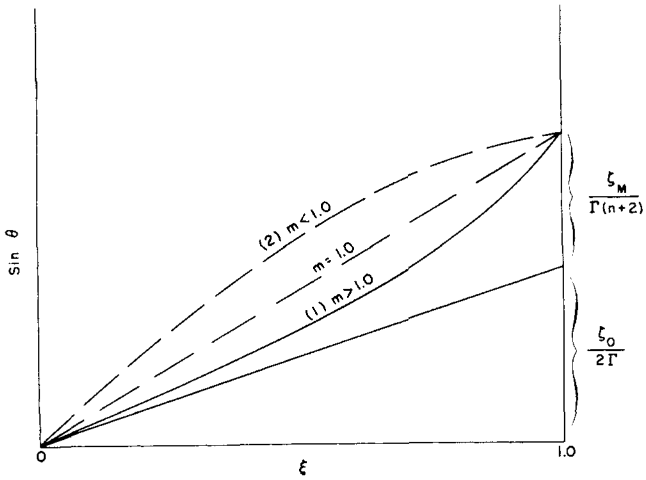

Fig. 2. Effect of m on sinθ curve.

DEDUCTIONS FROM THE DEVELOPED EQUATIONS

The above equations indicate some basic mathematical characteristics about menisci.

1. Sinθ is a linear function of ξ when $\zeta_0 >>> \zeta'_M$. When this condition is met, the second term in Equation (3) is very small compared with the first. This condition is that realized in a capillary rise experiment.

Many times in such an experiment, sinθ at the wall is in doubt and is assumed to be equal to 1.0 for convenience. However, if the meniscus can be photographed without distortion and the sinθ as a function of ξ calculated, then sinθ at $\xi = 1$ can be determined by drawing a best fit straight line through the sinθ data.

If the function $\sin\theta = S_R\xi$ does approximately apply to the meniscus, as is the case in capillaries, the approximating curve is a circular arc. This result can be produced by integrating Equation (8). S_R is the sinθ at $\xi = 1$ and is a constant equal to $\zeta_0/2\Gamma$ as indicated by Equation (3):

$$\sin\theta = \frac{d\zeta'/d\xi}{\sqrt{1+(d\zeta'/d\xi)^2}} = S_R\xi \tag{8}$$

The integrated result is given in Equation (9):

$$\zeta' = \frac{1}{S_R} - \sqrt{\left(\frac{1}{S_R}\right)^2 - \xi^2} \tag{9}$$

To show that this is the equation of a circle, substitute $\chi = 1/S_R - \zeta'$ into Equation (9). Equation (10) results:

$$\chi^2 + \xi^2 = \left(\frac{1}{S_R}\right)^2 = (\beta)^2 \tag{10}$$

By substituting a series approximation for the square root term in Equation (9), the functional relationship of ζ' and ξ can be determined for the circular cross-section case. This relationship is shown as Equation (11):

$$\zeta' = \frac{\xi^2}{2\beta} + \frac{\xi^4}{8\beta^3} + \frac{\xi^6}{16\beta^5} + \ldots \tag{11}$$

Thus, the function is approximately parabolic for small ξ.

2. m is always equal to or greater than 1. Equation (7) indicates that ζ is equal to zero at $\xi = 0$ unless $m = 1$. With $m = 1$, then $\lim_{\xi\to 0} \zeta = 2\Gamma S_M = \zeta_0$, where ζ_0 is the capillary rise.

Comparison of Equations (3) and (6) also indicates that m must have a lower bound of 1.0. Figure 2 indicates the effects of the two terms in Equation (3). n is always positive and, as a result, produces curve (1) which is concave upward. If m were less than 1, then a curve like curve (2) would result which is convex and would require the second term in Equation (3) to be negative.

