= space time

Subscripts

= final conditions

= component of vector

= initial conditions

= optimum

Superscripts

= iteration number

= transposition operator

= rough estimate

(0)= initial estimate

LITERATURE CITED

1. Denn, M. M., and Rutherford Aris, AIChE J., 4, 7 (1965).

 Horn, F., Chem. Eng. Sci., 14, 77 (1961).
 Aris, Rutherford, "The Optimal Design of Chemical Reactors; A Study in Dynamic Programming," Academic Press, New York, (1961).

4. Lapidus, Leon, and Rein Luus, "Optimal Control of Engineering Processes," Ginn-Blaisdell, Waltham, Mass.

5. Pontryagin, L. S., V. G. Boltyanskii, R. V. Gamkrelidze, and E. F. Mischenko, "The Mathematical Theory of Optimal Processes" (English translation by K. N. Trirogoff), Interscience, New York (1962).
6. Fan, L. T., "The Continuous Maximum Principle; a Study

of Complex Systems Optimization," Wiley, New York

(1966).

7. Schechter, R. S., "The Variational Method in Engineering," McGraw-Hill, New York (1967).

8. Lee, E. S., "Quasilinearization and Invariant Imbedding," Academic Press, New York (1968).

9. Washburn, E. W., ed., "International Critical Tables," Vol. VII, McGraw-Hill, New York (1930).

10. Frost, A. A., and R. G. Pearson, "Kinetics and Mechanism; A Study of Homogeneous Chemical Reactions," Wiley, New York (1961)

11. Jaspan, R. K., Ph.D. dissertation, Univ. Pittsburgh, Pa. (1969).

 Crane, R. L., and R. W. Klopfenstein, J. Assoc. Comp. Mach., 12, 227 (1965).
 Szabo, Z. G., "Advances in the Kinetics of Homogeneous Gas Reactions" (translated by K. J. Ivin), Methuen, London (1964).

14. Fine, F. A., and S. G. Bankoff, Ind. Eng. Chem. Fundamentals, 6, 288, (1967).

15. Padmanabhan, L., and S. G. Bankoff, Intern. J. Control, 9,

-, J. Opt. Theory and Appl., in press.

17. Kliesch, H. C., Ph.D. dissertations, Tulane Univ., New Orleans, La. (1967).

18. Lapidus, Leon, "Digital Computation for Chemical Engineers," McGraw-Hill, New York (1962).

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Liquid Bridges Between Cylinders, in a Torus, and Between Spheres

MICHAEL A. ERLE, D. C. DYSON

Rice University, Houston, Texas

and NORMAN R. MORROW

Esso Production Research Company, Houston, Texas

The stability of a capillary liquid bridge of given volume between two small, solid, equal, separated spheres is investigated by formulating and treating a minimum energy problem in the calculus of variations and by experiment. A conjecture is made that in the case of two solutions one and only one is minimizing, and that the case of one solution represents the limiting stable bridge. This theory agrees accurately with our stability experiments. Furthermore, it is possible to predict the cohesive force. For the case of spheres in contact, the theory presented here is in agreement with some experimental work and also with the theory of Fisher and calculations of cohesive force based on Melrose and Wallick's solution to the bridge problem. For the case of separated spheres, the agreement with the only available experimental data is excellent except for close separations.

Recently there has been a revival of interest in the classical problems (4, 17) concerning the configuration of a mass of liquid which bridges a gap between solid surfaces, being supported by capillary attraction. These liquid bridges are concepts in theories of oil recovery from porous media, adsorption hysteresis in porous adsorbents (7), capillary condensation (13), particle sedimentation (18), soil properties (10), and space exploration. At the present time very few exact solutions to liquid bridge problems

have been obtained; for example, the cylinder between flat plates (1).

One system which has received considerable attention is that of two solid spheres, either in contact or slightly separated with a liquid bridge held between them by capillary attraction, under conditions where gravitational forces may be ignored. The force required to hold the spheres apart has been measured by Mason and Clark (13) as a function of separation, from contact until breakage of the liquid bridge. When the separation of the spheres is increased slowly, the meniscus displaces until a certain critical bridge configuration is attained, at which stage the bridge becomes unstable and snaps.

The neck diameter of this critical bridge is unquestion-

M. A. Erle is deceased.

N. R. Morrow is with the Petroleum Recovery Research Institute, University of Calgary, Alberta, Canada.

ably greater than zero. We have determined experimentally the relation between the sphere separation and the minimum neck diameter and have developed a theory. The theory is at the moment incomplete; however, by adding to it a plausible conjecture, we have been able to explain adequately both our experimental observations and those of Mason and Clark (13) for large separations. The particular case of spheres in contact has been treated before. In this case our results agree with the work of Fisher (9) and of Melrose and Wallick (15).

