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THE USE OF DELAUNAY CURVES FOR THE WETTING OF AXISYMMETRIC BODIES

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Abstract. The wetting of a given solid figure is of importance in many fields of science ranging from physics and materials science to geology and medicine. An important special case that is generic to many situations is the wetting of an axisymmetric solid by a liquid of the same material. This problem is equivalent to minimizing the total surface area of the condensed phase (liquid + solid). Its solution is a mosaic of wet and dry regions on the solid. The shape of the wet regions is described by Delaunay curves. The analytic properties of these curves are discussed, and the wetting of several interesting solid configurations is presented.

I. Introduction. The phenomenon of wetting a given solid has important applications in many fields of science [1], including the sintering of powders in materials science [2], the wetting of porous media in hydrology and geology [3], the formation of hailstones in meteorology, and the transport of liquids on irregular and heterogeneous surfaces in engineering and medicine. The description of the wetted solid requires finding the solid-liquid configuration that minimizes the total free energy. However, the determination of the exact shape of the optimal configuration for the most general solid is prohibitively complicated. Consequently, much effort has been devoted to the study of basic solid configurations and the optimal surfaces resulting from the addition of liquid volume [2, 4–7].

However, in three dimensions there exists no simple analytical solution describing the shape of the wetted solid, not even for simple arrangements like two overlapping spheres. While there has been much concern with general questions of existence and uniqueness [7, 8], the problem of generating solutions in specific instances has been ignored in both the physics and mathematics literature. Recently, such solutions have been recognized to be important for the understanding of sintering processes [2, 4, 5, 9]. Basa et al. [5] have given an algorithm for the exact numerical treatment of the wetting of axisymmetric solids in general and of overlapping spheres in particular. Successful implementations of the algorithms developed in [5] rely on the analytical work presented here.

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Accordingly, we present the properties of the Delaunay curves, which describe the optimal shapes of the wet regions of axisymmetric solids, referred to as "puddles" in the text. We discuss how the constraints of the global wetting problem can be used to select the correct Delaunay curve(s) that minimize the combined solid-liquid surface area. Finally, we describe the wetting of configurations of two spheres, the wetting of an axisymmetric solid of constant mean curvature, and the wetting of a configuration consisting of a spherical pore inside two adjacent spheres. These examples demonstrate the use of Delaunay curves for describing nontrivial solid-liquid configurations of interest.

II. Formulation of the problem.

A. *The global problem—choosing the correct regions of the solid for wetting.* Quite generally, one can picture wetting as the result of covering a solid skeleton with liquid such that the total surface energy of the combined solid-liquid configuration is minimal. In particular, we are interested in the wetting of a homogeneous solid of revolution by a prescribed volume of liquid composed of the same material. The latter condition suggests our assumption that the surface tensions σ_{LG} and σ_{SG} along the liquid-gas and solid-gas boundaries are identical and that the surface tension σ_{LS} between the liquid and the solid vanishes. Such a situation occurs, for example, in homogeneous sintering processes, where there exists a mobile pool of material that wets the remaining solid skeleton of the same composition [2, 5, 9–11]. Furthermore, we assume that the material can be treated as homogeneous (and isotropic), which implies that the surface tension σ is constant.

Since σ_{LG} and σ_{SG} are identical and $\sigma_{\mathrm{LS}} = 0$, it follows from Young's law [12] that the liquid surface(s) will be tangent to the solid skeleton at the liquid-solid-gas boundaries. The physical quantity that is to be minimized during the wetting process is the free energy F. Unless additional physical phenomena are considered, the free energy corresponds to the surface energy $E_{\mathrm{s}} = \int \sigma \cdot dA$. Since σ is assumed to be a constant, this expression reduces to $E_{\mathrm{s}} = \sigma \cdot A$, where A is the combined liquid-solid surface area. Therefore, we are dealing with the problem of distributing a given liquid volume over the solid skeleton such that the resulting liquid-solid surface area is minimal. As described elsewhere [4] this represents a new and interesting generalization of the Plateau problem.

Specifically, consider a solid of revolution generated by revolving a piecewise smooth function $y = g(x) \geq 0$ about the x-axis. The global configuration of the wetted solid with liquid volume V_{L} consists of puddles of liquid V_i, $i = 1, \ldots, n$, placed onto certain regions of the surface of the solid so as to minimize the combined surface area. The generating function of the resulting liquid-solid configuration is then composed of pieces $y = g(x)$ in those regions where the solid is not covered by a puddle and by functions $y = W_i(x)$, $i = 1, \ldots, n$, describing the shape of the n puddles wetting the solid.

To achieve a minimum total surface area for the liquid-solid configuration, one must first determine which regions of the solid lead to a minimal combined surface area when covered by a liquid puddle. To do this, we interpret the mean curvature at every point of the solid-liquid configuration as measuring the local rate of change of the combined surface area per unit of additional volume

$$\kappa = \frac{dA}{dV} \tag{1}$$

where $\kappa(x)$ is the local mean curvature of the solid-liquid configuration. While related results abound [7], there appears to be no statement of Eq. (1) in the mathematical literature. We provide a derivation in the appendix. For a figure of revolution generated by the function $y(x)$, the mean curvature is given by [13]

$$\kappa = \frac{-1}{2\sqrt{1+y'(x)^2}}\left[\frac{y''(x)}{1+y'(x)^2} - \frac{1}{y(x)}\right]. \tag{2}$$

Using Eq. (1) we see that the greater the value of κ for a given region, the larger the change in surface area resulting from the addition of an incremental volume dV to this region. Thus, to achieve a minimal combined surface area upon addition of a small amount of liquid, it is most profitable to wet first those regions of the surface with the lowest value of κ. If, for example, $\kappa < 0$, an addition of liquid will result in a decrease of the local surface area in this region.

Equation (1) then gives us a local criterion by which to determine the global liquid-solid configuration for very small amounts of liquid added to the existing configuration. This is done by examining the individual regions R_i on the solid and finding those regions with the lowest mean curvature, i.e., where wetting will result in a minimal increase (or maximal decrease) of the combined liquid-solid surface area.

At corners where y' or y'' are undefined the mean curvature given by Eq. (2) is also undefined. At these points we shall use Eq. (1) to define the local mean curvature of the solid. We then interpret an inward-pointing corner, where an incremental increase in volume results in a decrease in net surface area, as having a local mean curvature equal to $-\infty$. Analogously, an outward-pointing corner, where an increase in volume results in an increase in surface area, is given a local mean curvature equal to $+\infty$. Thus, a minimal combined surface area will be achieved by first wetting those points (if any) on the solid that have an inward-pointing corner. Likewise, any outward-pointing corner should be wetted last. Notice that Eq. (1) also suggests a criterion to decide where to wet first, if two regions have the same local mean curvature. In this case, we have to compare $d\kappa/dV$.