To indicate the variation of exponents n and m and parameters ζ_M and S_M as a function of radial positions, four computed menisci are presented in Tables 2 through 5 in the appendix.* The Γ values for these menisci range from 11.23 to 0.013. The sine exponents $m_{i+1/2}$ are computed for these menisci, and the validity of the above statements is supported in all cases. m approaches 1.0 at $\xi = 0$ and monotonically increases as ξ increases. In Figures 3 and 4 are presented plots of $m_{i+1/2}$ and n_i from Tables 2 and 5.* m is a very well behaved function. It starts at 1.0 and increases almost linearly for most of the range of ξ. If Γ is large, above 5, $m \cong 1.0$ for the whole range of ξ. This observation supports the statements under 1 above.

3. $n = 2.0$ at $\xi = 0$ and > 2.0 as ξ increases. S_M, ζ'_N, m, and n are related by Equation (12) which was obtained by substituting Equations (1) and (6) into the definition of the sine:

$$(\xi^n{}_{i+1/2} - \xi^n{}_{i-1/2})\zeta'_M = \frac{(\xi_{i+1/2} - \xi_{i-1/2})S_M\,\xi^m}{\sqrt{1 - S_M{}^2\,\xi^{2m}}} \tag{12}$$

Equation (12) can be simplified by carrying out the division and then by letting $\Delta\xi$ go to zero. The result is Equation (13):

$$\zeta'_M(n\,\xi^{n-1}) = \frac{S_M\,\xi^m}{\sqrt{1 - S_M{}^2\,\xi^{2m}}} \tag{13}$$

Relationships between n and m and ζ'_M and S_m can be obtained from Equation (13) if assumptions are made as to how the equation should be divided up.

a. For $\xi \cong 0$, Equation (13) simplifies to Equation (14):

$$\zeta'_M(n\,\xi^{n-1}) = S_M\,\xi^m \tag{14}$$

Thus

$$n = m + 1 \geqq 2.0 \tag{15}$$

and

$$S_M = n\,\zeta'_M \tag{16}$$

The data in Tables 2 through 5* support these simplifications with $\xi \cong 0$.

b. For $\xi >> 0$, the separation of Equation (9) into two parts to indicate the relationships of ζ'_M and S_m and n and m cannot be readily made. However, the data in Tables 2 through 5* and Figures 1 and 2 indicate the

* The appendix has been deposited as document 01080 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

TABLE 1. COMPUTATIONAL RESULTS FOR METHODS WITH SHIFTED GRID TO MINIMIZE ERRORS AND WITH ITERATION TO ADJUST ζ_0

$\Gamma(\zeta')$ not shifted.
$\Gamma(S)$ n and ζ_M' indexes reduced 2½ units ($N = 25$).
$\Gamma(\Delta S1)$ n and ζ_M' indexes reduced 1.1 units ($N = 25$).

		Meniscus Table 2 $\Gamma = 11.236$ $\gamma = 1100.0$		Meniscus Table 3 $\Gamma = 1.0215$ $\gamma = 1000.0$		Meniscus Table 4 $\Gamma = 0.1021$ $\gamma = 1000.0$		Meniscus Table 5 $\Gamma = 0.01328$ $\gamma = 130.0$	
		γ	% Error	γ	% Error	γ	% Error	γ	% Error
$\Gamma(\zeta')$	No adjustment	1100.1	+0.009	1000.0	0.000	1000.9	+0.09	130.07	+0.05
$\Gamma(\zeta')$	ζ_0 iterated	1100.0	0.000	1000.0	0.000	1000.7	+0.07	130.15	+0.12
$\Gamma(S)$	No adjustment	1099.7	−0.027	996.7	−0.33	981.5	−1.85	122.65	−5.66
$\Gamma(S)$	Grid shifted	1099.9	−0.009	999.0	−0.10	993.6	−0.64	126.89	−2.39
$\Gamma(S)$	Grid shifted and ζ_0 iterated	1099.9	−0.009	998.9	−0.11	993.5	−0.65	126.95	−2.35
$\Gamma(\Delta S1)$	No adjustment	1100.4	+0.036	1002.5	+0.25	1009.0	+0.90	131.99	+1.53
$\Gamma(\Delta S1)$	Grid shifted	1100.1	+0.009	1000.8	+0.08	1003.6	+0.36	129.55	−0.35
$\Gamma(\Delta S1)$	Grid shifted and ζ_0 iterated	1100.1	+0.009	1000.8	+0.08	1003.4	+0.34	129.61	−0.30

following relationships: n is greater than 2.0 and is monotonically increasing, and $n \geqq m$.

c. If $n = m$, then

$$S_M = \zeta'_M m / (\xi \sqrt{1 + \xi^{2m-2} \zeta'^2_M m^2}) \tag{17}$$

Equation (17) applies for the region of fifteen through twenty-one increments in Figure 2.