There is a strong resemblance between our theory for bridges between spheres and the complete theory which has been worked out for bridges between two flat, round plates by Beer (2), Howe (12), and Hormann (11). In Howe's work the analog of our conjecture is the conjugate point criterion of the variational calculus.

We will also present the corresponding theory for a solid torus with a liquid in its hole and for two infinite separated solid cylinders with parallel axes. In these cases the theory is complete and in the case of the torus in agreement with experiments made by Plateau (4) and confirmed by our observations.

THEORY

We will discuss the problems in increasing order of difficulty. In all cases we ignore gravity and other body forces; use a continuum theory; and assume constant temperature, interfacial tensions, and densities of the fluids and solids. The surface tension becomes appreciably curvature dependent for pure substances only when radii of curvature approach molecular distances (16) when the continuum hypothesis also starts to fail. We are concerned with distances intermediate between these and those for which gravitational effects need consideration. Our main interest will be in the zero contact angle but we will remark in passing on cases of nonzero contact angle. The method employed is to formulate a problem of minimization of an energy integral, subject to the isoperimetric constraint of constant fluid mass, whose Euler-Lagrange equation is the static force balance equation and whose transversality conditions are equivalent to the contact angle statement.

If one is not interested in carrying the analysis beyond this, that is, beyond the theory of the first variation, then this energy approach has no advantage over the commonly used approach (9, 14, 18) which starts from the force balance, contact angle statements, except that a physical basis is provided for the contact angle (5). The force balance equations are equivalent to the statement that the interface be a surface of constant mean curvature. Now, Plateau (4, 17) pointed out long ago that all stable liquid bridges are surfaces of constant mean curvature (with the possible exception of extremely thin films), but that there exist surfaces of constant mean curvature, the form of which cannot be taken by the interfaces of any stable liquid bridge. In other words, if a liquid bridge of such a type is set up, then, although its surface is such that it satisfies the static force balance equation and the contact angle is correct, it will spontaneously transform into another figure; for example, a cylinder whose length/diameter ratio exceeds π between fixed circular end plates will break up (1, 4, 17).

It seems reasonable to suppose, then, that unless the energy integral is actually a local minimum (subject to the isoperimetric constraint) for a given surface, this surface cannot correspond to the interface of a stable liquid bridge.

For infinite cylinders and for the torus we will find bridging surfaces which truly satisfy all requirements of

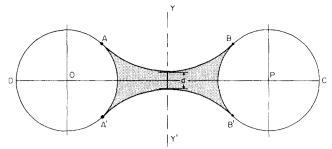


Fig. 1. Section through liquid bridge between infinite cylinders or in the hole of a torus. The shaded part is the liquid.

the minimization problem (at any rate on the basis of certain symmetry assumptions). The case of the two spheres is much more difficult. We will consider the totality of extremals (that is, integrals of the Euler-Lagrange equations) and show that for given sphere radii, separation, and bridge volume there are either two extremals, one extremal, or no extremals. Experiment supports the conjecture that in the case where there are two, one and only one is minimizing, and that in general the cases where there is only one represent the limits of stability.

We have assumed that the liquid density is constant so that the isoperimetric constraint becomes a constant liquid volume constraint. For the systems we have in mind this is very reasonable, although there are situations of physical importance where such an assumption would be invalid (14).

Two Infinite Separated Cylinders

We will assume that the liquid bridge is cylindrical, that is, its intersection with any plane normal to the axes of the solid cylinders will always be the same (curves AB, A'B', Figure 1). Now we are considering a liquid-solid system such that a drop of liquid placed on a solid surface will spread all over the surface. The continuum hypothesis implies that this will be the case, however small the drop or large the surface. Suppose we have a liquid bridging the gap, as shown in Figure 1. Then the entire surfaces of the cylinders will be covered, although to the left of AA' or to the right of BB' the covering will be taken to have zero thickness. The question to be resolved is: "What is the shape of the curve AB'?" We will assume also that the curve A'B' is the mirror image of AB in OP.

Because of our assumption about the cylindrical shape of the liquid bridge, we may conclude that the curve AB must have such shape that the total surface energy per unit length (perpendicular to the paper) is a local minimum subject to the constraint that the bridge area (shaded region) is constant. We will solve this minimum problem by finding the global minimum. The global minimum is certainly a local minimum, and in this case there are no other local minima.