As indicated above, not only can the mean curvature of the solid be interpreted as the change in area per unit change in volume, but the mean curvature of the individual puddles wetting the solid can be interpreted in the same manner. If this is the case we see that each puddle wetting the solid is itself a surface of constant mean curvature κ_i and that minimum surface area requires the same value $\kappa_i = \kappa$ for all puddles. This follows since the transport of liquid from a puddle with $\kappa = \kappa_1$ to a puddle with $\kappa = \kappa_2$, $\kappa_2 < \kappa_1$, would decrease the combined surface area. Furthermore, we notice that the mean curvature of the dry areas of the solid must be everywhere greater than the mean curvature of wet areas.

The foregoing arguments concerning the mean curvature suggest that the puddles should form and grow in regions where the mean curvature of the solid-liquid configuration is smallest. While this conclusion is correct for sufficiently small additional volumes, it is based on a linear analysis, and thus for larger liquid volumes its validity is limited. The true quantity to minimize is $\Delta A = \sum_j \Delta A_j$, where j indexes the regions of the solid-liquid configuration. Each $\Delta A_j = \int \kappa_j \, dV_j$ corresponds to the change in the area of a region on the liquid or solid surface. Thus, when adding more than infinitesimal amounts of liquid, it may pay to add liquid in places where the mean curvature is initially high, provided this enables us to reach configurations with lower values of κ, leading to a lowering of the surface area. For example, consider the case of removing liquid from puddles with mean curvature κ_1 in order to fill in a spherical pore with mean curvature $\kappa_2 > \kappa_1$: the more liquid we add to the pore, the lower κ_2 becomes, eventually reaching $-\infty$ when the pore disappears (cf. IV, Example C). Similarly, the mean curvature of a sphere will be reduced upon the addition of liquid. Thus, due to the global constraint of a fixed liquid volume, it can be advantageous to wet regions with initially high values of κ as an intermediate step, although this causes an initial increase in the total surface area. In such a situation, the system crosses a free energy saddle in order to go from a higher to a lower minimum.

We have limited our scope in this paper to shapes that have axial symmetry and can be generated by revolving the graph of a piecewise smooth function about an axis. In particular, this excludes those solids of revolution that contain cavities or create cavities by the formation of bridges.

B. *The local problem—the differential equation for the Delaunay curves.* The above arguments show that minimization of the total surface area requires us to choose the correct regions of the solid for wetting and that for sufficiently small liquid volumes these are exactly the regions with lowest mean curvature. Optimality further demands that the individual puddles must themselves have a shape that minimizes area. The configuration of each puddle of liquid volume V_i, characterized by the function $y = W_i(x)$, can then be found by solving a classical Calculus of Variations problem minimizing the surface area enclosing a given volume of liquid [8]. For surfaces of revolution, the Lagrangian $\mathscr{L}$ of the variation that minimizes surface area

$$A = 2\pi \int y\sqrt{1 + y'^2}\, dx \tag{3}$$

enclosing a given volume V_i

$$V_i = \pi \int y^2\, dx \tag{4}$$

is

$$\mathscr{L} = 2\pi y\sqrt{1 + y'^2} - \bar{\lambda}\pi y^2, \tag{5}$$

where $\bar{\lambda}$ is the Lagrange multiplier corresponding to the volume constraint. Noting that the Lagrangian has no explicit x-dependence, the associated Euler-Lagrange equation becomes

$$\mathscr{L} - y'\frac{\partial \mathscr{L}}{\partial y'} = 2\pi y\sqrt{1 + y'^2} - \bar{\lambda}\pi y^2 - y'\left(\frac{2\pi y y'}{\sqrt{1 + y'^2}}\right) = \overline{H}, \tag{6}$$

where $\overline{H}$ is a constant of integration. Equation (6) can be simplified to yield

$$\frac{y}{\sqrt{1+y'^2}} = H + \lambda y^2, \tag{7}$$

where we have set

$$\lambda = \frac{\overline{\lambda}}{2} \quad \text{and} \quad H = \frac{\overline{H}}{2\pi}. \tag{8}$$

Without loss of generality we may assume $y \geq 0$, in which case the above expression implies

$$H + \lambda y^2 \geq 0. \tag{9}$$

Equation (7) can be rewritten as

$$\frac{dy}{dx} = \pm\sqrt{\frac{y^2}{(H+\lambda y^2)^2} - 1}. \tag{10}$$

Solutions to Eq. (10) are functions $y = W_D(x)$ that describe the shape of the puddles wetting the solid. These functions represent a family of curves that, when rotated about the x-axis, generate surfaces of minimal area enclosing given volumes of liquid. They are called Delaunay curves [14], and the corresponding surfaces of revolution are called Delaunay surfaces. These surfaces can be classified as belonging to two families: the unduloids and the nodoids [15–17].

It is clear from our discussion in section IIA that the mean curvature $\kappa_i(x)$ of these surfaces will be constant. This can be seen explicitly by substituting Eq. (10) into the mean curvature in Eq. (2). We find that the mean curvature of the wetting curves $y_i = W_i(x)$ is just $\kappa_i(x) = \lambda_i$. Note that this verifies Eq. (1) for these surfaces, since for all constrained optimization problems the Lagrange multiplier λ_i associated with the constraint equals the change in the objective function with respect to the constrained quantity, i.e., $\lambda_i = dA/dV$. Furthermore, since $\kappa_i = \kappa$ for $i = 1, \ldots, n$, it follows that $\lambda_i = \lambda$ for $i = 1, \ldots, n$.

In determining the exact shape of the ith puddle, one needs to know more than which region should be covered. Solutions to the Euler-Lagrange equation (10) for a particular puddle require knowledge of the appropriate constants H and λ as well as the additional constant that comes from the integration of Eq. (10).

In addition, we have the boundary conditions requiring the tangency of the puddles to the solid surface, i.e., $g'(x) = W_i'(x)$ at the points of contact. In the language of classical capillarity, the contact angle between the surface of the liquid and the solid should be zero [12, 5].

In summary, in order to find the configuration of a puddle V_i wetting a region R_i of a solid of revolution, we must find a wetting curve $y = W_i(x)$ that:

(1) satisfies the Euler-Lagrange equation (10), i.e., it is composed of pieces of Delaunay curves;
(2) meets the generating function $y = g(x)$ of the solid with zero contact angle; and
(3) encloses a volume V_i between itself and the solid when rotated about the x-axis.

Since the Euler-Lagrange equation is independent of x, the shape of the Delaunay curve $W_i(x)$ is determined by the parameters H and λ and the inequality $H+\lambda y^2 > 0$. In order to attach a wetting curve with shape parameters H and λ to a particular region R_i, we must specify a point through which the wetting curve must pass. The most natural choice is the point where the wetting curve meets the generating function $g(x)$ of the solid. This prescribes the line element at such a point, since the contact must take place with a zero contact angle. In order to describe the configuration of a puddle covering region R_i of the solid, it is therefore sufficient to determine the H and λ parameters of the wetting curve and the points of tangency to the generating function of the solid.