USE OF THE EQUATIONS TO DETERMINE SURFACE TENSIONS FROM MENISCI

Equations (3), (4), (5), and (7) can be utilized to produce estimates of Γ for a given meniscus. Equations (18), (19), (20), and (21) are the finite difference representations of these equations. For the derivatives, first-order divided differences were used:

$$\Gamma_i(S) = \left(\frac{\xi_0}{2 \sin\theta_i}\right) \xi_i + \left[\frac{\zeta'_{M(i)}}{(n_i + 2)\sin\theta_i}\right] \xi_i^{n_i+1} \tag{18}$$

$$\Gamma_{i+1/2}(\Delta S1) = \frac{\zeta_0 \Delta\xi}{(2\,\Delta S1_{i+1/2})} + \frac{\zeta'_{M(i+1/2)}(n_{i+1/2} + 1)}{(n_{i+1/2} + 2)\Delta S1_{i+1/2}} \xi_{i+1/2}^{n_i+1} \Delta\xi \tag{19}$$

where

$$n_{i+1/2} = (n_i + n_{i+1})/2.0$$

and

$$\zeta'_{M(i+1/2)} = (\zeta'_{M(i)} + \zeta'_{M(i+1)})/2.0$$

$$\Gamma_{i+1}(\Delta S2) = \frac{\zeta'_{M(i+1)}(n_{i+1} + 1)(n_{i+1})\xi_{i+1}^{(n_i+1-1)} \Delta\xi^2}{(n_{i+1} + 2)\Delta S2_{i+1}} \tag{20}$$

$$\Gamma_{i+1/2}(\zeta') = (\zeta_0 + \zeta'_{i+1/2})/[(m_{i+1/2} + 1) S_{M(i+1/2)} \xi_{i+1/2}^{(m_{i+1/2}-1)}] \tag{21}$$

The gridwork used with the above equations is shown in Figure 5. The radius of the tube was divided into N increments (N was generally 25), and the height measurement for ζ' was made at the center of the increment. The positions for $\sin\theta$, n, ζ'_M, $\Delta S1$, m, S_m, and $\Delta S2$ are shown on the figure.

Application to Computed Menisci

The adequacy of the above equations was tested by determining surface tension from menisci that were computed by the numerical techniques outlined in reference 1. The relaxation iteration procedure used to calculate a meniscus was stopped when one hundred iterations produced a change in the meniscus heights ζ' which was not greater than 5×10^{-5}. The computation results for four menisci are shown in Tables 2 through 5*.

The results indicated that only one method was accurate over the whole range of Γ. That method was $\Gamma(\zeta')$ from Equation (21). The average surface tensions agreed within +0.006, +0.004, +0.09, and +0.06% of the input surface tensions, with Γ varying from 11.2 to 0.013 for the four menisci. As indicated by the tables which give surface tension as a function of radial position, no large variation of surface tension was found across the meniscus. The results from this method were sufficiently accurate to indicate when a meniscus had not been allowed to converge sufficiently in the numerical relaxation technique used to generate the meniscus.

The next best method was $\Gamma(\Delta S1)$ from Equation (19). The agreement of the average computed surface tensions with the input values was +0.037, +0.25, +0.09, and +1.6% for the four menisci.