Because the solid surfaces are everywhere in contact with liquid (even though the liquid thickness is arbitrarily small in some places), the surface energy per unit length of the liquid-solid interface may be ignored. The energy to be minimized then is the liquid-gas surface energy per unit length which is proportional to the length of the curve DABCB'A'D. If this is minimum, then certainly it must be minimum within the class of variations which leave invariant the points of attachment AB and A'B'. This is then equivalent to asking for the curve AB of minimum length which encloses given area (see Figure 2) (suppose this area is a) together with the chord. We will show that this curve AB must be the arc of some circle. Complete

the circle as shown; then this circle is well known to have the shortest perimeter possible for a curve enclosing the area A+a. Hence the assertion is correct because otherwise you could improve on the circle by altering the lower curve. It can also be shown that this minimization requires that the bridge must meet the solids with zero contact angle and that a bridge for which AB, A'B' are arcs of a circle and for which the contact angle is zero does have minimum energy/unit length. Furthermore, the surface satisfies the force balance as a requirement of the minimization problem.

The reader will note that the above proof merely requires that there be sufficient area for the distance d in Figure 1 to be greater than zero. In other words, there will exist stable bridges with arbitrarily small necks, in contrast to the case of two spheres.

Torus

In this case we assume symmetry of the bridge about the axis YY' of the torus Figure 1. The surface generated by revolution of the curve DABCB'A'D about YY' must be a local minimum subject to its volume of revolution being fixed.

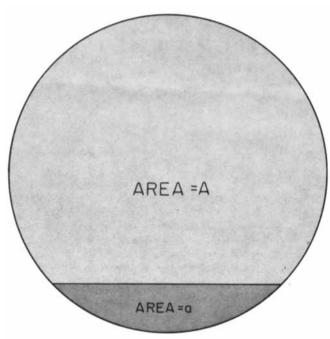


Fig. 2. Diagram to illustrate minimizing property of a segment of a

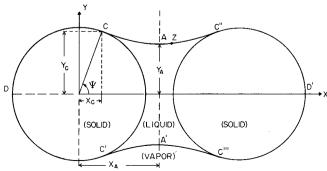


Fig. 3. Symmetrical liquid bridge between equal solid spheres with zero contact angle.

As with the case of two cylinders we will find the global minimum; it is easily shown that the surfaces AB, A'B' must be spherical. (The theorem we need is that the sphere has minimum surface area of all surfaces which enclose a given volume.) It can also be shown in this case that in order for the surface of revolution to have minimum area, the contact angle must be zero, and that the above conditions are sufficient as well as necessary, that is, spheres with zero contact angle minimize the energy.

Once more, in contrast to the case of the liquid bridge between spheres we have stability for all positive *d*, however small. One may treat the case of a nonzero contact angle by formulating a slightly different minimum problem. As the reader might expect, it turns out in this case that the liquid-air surfaces are spherical caps; for the two cylinders discussed above one also gets circular arcs.

Two Equal Spheres

The Variational Problem. Consider two spheres of radius R. Define dimensionless distances

$$X = x/R$$
 and $Y = y/R$ (1)

Figure 3 represents the two spheres joined by a bridge, the surface of which is assumed to be generated by the revolution of arc CAC'' about the axis DD'. For this case in which the liquid wets the entire solid surfaces, we must find for what values of X_A and V there exists an arc CAC'' which generates a surface of revolution whose area Q is locally minimum and which, together with the spherical surfaces, encloses the liquid volume $2\pi R^3 V$. In terms of dimensionless quantities this is equivalent to a minimization problem for the integral (2) subject to the integral constraint (3).

$$S = Q/4\pi R^2 = \frac{1}{2} \int_{X_D}^{X_{D'}} Y \sqrt{1 + Y^2} dX \qquad (2)$$

$$V = \text{liquid bridge volume}/2\pi R^3 = \frac{1}{2} \int_{X_D}^{X_{D'}} \Upsilon^2 dX - 4/3$$
(3)

where we use \dot{Y} to represent the derivative of Y with respect to X.