III. Properties of Delaunay curves.

A. *General considerations.* As was shown in Delaunay's original paper [14], if the variation in Eq. (5) is parametrized in terms of arc length, the Delaunay curves $W_D(x)$ can be seen to be generated by the trajectory of a focus when a conic section is rolled along the x-axis. The resulting $W_D(x)$ is a periodic function [14]. If the chosen conic section is an ellipse, the resulting figure is called an unduloid; and if the conic is a hyperbola, the figure is called a nodoid. Finn and Concus [15, 16] used these surfaces to study the shape of liquid drops, focusing on the questions of existence and stability. The present discussion, however, focuses on the description of wetting and sintering phenomena. While these surfaces can be completely characterized in terms of elliptic integrals [17, 15, 16], it is considerably easier to solve Eq. (10) directly to determine the properties of the Delaunay curves appropriate to a given physical situation. Note that Eq. (10) is of the rather accessible form $f' = G(f)$.

The $\pm$ sign in Eq. (10) shows that Delaunay curves exist as two separate branches considered as functions of the variable x, one branch with positive slope and the other with negative slope. For $W_D(x)$ to be smooth these two branches must meet at a point of zero slope (a horizontal tangent) or a point of infinite slope (a vertical tangent). The horizontal tangents occur when $f' = 0$ at f_0:

$$f_0 = \frac{\pm 1 \pm \sqrt{1 - 4H\lambda}}{2\lambda}. \tag{11}$$

It can be shown by formally integrating Eq. (10) that the Delaunay curves, viewed as functions $f(x)$, are symmetric about their extrema. Vertical tangents will occur if $f' = \pm\infty$, which implies that

$$f_v = \pm\sqrt{-\frac{H}{\lambda}}. \tag{12}$$

This implies that a vertical tangent can occur only when H and λ are of opposite sign, i.e., $H > 0$, $\lambda < 0$ or $H < 0$, $\lambda > 0$.

For those Delaunay curves that do not have vertical tangents ($\lambda > 0$, $H > 0$ and $\lambda < 0$, $H < 0$), we differentiate Eq. (10) to form the second derivative

$$f'' = \frac{Hf - \lambda f^3}{(H + \lambda f^2)^3}, \tag{13}$$

and setting f'' to zero we find the value of f at an inflection point as

$$f_{\text{in}} = \pm\sqrt{\frac{H}{\lambda}}\,. \tag{14}$$

Inflection points can only exist if H and λ are of the same sign, i.e., $\lambda > 0$, $H > 0$ or $\lambda < 0$, $H < 0$. At an inflection point the slope of the Delaunay curve takes on its maximum value of

$$\left|\frac{df}{dx}\right|_{\max} = \sqrt{\frac{1-4H\lambda}{4H\lambda}}\,. \tag{15}$$

The square root in the differential equation (10) describing the wetting curves gives the additional condition

$$\frac{f^2}{(H+\lambda f^2)^2} - 1 \geq 0\,. \tag{16}$$

Solving for the allowed values of $z = f^2$, we find that they must lie between

$$z_- = \frac{(1-2H\lambda) - \sqrt{1-4H\lambda}}{2\lambda^2} \tag{17a}$$

and

$$z_+ = \frac{(1-2H\lambda) + \sqrt{1-4H\lambda}}{2\lambda^2}\,, \tag{17b}$$

where $z_+ > z_- > 0$. Equivalently, $|f|$ must lie between $\sqrt{z_-}$ and $\sqrt{z_+}$, which correspond to the (appropriate) flat points given in Eq. (11). Furthermore, we notice that

$$1 - 4H\lambda \geq 0 \tag{18}$$

is a necessary condition for the existence of a Delaunay curve corresponding to the pair (H, λ). The case where $1 - 4H\lambda = 0$ represents a special Delaunay curve, which will be dealt with in Sec. IIIC.

B. *Delaunay curves belonging to specific regions in* (H, λ) *parameter space.*

Restrictions on the wetting curves. From Eqs. (19) and (20) it follows that the Delaunay curves must lie between an appropriately chosen pair of roots in Eq. (12). By examining $\sqrt{z_-}$ and $\sqrt{z_+}$ for different values of H and λ the appropriate values of extremal solutions f can be selected. These values are tabulated in Table 1.

TABLE 1

λ, H	f_0^{top}	f_0^{bottom}
$\lambda < 0, H > 0$	$\frac{-1-\sqrt{1-4H\lambda}}{2\lambda}$	$\frac{1-\sqrt{1-4H\lambda}}{2\lambda}$
$\lambda > 0, H < 0$	$\frac{1+\sqrt{1-4H\lambda}}{2\lambda}$	$\frac{-1+\sqrt{1-4H\lambda}}{2\lambda}$
$\lambda > 0, H > 0$	$\frac{1+\sqrt{1-4H\lambda}}{2\lambda}$	$\frac{1-\sqrt{1-4H\lambda}}{2\lambda}$
$\lambda < 0, H < 0$	$\frac{-1-\sqrt{1-4H\lambda}}{2\lambda}$	$\frac{-1+\sqrt{1-4H\lambda}}{2\lambda}$

We now exploit the additional restriction given by Eq. (9), $H + \lambda f^2 > 0$. If $\lambda < 0$, $H < 0$, then Eq. (9) is violated for all possible values of f, which implies no Delaunay curve generated with these parameter values can be used to solve the variational problem.

If $\lambda < 0$, $H > 0$, then Eq. (9) implies

$$f < \sqrt{-\frac{H}{\lambda}} = f_v, \tag{19a}$$

allowing us to use that portion of the Delaunay curve between f_v given above and f_0^{bottom} from Table 1 as a solution of the variational problem.

If $\lambda > 0$, $H < 0$, we find

$$f > \sqrt{-\frac{H}{\lambda}} = f_v, \tag{19b}$$

which allows us to use the section of the Delaunay curve between f_v and f_0^{top} from Table 1 as a solution of the variational problem.

Finally, if $\lambda > 0$, $H > 0$, then the condition is always satisfied. Thus, we can use the entire Delaunay curve generated by these parameter values; i.e., the allowed values of f may lie between f_0^{bottom} and f_0^{top} given in Table 1. We note that Eq. (10) does not distinguish between (λ, H) and $(-\lambda, -H)$.

By comparing f_{in} and f_v from Eqs. (14) and (12) with the midpoint f_{mid} of the interval $[f_0^{\text{bottom}}, f_0^{\text{top}}]$ for the different choices of H and λ, we find that the inflection points and points of vertical tangency all lie below the vertical center of the Delaunay curve.