The other two methods, $\Gamma(S)$ and $\Gamma(\Delta S2)$, were definitely inferior to the others. $\Gamma(S)$ average values exhibited errors of −0.031, −0.33, −0.33, −1.85, and −5.65% for the four menisci. The errors found for $\Gamma(\Delta S2)$ method were +3.0, −0.67, −0.70, and −1.21%. The second difference in sines, $\Delta S2$, is usually a small number and in many cases approaches the statistical errors in the computed menisci heights for large values of Γ. For experimental menisci, where the statistical errors due to measurement are relatively large, the $\Gamma(\Delta S2)$ method is very inadequate.

By empirically adjusting the indexes in Equations (18), (19), and (20), much of the error indicated above was removed. In all cases, the indexes for ζ'_M and n were shifted to smaller or larger numbers, while the indexes of $\sin\theta$, $\Delta S1$, and $\Delta S2$ were held to the values indicated by the equations. In Table 1 are summarized the results obtained with these shifts for four calculated menisci. To eliminate the errors, the indexes were made 2½ units smaller for $\Gamma(S)$, 1.1 units smaller for $\Gamma(\Delta S1)$, and 0.15 units larger for $\Gamma(\Delta S2)$. In these cases, the number of radial increments was 25. With the grid adjustments, all of the procedures gave satisfactory results.

Application to Experimental Menisci

Estimation of ζ_0. When an actual experimental meniscus is analyzed, the ζ_0 must be generated by the surface tension computation procedure itself. Only one of the pro-

* See footnote on p. 788.

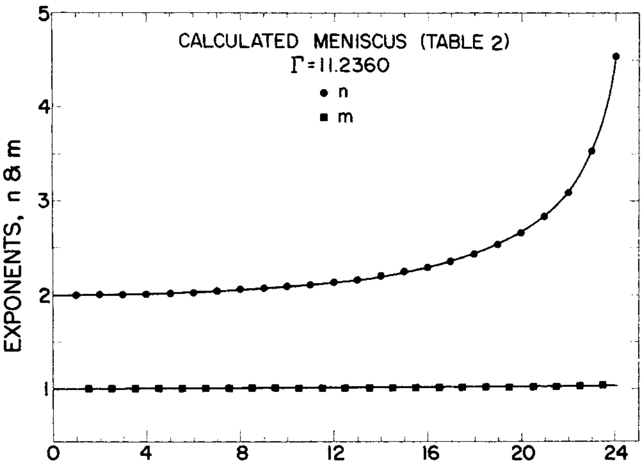

Fig. 3. Exponents n and m as a function of radius for a calculated meniscus with $\Gamma = 11.236$.

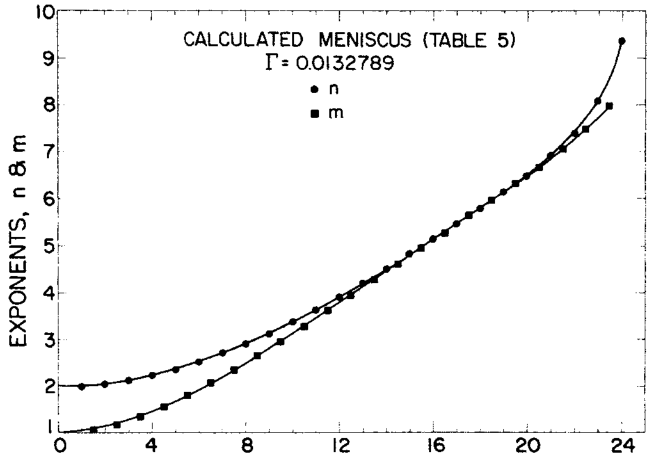

Fig. 4. Exponents n and m as a function of radius for a calculated meniscus with $\Gamma = 0.0133$.

cedures, $\Gamma(\Delta S2)$, does not require a value of ζ_0. But in this case, as explained above, statistical variations in the experimental data prohibit calculation of meaningful surface tension data. The other three methods require ζ_0 values.