If Y(X) is minimizing then the first variation of the integral (2) must vanish for all variations which do not alter the integral (3). Because the spheres are equal this means that the liquid bridge will be symmetric about the plane AA' in Figure 3, so an equivalent condition is that the first variation of the integral

$$K = \int_{X_C}^{X_A} \left[Y \sqrt{1 + \dot{Y}^2} + \frac{\lambda}{2} R Y^2 \right] dX$$

$$+ X_C + \frac{\lambda R}{2} (X_C - X_C^3/3 - 2/3) \quad (4)$$

vanish. λ is a Lagrange multiplier. It may be shown that this requires that the bridge meets the sphere at C with zero contact angle, the slope of CA is zero at A, and the Euler-Lagrange equation is satisfied by Y(X). Because the integral in Equation (4) does not depend explicitly on X, this latter equation has an integral:

$$\frac{2Y}{\sqrt{1+\dot{Y}^2}} + \lambda R Y^2 = B \tag{5}$$

There are two other properties of the minimizing function Y(X): it satisfies the Weierstrass necessary condition and

the condition that the second variation be non-negative. The former is the same for this problem as for the case where spheres are replaced by parallel coaxial end plates, and has been shown by Howe and Hormann to be satisfied by all extremals so it provides no stability criterion. The condition on the sign of the second variation was shown by Howe to give the stability result for the flat end plate problem, and also to have a geometrical interpretation. For the sphere problem the second variation criterion has not yet been resolved. However there is experimental evidence that supports a geometrical criterion to be discussed later, which is analogous to Howe's.

The Mechanical Problem. We now make a force balance on an element of the bridge and show that this leads to a differential equation equivalent to Equation (5). In this way we are able to identify the constants λ and B of Equation (5) with physical quantities.

Consider two planes perpendicular to DD' in Figure 3 cutting the bridge at Z and A. Then if the forces acting on the resulting bridge segment in the X direction are put in balance, the following equation is obtained:

$$\frac{2Y}{\sqrt{(1+\dot{Y}^2)}} + \frac{R(P_2 - P_1)}{\gamma} Y^2 = \frac{R(P_2 - P_1)}{\gamma} Y_A^2 + 2Y_A$$
(6)

Now employ the equation for mechanical equilibrium at the meniscus (8)

$$\frac{(P_2 - P_1)}{\gamma} = J \tag{7}$$

where J is the mean curvature at the surface and is defined in terms of the principal radii of curvature r_1 and r_2 by the relation

$$J = \frac{1}{r_1} + \frac{1}{r_2} \tag{8}$$

[Equation (7) can also be derived without explicit recourse to thermodynamics by differentiating Equation (6) with respect to X, and thus obtaining an equation in which $(P_2 - P_1)/\gamma$ equals the sum of two terms well known as the principal curvatures of a surface of revolution (14).]

Equations (5) and (6) both describe the arc CA. Comparing these equations and using Equation (7), we obtain

$$\lambda = J$$

and

$$B = JR Y_A^2 + 2Y_A \tag{9}$$

Evaluating Equation (5) at C (recalling that the contact angle is zero) and using Equation (9), we obtain

$$B = (2 + JR) Y_C^2 (10)$$

Now, if we calculate the cohesive force acting on one of the spheres (surface tension plus pressure difference) we see that it is just $\pi R \gamma B$. We define the dimensionless cohesive force F by F = B/2.

Numerical Integration of the Euler-Lagrange Equation. It can be shown (3) that all integrals of the Euler-Lagrange equation satisfy Equation (5) and all integrals of Equation (5), other than Y = const., satisfy the Euler-Lagrange equations. Numerical integration of Equation (5) starting from the point X_A , Y_A is to be avoided, because at that point the Lipschitz condition is not satisfied and for all values of JR the equation is satisfied by Y = const., which of course only satisfies the Euler-Lagrange equation for $JR = -1/Y_A$. For this reason we express B in terms of Y_C by use of (10), substitute in (5), and solve for \dot{Y} , obtaining

$$\dot{Y} = -\sqrt{\frac{4Y^2}{\{(2+JR)Y_{c^2} - JRY^2\}^2} - 1}$$
 (11)

This form of the first integral of the Euler-Lagrange equation is integrated for chosen values of JR and ψ . Boundary conditions at C are specified by ψ because $Y_C = \sin \psi$ and $X_C = \cos \psi$ (see Figure 3). Integration is stopped when the boundary condition at A is met, that is, $\dot{Y} = 0$. A predictor-corrector integration scheme is used employing Euler's method as the predictor and the trapezoidal rule as the corrector. Along with X_A and Y_A , the quantities V and S were computed for each integration. The following checks were made on the integration procedures:

- 1. Independent calculations were made of Melrose and Wallick's (15) solutions for spheres in contact (see Figure 4).
- 2. When J=0 the bridge becomes a catenoid, and its equation is readily found in closed form (see Appendix), so that the numerical results can be compared with analytical results in this case.
- 3. The behavior of the numerical solution was studied as a function of step size to determine the stability of the method over the range of JR and ψ considered in this study.
- 4. Expressions for bridge parameters in terms of elliptic integrals were obtained using a transformation first given by Woodrow, Chilton, and Hawes (18). The case of an arbitrary contact angle is treated; for formulas see the Appendix. Bridge parameters calculated in this way agreed well with those calculated using the numerical integration scheme discussed above.