It is sometimes of interest to know the curvature of the Delaunay curves at their extrema. This is found to be

$$\kappa_0 = \frac{-Hf_0 + \lambda f_0^3}{(H + \lambda f_0^2)^3} = \lambda - \frac{H}{f_0^2}. \tag{20}$$

Specifically, for the parameters $H > 0$, $\lambda > 0$, where the complete Delaunay curve can be used to solve the variational problem, we find by using Table 1 that $\kappa_0^{\text{bottom}} < \kappa_0^{\text{top}}$. As far as the magnitude of κ_0^{bottom} and κ_0^{top} are concerned, it follows from Eq. (20) that

$$|\kappa_0^{\text{bottom}}| \geq |\kappa_0^{\text{top}}|. \tag{21}$$

C. *Special Delaunay curves.* For certain values of the parameters H and λ, the resulting Delaunay curves are given by simple functions.

If we set $H = 0$ and $\lambda = 0$ then Eq. (7) gives

$$\frac{f}{\sqrt{1 + f'^2}} = 0, \tag{22}$$

and the only curve that satisfies this equation is given by $f \equiv 0$. Therefore, the special Delaunay curve corresponding to $H = 0$, $\lambda = 0$ is the horizontal line through the origin

$$y = f \equiv 0\,. \tag{23}$$

Next, we set $\lambda = 0$, $H = \text{constant} > 0$. Then Eq. (7) becomes

$$\frac{f}{\sqrt{1 + f'^2}} = H\,. \tag{24}$$

We recognize this as the classical problem of minimizing the surface area associated with (axisymmetric) soap films. The function satisfying Eq. (24) is the well-known catenoid

$$y = H \cosh\left(\frac{x + x_0}{H}\right)\,. \tag{25}$$

Therefore, the special Delaunay curve associated with $\lambda = 0$, $H \neq 0$, is the hyperbolic cosine, where the value of x_0 is given by the boundary conditions of the problem.

Similarly, if we take $H = 0$ and $\lambda = \text{constant} > 0$ in Eq. (7), we obtain

$$\frac{f}{\sqrt{1 + f'^2}} = \lambda f^2 \tag{26a}$$

or

$$f'^2 = \frac{(1/\lambda)^2 - f^2}{f^2}\,. \tag{26b}$$

We recognize this as describing the classical isoperimetric problem whose solution is a circle centered on the x-axis with radius $r = 1/|\lambda|$. Since we are assuming $f \geq 0$, the special Delaunay curves associated with $H = 0$ are semicircles.

It is of interest to know which nontrivial Delaunay curves with finite (H, λ) intersect the symmetry axis. From Eq. (7) it follows that, in order to allow $f(x) = 0$ at some point x, $H = 0$ must hold. Thus, any Delaunay curve that intersects the x-axis is a circle.

Finally, let us consider the case that H and λ are chosen such that $1 - 4H\lambda = 0$. This can only occur if $H\lambda > 0$. For $H > 0$, $\lambda > 0$, the interval given in Table 1 shrinks to a point

$$f_0^{\text{top}} = f_0^{\text{bottom}} = f_{\text{in}} = \frac{1}{2\lambda}\,, \tag{27}$$

and the curve is the horizontal line

$$y \equiv \frac{1}{2\lambda}\,. \tag{28}$$

The case $H < 0$, $\lambda < 0$ has already been excluded using Eq. (9).

D. *The question of uniqueness.*

The Jacobi condition. In order to judge, whether the extremals given by the Euler-Lagrange equations are in fact minima, we examined the necessary conditions of Legendre and Jacobi [18]. We find that although the Legendre test is positive, the

Jacobi test is inconclusive. As will be seen below, this result is not unexpected, since we do find that for some examples it is possible to find several Delaunay curves that solve the Euler-Lagrange equation. In particular, our investigations have led us to believe that for reasons of stability it is never appropriate to use more than a full period of a Delaunay curve as a wetting curve. The work of Vogel [19] shows the importance of the boundary conditions in determining the stability of solutions. He shows that for the case of a liquid drop suspended between two parallel plates with contact angle 90°, it is not possible to find a stable solution using more than one period of a Delaunay curve. Furthermore, he shows in an extension of Lord Rayleigh's analysis [20, 21] that a cylindrical column of liquid will become unstable if its height exceeds half its circumference. We expect that his proof could be adapted to our problem.

The boundary conditions revisited. We now return to the problem of specifying the correct Delaunay curve covering a region R_i. We must impose a number of conditions, which fall into three categories:

1. The liquid volume enclosed by the Delaunay curve(s) must equal a prescribed number V_L, and the liquid surface must lie above the solid surface.

2. For a given puddle, we need to specify the distance $x_2 - x_1$ along the rotation axis between the two points $(x_1, g_1(x_1))$ and $(x_2, g(x_2))$ where the Delaunay curve is to touch the generator $y = g(x)$ of the underlying solid.

3. We demand that the Delaunay curve $f(x)$ be tangent to the solid at the points of contact; i.e., we require that $f_1 = f(x_1) = g(x_1)$, $f_2 = f(x_2) = g(x_2)$, $f'_1 = f'(x_1) = g'(x_1)$, and $f'_2 = f'(x_2) = g'(x_2)$.

We will first address conditions 2 and 3. We can identify two distinct cases, the symmetric arrangement, $f_1 = f_2$ (in which case $f'_1 = -f'_2$), and the nonsymmetric one.

Let us begin with the latter. Inserting the boundary condition at points 1 and 2 into Eq. (7), we find a unique pair of values (H, λ) that specify the appropriate Delaunay curve:

$$H = \frac{f_1^2 f_2^2}{f_2^2 - f_1^2}\left(\frac{1}{f_1\sqrt{1+f_1'^2}} - \frac{1}{f_2\sqrt{1+f_2'^2}}\right), \tag{29a}$$

$$\lambda = \frac{1}{f_1^2 - f_2^2}\left(\frac{f_1}{\sqrt{1+f_1'^2}} - \frac{f_2}{\sqrt{1+f_2'^2}}\right). \tag{29b}$$

We now must take into account the fact that line elements 1 and 2 are located at two fixed x-values on the solid. In order to match the Delaunay curve with one of these points, e.g., point 1, we can always simply shift it along the x-axis by a constant x_0. But once this degree of freedom has been used, we have no remaining free parameter that would allow us to match the prescribed distance Δx between points 1 and 2. Thus, in general, there will exist no Delaunay curve between two arbitrarily chosen line elements on the solid.

For an application of our Delaunay curves to any practical problem, it is therefore necessary to fix, e.g., only the location of point 1, and then to vary the location of point 2 on the "other side of the puddle", until we succeed in fulfilling both conditions 2 and 3 [5]. We find that there exist either zero, one, or two curves that fulfill both conditions. We will discuss the case of two solutions below in subsection iii as part of our discussion of global vs. local minima.

However, it is possible, especially if the range of Δx values is restricted in some way, that no Delaunay curve might exist from point 1 to *any* point on "the other side of the puddle" while fulfilling the condition that we use at most one period of a Delaunay curve. Such a restriction may occur, e.g., if the solid under consideration consists of several disconnected pieces, and the Delaunay curve is employed to form a bridge using only a very small amount of liquid. This suggests the concept of the least feasible bridge, i.e., the configuration connecting two disjoint pieces by a Delaunay curve that requires the least amount of liquid volume.