The ζ_0 value can be estimated by utilizing the fact that ζ_0 has a greater influence on the surface tension values near the center of the meniscus than at the outside. Thus, an iteration procedure can be generated which adjusts ζ_0 until the average surface tensions for the inside half of meniscus equals that for the outside half of the meniscus. The adjustment in ζ_0 by this method is indicated in Equation (22). The iteration

$$\zeta_{0(k+1)} = \zeta_{0(k)} \left(\frac{\gamma_{\text{avg}}\ (\text{outside half})}{\gamma_{\text{avg}}\,(\text{inside half})} \right)^b \qquad (22)$$

is terminated when the total average surface tension agrees within a set limit with the previous surface tension before the iteration. The limit was set at 1 dyne/cm. for γ greater than 500 and 0.1 dyne/cm. for smaller values of surface tension. In general, less than twenty iterations were required for convergence. This technique worked satisfactorily with both $\Gamma(\zeta')$ and $\Gamma(\Delta S1)$ methods, since the change of γ with ξ was essentially zero. $\Gamma(S)$ could not be used, since the surface tension decreased with increasing ξ.

The exponent b was adjusted to speed convergence and not produce instabilities. The following values were found to be satisfactory:

Γ in the 0.01 to 0.1 range: $b = 1.0$.
Γ in the 0.1 to 1.0 range: $b = 2.0$.
Γ in the 1.0 to 10.0 range: $b = 3.0$.

The ζ_0''s for the four menisci listed in Tables 2 through 5* were determined by the iteration procedure. The surface tensions determined and resulting errors are listed in Table 1. In all cases, the iterations produced effectively no change in the surface tensions, and the errors inherent to the calculational method were unaltered.

Smoothing of Menisci. The surface tension calculational procedures work best on menisci that are smooth functions of ξ. Each surface tension value from methods $\Gamma(\zeta')$ and $\Gamma(\Delta S1)$ utilizes three $\zeta'_{i-1/2}$ values, and $\Gamma(S)$ uses two $\zeta'_{i-1/2}$ values. Therefore, to minimize wild fluctuations in γ as a function of ξ, the values of $\zeta'_{i-1/2}$ should be smoothed to produce functions of $\sin\theta$, n, m, and $\Delta S1$. Attempts to effect such smoothing operations on the computer were made with varying degrees of success. Below are listed five smoothing procedures. The simplest programs utilized only averaging procedures, while others applied some of the mathematical characteristics of menisci such as $n \geqq 2.0$ and $m \geqq 1.0$. The detailed procedures are given in the appendix.* Below are summarized the main features of the procedures.

Smoothing Procedure 1: Averaging of n. $n_i(\text{avg})$ was obtained by averaging the experimental n values at n_{i-1}, n_i, and n_{i+1}. $\xi'_{i+1/2}$ was then recalculated from the smoothed $n_i(\text{avg})$, and an assumed value for $\zeta'_{N-1/2}$. $\zeta'_{N-1/2}$ was adjusted to minimize the sum of squares between the experimental and calculated $\zeta'_{i-1/2}$ values. (The minimization was also made with two other summing methods as outlined in the appendix.* The adequacy of each method was tested by smoothing both calculated and experimental menisci.)

Smoothing Procedure 2: Averaging of n with $n \geqq 2.0$. $n_i(\text{avg})$ was obtained as above, and then any $n_i(\text{avg})$ values less than 2.0 were set equal to 2.0.

Smoothing Procedure 3: Averaging of m. $m_{i+1/2}(\text{avg})$ was obtained by averaging $m_{i-1/2}$, $m_{i+1/2}$, and $m_{i+1\ 1/2}$. Sinθ and then $\zeta'_{i-1/2}$ were recalculated from the smoothed $m_{i+1/2}(\text{avg})$ values and an assumed $\sin\theta_{N-1}$. Sinθ_{N-1} was adjusted to minimize one of the sums indicated in procedure 1.

Smoothing Procedure 4: Averaging of m with $m \geqq 1.0$. Procedure 3 was followed except m was set equal to 1.0 if the averaged value was less than 1.0.

Smoothing Procedure 5: Averaging of n and then m with $m \geqq 1.0$. Procedures 1 and 4 were combined. The meniscus was smoothed with 1, and the resulting meniscus was smoothed with 4.