From these tests we conclude that the results of the numerical procedure (expressed in terms of $X_A - X_C$) are not in error by more than four parts in 10,000.

DISCUSSION

Torus

Plateau (4) performed experiments with a liquid mass removed from the influence of gravity and placed inside a short, hollow, circular cylinder. He found that the two free liquid surfaces took the shape of twin spherical concavities. When sufficient liquid was withdrawn from this mass the spherical surfaces almost touched. Further withdrawal of liquid resulted in the formation of a thin flat film where the two free surfaces came closest together. Plateau pointed out that this figure no longer had the property of constant mean curvature over its entire surface. (Whether this is due to nontrivial flow fields is not known.) We have observed the behavior of a drop of acetone placed in the hole of a small wire torus. As the bridge volume is reduced by evaporation, one observes similar phenomena to those reported by Plateau. The central flat film gets thin enough for interference colors to be observed in it (when illuminated by white light). Thus stable bridges exist in the hole of a torus with extremely small neck thicknesses in accordance with our theory.

Dichotomy of Solutions for Bridges Between Spheres

In order to calculate the equation for the curve describing a liquid bridge given the sphere radius, the separation, and the liquid volume, we first compute a map of solutions to the Euler-Lagrange equation for a rectangular grid of values of IR and ψ . Values of IR between -2 and +23 (in increments of 0.2) and values of ψ between 0 and 90 deg. (in increments of 5 deg.) were used. The lower limit of IR is a natural boundary, because for IR = -2 the solution to the Euler-Lagrange equation is a sphere of radius

R (that is, the bridge degenerates to two films, one attached to each sphere) and for smaller values of the curvature the (zero contact angle) solutions lie inside the solid spheres.

By means of interpolation and classification we develop from the grid of solutions subsets of solutions whose elements all have the same volume and other subsets whose elements all have the same separation. Some of this information is presented in Figure 4 in which these subsets are labeled curves of constant volume and constant separation, respectively. Now, when we try to locate a solution having a volume of, say 0.005, and a separation specified by $X_A = 1.15$, we find by looking at the map that there are two distinct solutions (Figures 4 and 5). For other values of the parameters such as V = 0.001 and $X_A = 1.10$ we see that there are no solutions.

Suppose now we consider the separations of bridges along a curve of constant volume. There will be one solution on this curve which has greater separation than any other solution. If we call this separation X_{max} , then this solution of maximum separation is located at the point of tangency of the constant volume curve with the curve of constant separation corresponding to $X_A = X_{\text{max}}$. By considering all constant volume and constant separation curves we define a locus of tangency which is plotted approximately in Figure 4. We have plotted this line by drawing a curve through all the points of greatest separation on the constant volume curves (which are also points of least volume on some constant separation curve). Note that all solutions lying on the locus of tangency are unique, and that if two distinct solutions have identical volume and separation one must lie to the right of the locus of tangency and one to the left.

We have not yet established the subset of solutions to the Euler-Lagrange equation whose elements represent physically observable liquid bridges. However, in the discussion of experiments performed on liquid bridges a plausible criterion will suggest itself for the elimination of some of the solutions.

EXPERIMENTS WITH SPHERES

The minimum stable neck diameter of a liquid bridge between two spheres was measured for various sphere separations. Two chrome-steel ball bearings of 4.775 mm. diam. were selected for roundness and cleaned with acetone. The spheres were seated over 2.5-mm. diameter holes drilled in a Lucite plate. The holes were spaced so that

the distance of separation between the spheres could be changed by increments of about 0.05 mm. With the two spheres in a set position, a drop of n-heptane was introduced to form a liquid bridge between the spheres. The heptane spread on the steel surface to give zero contact angle. For wider sphere separations, the liquid bridges were formed by introducing the liquid with the spheres touching and then moving the spheres apart until seated.

The volume of heptane in the bridge decreased by evaporation into the surrounding air until the bridge ruptured. The evaporation was held at a rate convenient for observation purposes by partially enclosing the liquid bridge assembly in a Lucite box containing a few drops of heptane. The observation period prior to rupture usually ran from 1 to 5 min. The position of one side of the heptane-air interface was followed at the thinnest part of the bridge (that is, the neck) with the crosshairs of a traveling microscope.