The case of a symmetric arrangement poses some additional complications. Let us assume first that the relevant Delaunay curves are symmetric themselves. In this case, we can no longer use the two points of tangency, in order to determine the unique values of H and λ, since Eq. (7) is identical for both end points. This means that we have a one-parameter family of Delaunay curves that fulfill condition 3. We parametrize this family by the height f_0 of their flat points $(f_0, f'_0 = 0)$, halfway between the end points, in order to be able to solve for λ and H as required for the numerical integration [5]. We now can use condition 2 to choose the allowable Delaunay curve(s) among the members of this family. We find either two, one, or no such curve.

The fact that the boundary conditions are symmetrical does not in general preclude the existence of asymmetric solutions. However, it follows from the reflection symmetry of the Delaunay curves about their flat points together with the requirement that at most one period of a Delaunay curve may be used for a given puddle, that for symmetric boundary conditions no solution consisting of an asymmetric piece of a Delaunay curve exists.

Nevertheless, it is still conceivable that for a given symmetric solid configuration we can choose asymmetric boundary conditions resulting in an asymmetric liquid surface. For some symmetric solid configurations, it can be shown that this possibility does not exist. Consider, for example, whether it is possible to have a Delaunay curve tangent to two identical separated semicircles at heights y_1 and y_2, with $y_1 \neq y_2$. According to Eq. (29), we then can find the values for H and λ for a curve between two semicircles to be given by

$$H + \lambda y_1^2 = y_1^2, \qquad H + \lambda y_2^2 = y_2^2. \tag{30}$$

These equations imply that $y_1 = y_2$. Since this contradicts the assumption that $y_1 \neq y_2$, we conclude that for two identical separate spheres we cannot have an asymmetric liquid bridge. However, if we place all the liquid on only one of the two spheres, this configuration is found to represent the optimal solution of the global problem for very small liquid volumes. Thus an asymmetric solution is possible.

Returning to the general case, if two solutions do exist between $(x_1, g(x_1))$ and $(x_2, g(x_2))$, they will enclose different liquid volumes. However, condition 1 cannot be used in a straightforward manner to eliminate one of the two Delaunay curves. By applying condition 1, we ensure that the surface encloses the required volume. In many cases of interest, this selects the appropriate starting point 1 uniquely. However, sometimes, for example in the symmetric case, two different starting points, 1 and $1'$, will yield Delaunay curves that enclose the same volume. If this is the case, we have to determine explicitly the total liquid-solid surface areas and choose the curve with the lower one. For example, for two disjoint identical spheres two Delaunay curves originate from all feasible starting points on the sides of the spheres that face each other. These curves can be classified into a "lower" and an "upper" family. For all cases of interest, we must choose a member of the "upper" family, in order to achieve the minimal surface area.

Finally, we have the global condition that the liquid surface must lie everywhere above the solid surface. This condition is not implemented automatically by the choice of a Delaunay curve via the conditions 2 and 3 discussed above. Instead, we must check, in principle, for any given Delaunay curve whether it fulfills this condition. Obviously, if a graph of the solid curve, $g(x)$, is available, one will try from the outset to choose regions $R_i(x)$ containing the starting points and end points of the Delaunay curves in such a manner that no solid obstacle will be encountered by the wetting curve. Nevertheless, it is important to verify this assumption.

As an example, we again consider the case of two identical spheres. We show that for this case it is not possible for the Delaunay curve to be tangent to both semicircles and also pass through them. We assume the Delaunay curves contain at most one period and originate and end on the adjacent sides of the semicircles. Given that the Delaunay curve is tangent to the semicircle at some point y and has a horizontal tangent at y_0, we can solve for its H and λ values.

If the Delaunay curve is tangent to the semicircles at y, the only way it can then pass through this semicircle is for the slope of the Delaunay curve to increase faster than the slope of the semicircles themselves. This can only occur if: (a) the Delaunay curve under consideration has an inflection point, $y_{\text{in}}\sqrt{H/\lambda}$, with a slope greater than the slope of the semicircles at the same height and (b) the point of tangency, y, must be above the inflection point.

We first notice that, in order for an inflection point to exist within a valid region of the Delaunay curve, we need $\lambda > 0$. Condition (a) leads to $\lambda < 1/2$, and since $y > y_0$, we find as a necessary condition that

$$y_0^2 - 2y_0 + y^2 < 0. \tag{31}$$

From condition (b) we deduce that

$$1 > (1 - y_0)y_0/(y^2 - y_0). \tag{32}$$

Since $\lambda > 0$, we have $y^2 - y_0 > 0$, and we obtain the inequality

$$0 < y_0^2 - 2y_0 + y^2, \tag{33}$$

which contradicts the inequality derived from condition (a).

Global minima vs. local minima—different suboptimal configurations. The symmetric case studied above has already pointed to the fact that we can have two or more allowed Delaunay curves that will enclose the same amount of liquid volume. Thus, we are dealing with a multiplicity of stationary solutions. In certain cases (e.g., two identical disjoint but close spheres), we can identify the curve with the lowest total liquid-solid surface area from the outset. But in more general solutions, we have to perform a combinatorial (configurational) optimization. In Sec. IV we will show, for the examples of (i) two disjoint spheres and (ii) a small cavity in competition with a neck, how such an optimization proceeds in two simple cases.

IV. Solutions of typical configurations. In this section we will present the Delaunay curves associated with the wetting of some simple but interesting configurations: two overlapping spheres of different radii, two disjoint spheres of different radii, two adjacent spheres containing a spherical cavity, and a solid of constant mean curvature. We have chosen these examples, since they are simple enough to allow the determination of the appropriate Delaunay curves and at the same time represent generic examples of great interest for practical applications.

A. *The wetting of two overlapping spheres with different radii.* The first configuration consists of two spheres with radii r_1 and r_2. Since the shape of the final liquid-solid configuration is scale invariant [5], we can restrict ourselves to the case $r_2 = 1$, $r_1 < 1$. We assume that these spheres are overlapping with an overlap parameter h $(h \geq 0)$. (If d is the distance between the centers of the spheres, then $2h = r_1 + r_2 - d$.) Using numerical techniques [5] based on the results presented here, it is possible to calculate the Delaunay curves associated with the wetting of the two spheres. In Figs. 1a–d (see pp. 14, 15), we show several examples of such curves for each of the chosen values of r_1 and h.