The adequacy of the smoothing and computational procedures was tested in two manners. First, computed menisci were smoothed, and then the surface tensions were determined from the meniscus by the calculational procedures. The change in surface tension was then compared with the change without smoothing. Second, experimental menisci from mercury, water, cobalt-cerium, and plutonium-cobalt-cerium which had been processed by the methods outlined in reference *1* and *2* were smoothed and then analyzed by the new calculation method proposed in this paper. A comparison of the previously determined values and the new values for these menisci gave an indication of the utility of the smoothing and computation techniques.

* See footnote on p. 788.

* See footnote on column 1.

Results from Smoothing Calculated Menisci

If ζ_0 is known, the smoothing of the calculated meniscus produces little change in the average value of surface tension determined from the smoothed meniscus. However, the smoothing operations do produce enough distortion in the computed menisci to generate errors in the ζ_0 iteration procedure. The errors produced for the four computed menisci are listed in Table 6 in the appendix.* The errors varied as follows:

	% error	
Γ	Smoothing methods 1, 2, and 5	Smoothing methods 3 and 4
0.013	−0.1	−0.2
0.102	−0.5	−0.9
1.02	−2.1	−1.5
10.2	−14	−0.5

Thus, the sine averaging smoothing procedures, 3 and 4, gave the best overall results, even at high Γ values. However, below $\Gamma = 1.0$, the results of all smoothing methods were comparable. Of the three minimization procedures, the sum of meniscus height differences, $(\mathrm{SUM})_S$, produced the best results.

When actual experimental menisci were run, the utilization of all five smoothing methods with the three computation techniques was found to give a better estimate of the surface tension than any single smoothing method with a single computation procedure. The effect of using the average of all fifteen combinations on the computed menisci is also given in Table 6.* The combined calculation method is summarized in the appendix.*

This combined calculational method gives a number of merit to indicate the degree of distortion on the meniscus and the adequacy of the final surface tension obtained. This number of merit is defined as follows: $(CI_\xi)_{\mathrm{avg}}$ = the overall average 95% confidence interval of the overall surface tension average. This value indicates the variation of γ as a function of ξ.

Results from Use of Procedure on Experimental Menisci

Twenty-one menisci which were analyzed by the meniscus comparison method and reported in references *1* and *2* were reprocessed with the composite procedure outlined above. All but one of these menisci met the minima criteria of the comparison procdure and, as a result, were relatively undistorted. The results from the new computation and the comparison with the old values from the comparison method are presented in Table 7 in the appendix.*

The agreement between the old and new values was very good. A breakdown of the number of menisci with percentage difference between the old and new values is given below:

Range of disagreement	No. of menisci
0 to 2%	5
2 to 5%	9
5 to 8%	4
8 to 16%	3

The percentages of disagreement between the old and new values were averaged to indicate if there existed any significant bias between the methods. The average was −1.70%, with a 95% confidence interval of ±3.30%. Since the confidence interval easily included 0%, there was no significant bias between the new and old calculational methods, at least in the Γ range of 0.06 to 0.6.

* See footnote on p. 788.

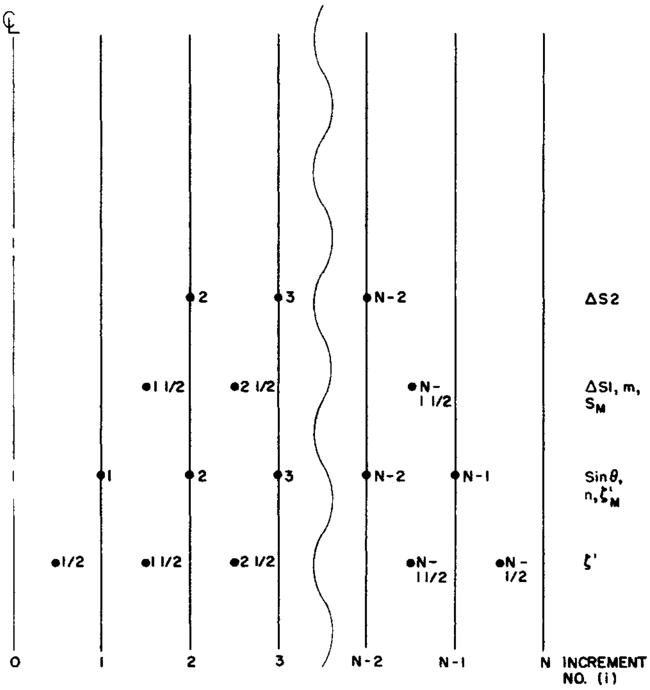

Fig. 5. Grid used in computations.