Instability was indicated by a rapid acceleration of the interface. Consecutive frames of a high-speed movie showed that the interface velocity changed from a few millimeters per minute just before rupture to at least 20,000 mm./min. at rupture. The position of the interface with respect to the spheres at the onset of instability gave the minimum stable neck diameter. The distance of separation between the spheres was measured accurately with the traveling microscope. Reproducibility was usually within \pm 0.01 mm. A plot of distance of separation versus neck diameter is shown in Figure 6.

In the model study it was assumed that the liquid bridge had perfect symmetry. When the liquid bridges were viewed in the vertical plane with a cathetometer, it appeared that distortion of the bridge due to gravity would have only a minor effect on the experimental results, except perhaps for wider separations where the weight of liquid forming the bridge is relatively high.

Because the bridge volume was decreased by evaporation, the temperature of the liquid bridge must have been slowly decreasing throughout the experiment. If the heptane held any small dust particles, these showed quite clearly the convection currents set up by the evaporative cooling. The convection served to keep the temperature uniform throughout the bridge. According to theory, the bridge shape and the limiting configuration of the bridge should, of course, be independent of temperature. Since the point of rupture, as indicated by a rapid inward acceleration of the interface, was distinct and reproducible, it seems safe to assume that the experimental results cor-

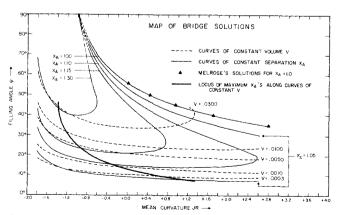


Fig. 4. Curves of constant volume, or constant separation in the filling angle mean curvature plane. The heavy line is the locus of points of contact of curves of the two families.

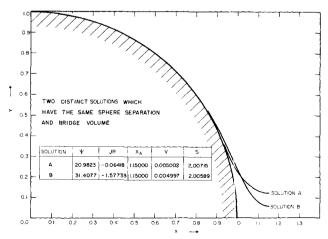


Fig. 5. Examples of dichotomy of solutions: solution A is stable, solution B is not.

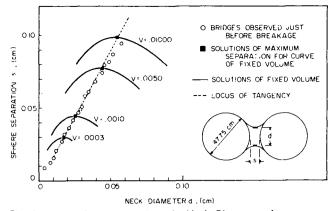


Fig. 6. Curves of constant volume in Neck Diameter sphere separation plane. The maxima (squares) correspond to the limit of stability shown by the broken line. Experimental determination of limiting stable neck diameter for various separations are plotted as circles.

responded very closely to those that would be given by reversibly varying the liquid volume down to its limiting stable configuration.

INTERPRETATION OF EXPERIMENTS ON SPHERES: BASIS FOR CONJECTURE

The neck diameter and sphere separation have been evaluated for points on constant volume curves in Figure 4. These are plotted in Figure 6. The locus of maxima of the constant volume curves (in Figure 6) is indicated by the broken lines labeled "locus of tangency" because it corresponds to the locus of tangency in Figure 4.

The circles in Figure 6 arise from the experiments on stability described above. The locus of tangency (developed by theory alone) can be seen to fit these circles very well, except for large bridge volumes where the slight disagreement could be put down to gravitational effects. This could easily be tested, for example, by experimenting with spheres of smaller diameter.

We will conjecture at this stage that the locus of tangency divides Figures 4 and 6 into two parts such that points on the right-hand side (and only on the right-hand side) of the locus correspond to physically realizable bridges. [In general, a point (JR, ψ) specifies a bridge completely and, in particular, determines the volume and the separation. However, the point (-1, 90 deg.) is exceptional since all cylindrical bridges with zero contact angle correspond to this point, whatever the separation.] This conjecture has experimental support from both our work and that of Mason and Clark, which we will now discuss.

Mason and Clark (13) have conducted somewhat different experiments in which the cohesive force of liquid bridges was measured for a constant volume of liquid while the spheres were pulled apart from zero separation to a separation sufficient to break the bridge. In Figure 7 their experimental force versus separation curves (broken lines) are compared with curves constructed by evaluating the cohesive force and separation according to our theory for points along constant volume curves (to the right of the locus of tangency) in Figure 4. Force curves constructed by evaluating force and separation of points to the left of the locus of tangency do not agree with Mason and Clark's data.

Near the point of breakage the force versus separation curves are quite similar for the experimental bridges and our theoretical bridges having nearly the same volume. For small separations the agreement is not so good. We feel that this is due to experimental difficulties, because

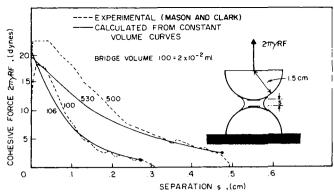


Fig. 7. Separation versus cohesive force for bridges with volumes shown: the full lines are calculated according to our theory with the right hand end points (large dots) representing the limiting stable bridges. The broken lines are taken from Mason and Clark (13).