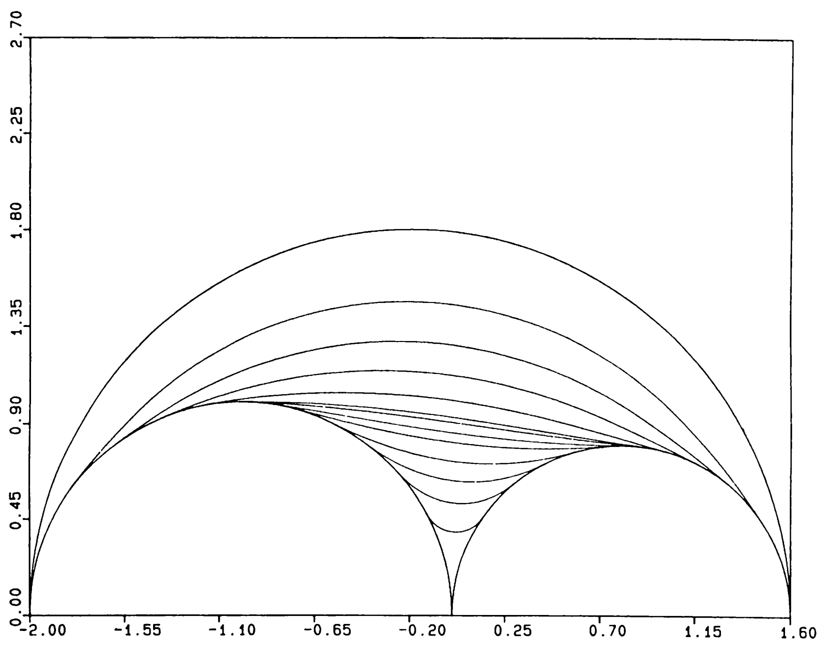

FIG. 1(a). Delaunay curves for the wetting of two spheres. $r_2 = 1$, $r_1 = 0.8$, $h = 0$.

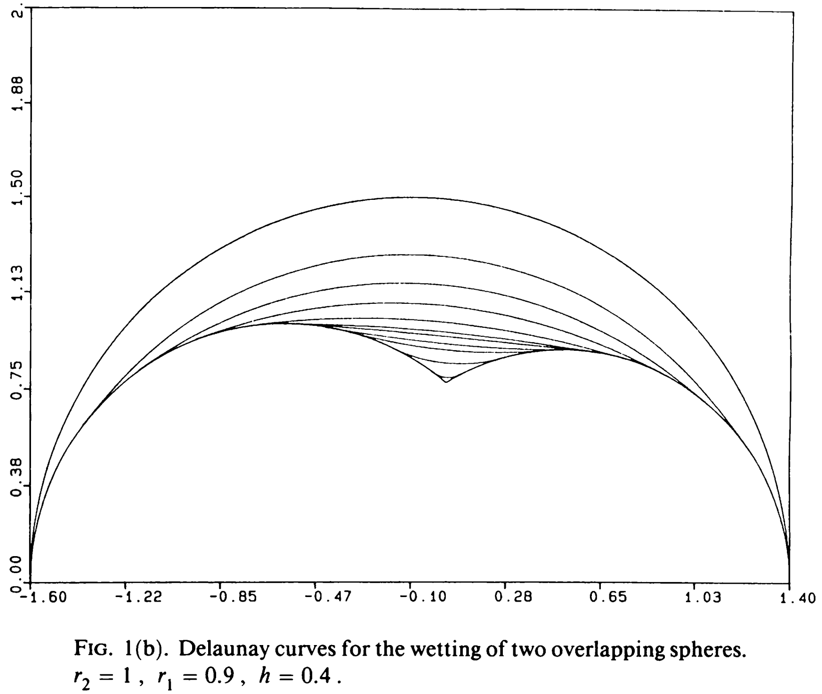

FIG. 1(b). Delaunay curves for the wetting of two overlapping spheres. $r_2 = 1$, $r_1 = 0.9$, $h = 0.4$.

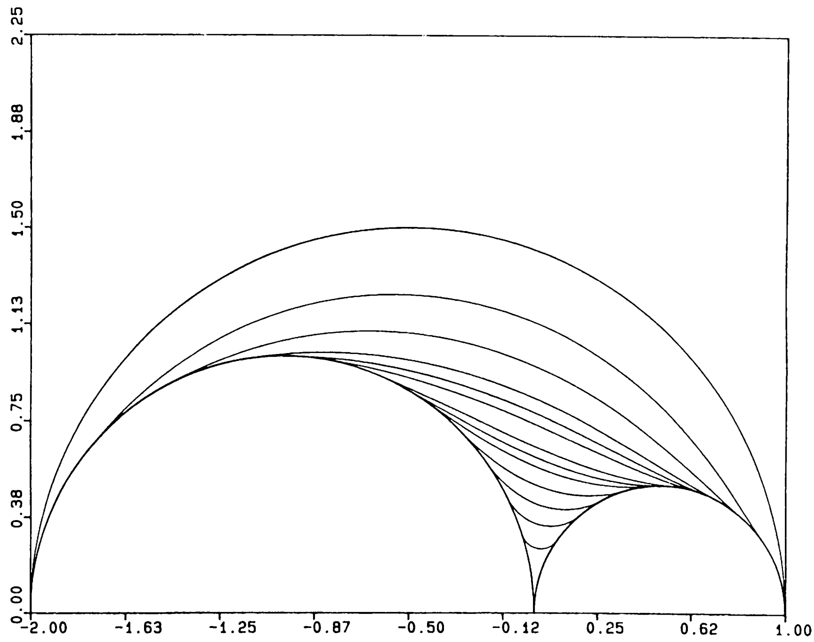

FIG. 1(c). Delaunay curves for the wetting of two spheres. $r_2 = 1$, $r_1 = 0.5$, $h = 0$.

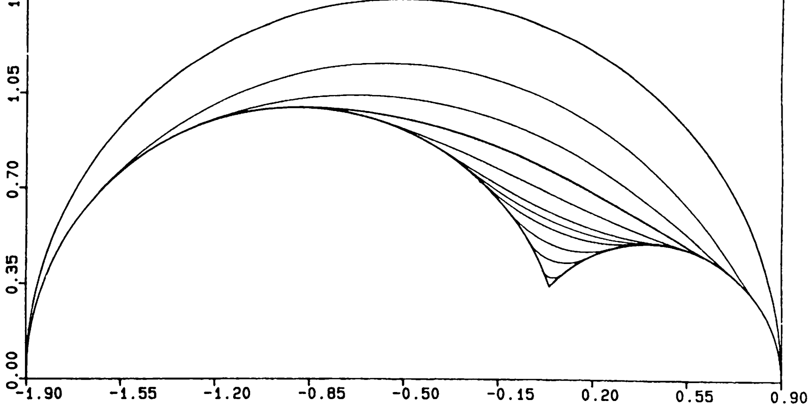

FIG. 1(d). Delaunay curves for the wetting of two overlapping spheres. $r_2 = 1$, $r_1 = 0.5$, $h = 0.1$.

B. *The wetting of two disconnected spheres.* In this example, we have to select between several possible solutions. In Fig. 2a we show two Delaunay curves that would form bridges upon rotation about the symmetry axis. We notice that these curves belong to two families. For a given liquid volume, it is always the upper curve that represents the actual minimum surface area solution.