Use of Numbers of Merit

The confidence interval $(CI_\xi)_{\mathrm{avg}}$ gave a good indication of the accuracy of the average surface tension values and the degree of distortion in the meniscus. Certain limits on the confidence interval appeared to be correlated with the degree of disagreement between the new and old calculations. A listing of these limits and the degree of disagreement are presented below:

Limit on $(CI_\xi)_{\mathrm{avg}}$ %	No. of menisci in range of disagreement between old and new values: 0 to 2%	2 to 5%	5 to 8%	8 to 16%
0 to 7.6	4	0	0	0
7.6 to 11.0	1	2	1	
11.0 to 13.0	0	3	3	1
13.0 to 20.0	0	1	0	2
20.0 to 30.0	0	2	1	0

Bias in Smoothing Methods

The calculations on the twenty-one menisci also indicated whether or not the smoothing methods produced a bias in the surface tension when actual experimental menisci were used. For each smoothed meniscus, calculations with $\Gamma(\zeta')$, $\Gamma(S)$, and $\Gamma(\Delta S1)$ were made. The values were compared with the overall average produced by all smoothing and calculational methods. The results indicate that methods 1 and 2 are biased high, method 3 is unbiased, and methods 4 and 5 biased low. Also, if the meniscus is very well formed, all of the smoothing methods fall within an acceptable range. These data show that if one smoothing method should be chosen for this range of Γ (0.06 to 0.6), that method should be number 3.

Bias of Calculational Methods

The experimental meniscus calculations were analyzed to indicate any bias that might exist in the three calculational methods. In this case, the acceptable range of ±3% of the overall average was established. The average surface tensions from the three calculation methods were then compared with this range. This comparison showed that the $\Gamma(\zeta')$ method was unbiased, while $\Gamma(S)$ was biased slightly low and $\Gamma(\Delta S1)$ biased high. If the meniscus was well formed, all three calculations gave nearly the same result.

SUMMARY AND CONCLUSIONS

By expressing the meniscus heights, $\zeta'_{i-1/2}$ and the meniscus $\sin\theta_i$ values as simple experimental functions of ξ, a new calculational procedure for determining surface tensions from menisci has been developed. Three separate equations for calculating the surface tensions as a function of ξ were generated. Also, to use the equations on actual experimental menisci, five meniscus smoothing methods were produced. The overall procedure which combined the three calculation methods and five smoothing techniques was tested on both experimental and calculated menisci. The results from the procedure when used on calculated menisci agreed within 1.5% with the original surface tension used to generate the meniscus for Γ values below 1.0. The agreement from experimental menisci with this method and the comparison method previously reported (*1, 2*) was within ±8% in general and less than ±2% for the best formed menisci.

The data from experimental menisci indicated that one meniscus smoothing method and one computational equation were superior to the other methods and equations tested. The best smoothing technique was method No. 3 in which the exponents $m_{i+1/2}$ from the $\sin\theta$ exponential equations were averaged in groups of three. The best computational equation which showed no bias with either computed or experimental menisci was $\Gamma(\zeta')$ which was generated by substituting $\sin\theta = S_M \xi^m$ into the Laplace-Young equation.

As indicated above, the new calculational procedure produced results which were as accurate as those generated by meniscus comparison methods. Also, both of these methods generated parameters in the calculations or in the comparison which indicated whether or not a meniscus was possibly distorted. However, the big advantages of the new procedure were that the computer time to generate a surface tension value was small, and no manual graphing and data interpretation were necessary. The total procedure involving the five smoothing methods and three computing techniques required above 0.3 min. of time/meniscus, while the comparison method required up to 20 min. if the comparison menisci had to be calculated. When only smoothing method No. 3 and equation $\Gamma(\zeta')$ were utilized, the computational time was approximately 0.02 min.