Mason and Clark's (13) data for the limiting case of zero separation differ significantly from the experimental data of Cross and Picknett (6), which not only agree with our results but also with the forces calculated from the parameters given by Fisher (9) and by Melrose and Wallick (15).

It seems likely that our conjecture will turn out to be equivalent to the requirement that the second variation of the integral (2) be non-negative for all variations which leave the integral (3) invariant, at any rate over the portion of Figure 4 corresponding to the experiments described above; this conjecture is precisely analogous to the geometrical criterion shown by Howe to provide necessary and sufficient conditions for an extremal to be minimizing for the problem of the finding the curve which generates simultaneously minimum area of revolution and a given volume of revolution.

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NOTATION

3 = integration constant equal to twice the dimensionless cohesive force

e thickness of the thinnest part of a bridge between cylinders or in a torus

 $E(k, \theta)$ = Lagrange's elliptic integral of the second kind

F = dimensionless cohesive force $F(k, \theta)$ = Lagrange's elliptic integral of the first kind

JR = dimensionless mean curvature

K = functional representing surface energy of a bridge

 P_1 = pressure inside the bridge P_2 = pressure outside the bridge

 $Q = \frac{1}{\text{surface area of liquid-vapor interface}}$

 \tilde{R} = sphere radius

 $r_1, r_2 = \hat{p}$ rincipal radii of curvature

= dimensionless surface area of liquid-vapor interface

s = separation of two spheres

V = dimensionless liquid volume of bridge

= dimensionless distance along line between centers of spheres

= distance along line between centers of spheres

Y = dimensionless radial distance from axis of revolu-

y = radial distance from axis of revolution

Greek Letters

X

 $\gamma = surface tension$

= contact angle

= Lagrange multiplier equal to JR λ

= ratio of circumference to diameter of a circle π

= filling angle

= (area of revolution of the curve CAC" about the Σ. axis DD')/ $4\pi R^2$. See Figure 3.

LITERATURE CITED

1. Almansi, E., Ann. Matematica Ser. 3, 12, 1-17 (1905).

Beer, A., Dissertation, Bonn (1857).
 Bolza, O., "Lectures on the Calculus of Variations,"

Dover, New York (1961).

4. Plateau, J. A. F., "Experimental and Theoretical Researches"." on the Figures of Equilibrium of a Liquid Mass. translation in Ann. Rept. Smithsonian Institution (1863-1866).

5. Collins, R. E., and C. E. Cooke, Trans. Faraday Soc., 55, 1602 (1959).

 Cross, N. L., and R. G. Picknett, "International Conference on Mechanism of Corrosion by Fuel Impurities," Marchwood Eng. Lab., England (1963).
7. Everett, D. H., in "The Solid-Gas Interface," E. A. Flood,

ed., Marcel Dekker, New York (1967).
Denbigh, K. G., "The Principles of Chemical Equilibrium,"
Cambridge Univ. Press (1964).

9. Fisher, R. A., J. Agr. Sci., 16, 492 (1926).

10. Haines, W. B., ibid., 20, 97 (1930).

11. Hormann, G., Dissertation, Göttingen (1887).

12. Howe, W., Dissertation, Berlin (1887).

13. Mason, G., and W. C. Clark, Chem. Eng. Sci., 20, 859

14. Melrose, J. C., AIChE J., 12, 986 (1966). 15. ——, and G. C. Wallick, J. Phys. Chem., 71, 3676 (1967).

16. Melrose, J. C., Ind. Eng. Chem., 60, 53 (1968).
17. Plateau, J. A. F., "Statique experimentale et théorique des liquids soumis aux seules forces moléculaires," Gauthier-

Villars, Paris (1873).

18. Woodrow, J., H. Chilton, and R. I. Hawes, J. Nucl. Energy, Pt. B, Reactor Techn., 1, 229 (1961).

APPENDIX: ANALYTIC SOLUTION TO LIQUID BRIDGE PROBLEM

The following equations are valid for the case

$$\psi + \delta \leq \frac{\pi}{2}$$

Note: The contact angle δ is the positive angle measured from the solid-liquid to the liquid-vapor interface measured through the liquid.