However, we observe that the first allowable Delaunay surface, i.e., the smallest feasible bridge, already encloses a nonzero volume of liquid V_1. This means that, for liquid volumes smaller than V_1, the liquid has to be distributed on the surface of two spheres in such a manner as to minimize the total liquid-solid surface area. In this case, we have to add all of the liquid to the larger of the two spheres (the corresponding Delaunay curve is, of course, a circle). For two identical spheres, it pays to break the symmetry and choose one of the spheres to remain dry.

For liquid volumes slightly larger than V_1, we sometimes find that the minimal surface area is still achieved by placing all the liquid onto the bigger sphere. But, if the distance $d(= -h)$ between the two spheres is not too large, there will be a liquid volume V_2, where the surface area associated with the bridge is smaller than the surface area of the separated spheres. From then on, the minimal surface is given by one of the Delaunay curves in Fig. 2b. For this specific example, we have marked the critical curve, i.e., the first actually realized bridge, by a dashed line.

C. *The wetting of two adjacent spheres containing a spherical cavity.* A similar optimization procedure is necessary for the case of the wetting of two adjacent spheres, one of which contains a spherical cavity (see Fig. 3a on p. 18). In this configuration, there are two regions where wetting will occur: inside the cavity and at the neck, i.e., the point of contact between two spheres. The optimal wetting with progressively larger volumes proceeds as follows: We begin by filling the neck first, while leaving the cavity dry. Beyond a critical value of liquid volume, we begin adding liquid within the cavity and transferring some liquid from the neck into the cavity as well. During this process, we ensure that the mean curvature of the two Delaunay surfaces at the neck and within the cavity remain identical. When we add enough liquid volume to fill the cavity exactly, all the liquid resides in the cavity, while the neck is dry. Addition of further liquid will result in the rewetting and growth of the neck. In Fig. 3b on p. 18 we plot the total reduction of liquid-solid surface area as a function of added liquid volume. The solid line is the optimal curve, while the dotted line and the dashed line represent the extreme cases of filling only the neck or the cavity, respectively.

D. *The wetting of a solid of constant mean curvature.* In the process of sintering, it often occurs that the liquid wetting the solid particles freezes after wetting the solid, thus forming a new solid containing regions of constant mean curvature. It is therefore of interest to study the wetting of axisymmetric solids where the generating function $g(x)$ itself is a Delaunay curve. These require different Delaunay curves tangent to $g(x)$ as shown in Figs. 4a–c (see pp. 19 and 20) for several examples.

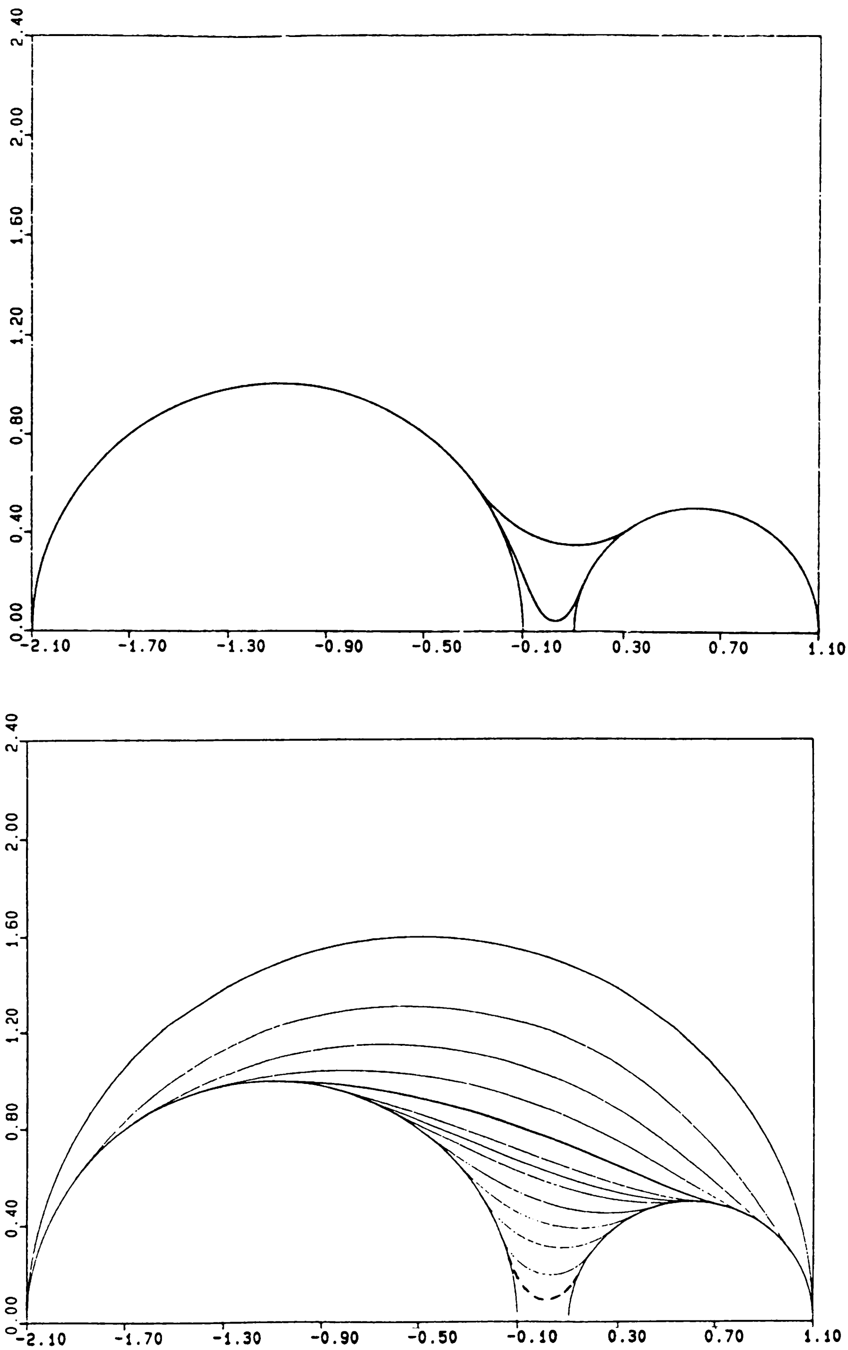

FIG. 2. Delaunay curves for the wetting of two disconnected spheres: $r_2 = 1$, $r_1 = 0.5$, $h = -0.1$. (a) Two Delaunay curves being tangent to the larger sphere at the same point, belonging to the upper and lower family, respectively. (b) Delaunay curves representing optimal surfaces. The dashed line indicates the least globally optimal bridge.