In addition to the time advantage in calculating surface tensions, this method of expressing local segments of the meniscus as exponential functions of radial position has indicated some interesting and useful characteristics of menisci. For instance, $\sin\theta$ is approximately a linear function of radial position for menisci formed in small capillaries. Therefore, the contact angle of the edge of the capillary can be determined by a linear extrapolation of $\sin\theta$ data from a photographed meniscus, if a distortion free photograph can be made. For all menisci, n, the meniscus height radial exponent, is greater than or equal to 2.0 and is monotonically increasing with radius. The $\sin\theta$ radial exponent m is greater than or equal to 1.0 and is also monotonically increasing with radius. These properties can be used to check the consistency of experimental meniscus data.

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NOTATION

$(ABSUM)_s$ = sum of absolute values of experimental minus smoothed meniscus heights divided by N
b = exponent for adjusting ζ_0 by Equation (18)
CI_ξ = 95% confidence interval of the average of surface tensions determined as a function of ξ across the meniscus
$(CI_\xi)_{avg}$ = average of the 15 CI_ξ from the five smoothed menisci and the three computational methods
g = acceleration due to gravity, cm./sec.^{2}
i = radial increment index number
k = iteration number
m = exponent used in Equation (6) which expresses $\sin\theta$ as a function of ξ
n = exponent used in Equation (1) which expresses ζ as a function of ξ
N = total number of radial increments
r = distance from centerline to any radial position, cm.
r_0 = radius of tube, cm.
S_M = parameter used in Equation (6) which expresses $\sin\theta$ as a function of ξ
S_R = $\sin\theta$ at wall of tube
$(SUM)_s$ = sum of experimental meniscus heights minus smoothed meniscus heights divided by N
SD_s = standard deviation of experimental minus smoothed meniscus heights
z = height of meniscus above datum plane, cm.
z' = height of meniscus above plane tangent to base of meniscus
z_0 = height of meniscus above datum plane at center of cylinder, cm.

Greek Letters

β = dimensionless radius of circular curve approximating the meniscus in a capillary
γ = surface tension, dynes/cm.
Γ = dimensionless surface tension, $\gamma/[(\rho_1 - \rho_2)g r_0^2]$
$\Gamma(S)$ = dimensionless surface tension calculated from $\sin\theta$, Equation (14)
$\Gamma(\Delta S1)$ = dimensionless surface tension calculated from first sine difference equation, Equation (15)
$\Gamma(\Delta S2)$ = dimensionless surface tension calculated from second sine difference equation, Equation (16)
$\Gamma(\zeta')$ = dimensionless surface tension calculated from meniscus heights, Equation (17)
$\Delta S1_{i+1/2}$ = first sine difference, $\Delta S1_{i+1/2} = \sin\theta_{i+1} - \sin\theta_i$
$\Delta S2_i$ = second sine difference, $\Delta S2_i = \Delta S_{i+1/2} - \Delta S1_{i-1/2}$
ζ = dimensionless height of meniscus above the datum plane, z/r_0
ζ_0 = dimensionless height of meniscus at center line of cylinder, z_0/r_0
ζ' = dimensionless height of meniscus above horizontal plane tangent to base of the meniscus, z'/r_0
ζ_M' = parameter used in Equation (1) which expresses ζ as a function of ξ
θ = angle between horizontal and tangent to meniscus curve at any position ξ
ξ = dimensionless radius, r/r_0
ρ_1 = density of more dense fluid, g./cc.
ρ_2 = density of less dense fluid, g./cc.
χ = dimensionless vertical distance, $\beta - \zeta'$

LITERATURE CITED

1. Biery, J. C., and J. M. Oblak, *Ind. Eng. Chem. Fundamentals*, 5, 121-128 (1966).
2. Biery, J. C., *J. Electrochem. Soc.*, 114, 225-231 (Mar., 1967).

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