General Formula for the Neck Radius

$$Y_A = \begin{cases} (1/JR) \left\{ \sqrt{1 + JR\sin\psi \left[2\sin(\psi + \delta) + JR\sin\psi \right]} - 1 \right\} : JR \neq 0 \\ \sin\psi\sin(\psi + \delta) : JR = 0 \end{cases}$$

We now consider three cases: (I) JR > 0, the bridge is a nodoid. (II) JR = 0, the bridge is a catenoid. (III) 0 > JR, the bridge is an unduloid.

I. Nodoid

Define

A)
$$\Omega = \pi/2 - (\psi + \delta)$$

B)
$$k = 1/(Y_A J R + 1)$$

$$X_A = \left(\frac{Y_A}{1-k}\right)$$

$$\{k\sin\Omega+(1-k^2)\ F(k,\Omega)-E(k,\Omega)\}+\cos\psi$$

$$\Sigma = \left(\frac{\Upsilon_A}{1-k}\right)^2$$

$$\{2kE(k,\Omega) + k(k^2-1) \ F(k,\Omega) - 2k^2 \sin \Omega\}$$

$$V = \left(\frac{Y_A}{1-k}\right)^3 \left\{ (1-k^2) k \sin \Omega + 4k^3 \left[\sin \Omega - (\sin^3 \Omega)/3 \right] \right.$$
$$\left. - (4/3) \Delta (k, \Omega) k^2 \sin \Omega \cos \Omega - \left[1/3 + (7/3)k^2 \right] \right.$$
$$\left. E(k, \Omega) + (1/3 + 2/3 k^2 - k^4) F(k, \Omega) \right\}$$
$$\left. + \cos \psi - \frac{\cos^3 \psi}{2} - 2/3 \right.$$

where

$$\Delta(k,\Omega) = \sqrt{1 - k^2 \sin^2 \Omega}$$

II. Catenoid In this special case

$$X_A = -\sin\psi\sin(\psi + \delta)\ln\left\{\frac{\sin(\psi + \delta)}{1 + \cos(\psi + \delta)}\right\} + \cos\psi$$

$$\Sigma = -(\frac{1}{2})\sin^2\psi \left\{-\cos(\psi + \delta)\right\}$$

$$+\sin^2\left(\psi+\delta\right)\ln\left[\frac{\sin\left(\psi+\delta\right)}{1+\cos\left(\psi+\delta\right)}\right]$$

$$V = - (\frac{1}{2}) \sin^3 \psi \sin (\psi + \delta) \left\{ -\cos (\psi + \delta) \right\}$$

$$+ \, \sin^2 \left(\psi + \delta \right) \, \ln \left[\frac{\sin \left(\psi + \delta \right)}{1 + \cos \left(\psi + \delta \right)} \right] \bigg\}$$

$$+\cos\psi - (1/3)\cos^3\psi - 2/3$$

III. Unduloid

Define

A)
$$k = -Y_A J R - 1$$

B)
$$\Gamma_1 = \arcsin \left[-\frac{1}{k} \cos \left(\psi + \delta \right) \right];$$

$$0 \le \Gamma_1 \le \pi/2$$

C) $\Gamma_2 = \pi - \Gamma_1$

For

a)
$$- [\sin(\psi + \delta)]/\sin \psi \leq JR < 0$$
 use $i = 1$

b) $JR < -[\sin(\psi + \delta)]/\sin\psi$ use i = 2 in the following formulas

$$X_A = \left(\frac{Y_A}{k+1}\right) \left\{ k \sin \Gamma_i + E(k, \Gamma_i) \right\} + \cos \psi$$
$$\Sigma = \left(\frac{Y_A}{k+1}\right)^2$$

$$\frac{\sqrt{y+\delta} + \beta + JR\sin\psi}{\left\{2K\sin\Gamma_{i} + 2E\left(k,\Gamma_{i}\right) + (k^{2} - 1)F(k,\Gamma_{i})\right\}}$$

$$V = \left(\frac{\gamma_{A}}{k+1}\right)^{3}$$

$$\left\{-(4/3)(1-k^{2})F(k,\Gamma_{i}) + (7/3 + (1/3)k^{2})E(k,\Gamma_{i}) + (k^{3} + 3k)\sin\Gamma_{i} + (4/3)k^{2}\Delta(k,\Gamma_{i})\sin\Gamma_{i}\cos\Gamma_{i} - (4/3)k^{3}\sin^{3}\Gamma_{i}\right\} + \cos\psi - \frac{\cos^{3}\psi}{3} - 2/3$$
where

where

$$\Delta (k, \Gamma_i) = \sqrt{1 - k^2 \sin^2 \Gamma_i}$$

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