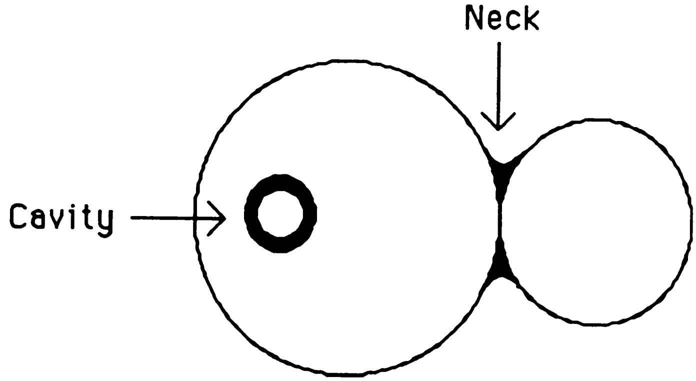

FIG. 3(a). Configuration consisting of two adjacent spheres of radii 1 and 0.5 containing a spherical cavity of radius 0.1 : $r_2 = 1$, $r_1 = 0.5$, $h = 0$, $r_{cav} = 0.1$. Liquid wetting this configuration is indicated by shading.

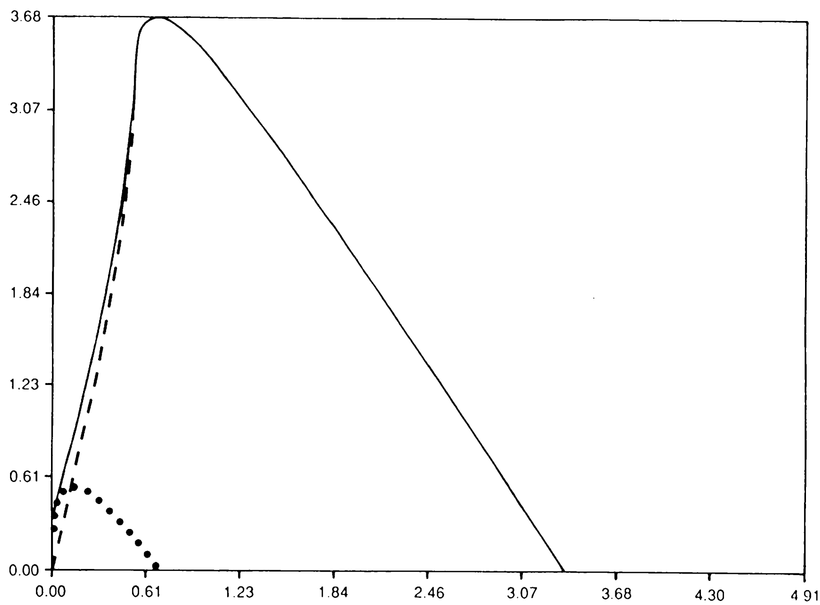

FIG. 3(b). Total reduction in liquid + solid surface area vs. liquid volume added for the wetting of two adjacent spheres of radii 1 and 0.5 containing a spherical cavity of radius 0.1 : $r_2 = 1$, $r_1 = 0.5$, $h = 0$, $r_{cav} = 0.1$. The solid line is the optimal curve, while the dotted line and the dashed line represent the extreme cases of filling only the neck or the cavity, respectively. Remember that the optimal configuration will have maximal reduction in total surface area for a given liquid volume.

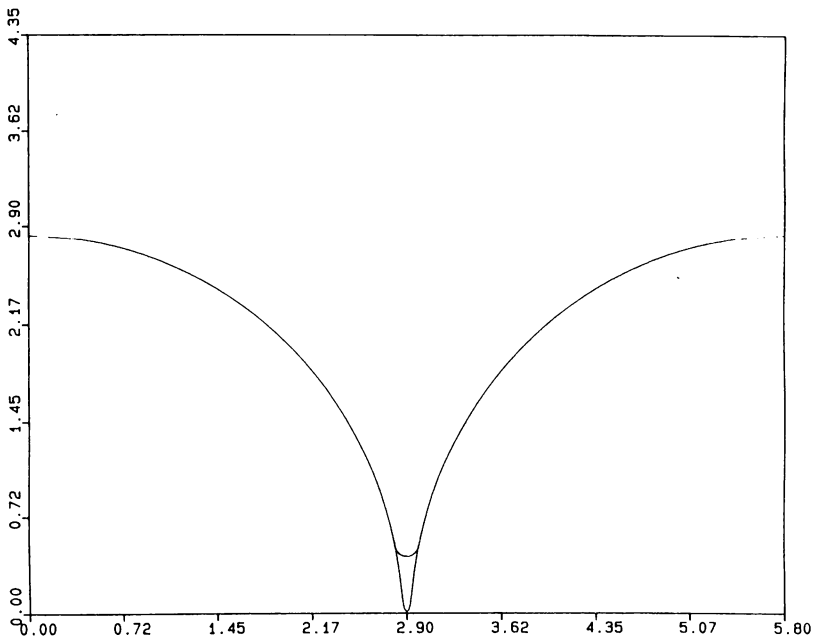

FIG. 4(a). Delaunay curve y_c of negative mean curvature λ for the wetting of Delaunay surface y_s with positive mean curvature λ_s. $\lambda < 0$.

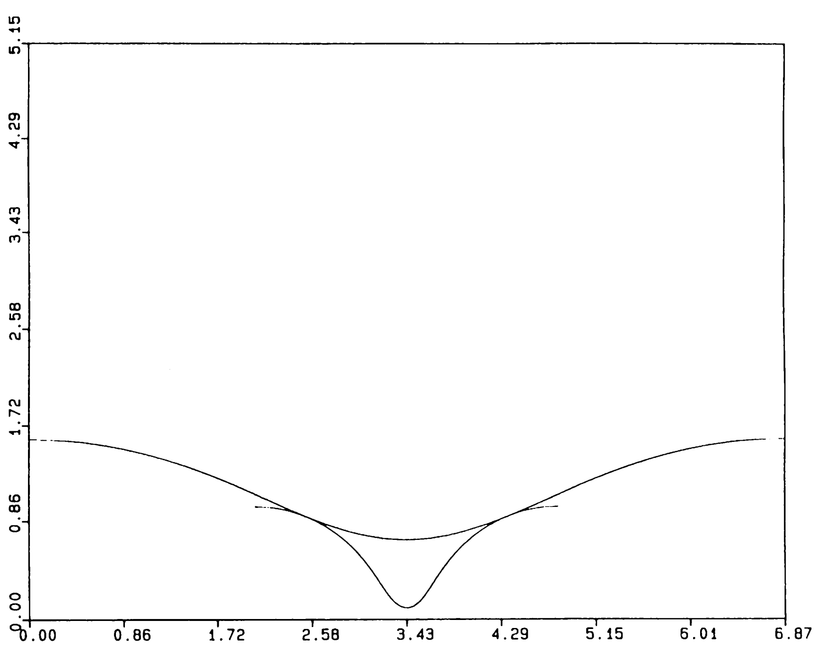

FIG. 4(b). Delaunay curve y_c of positive mean curvature λ for the wetting of Delaunay surface y_s with positive mean curvature λ_s. $\lambda > 0$.

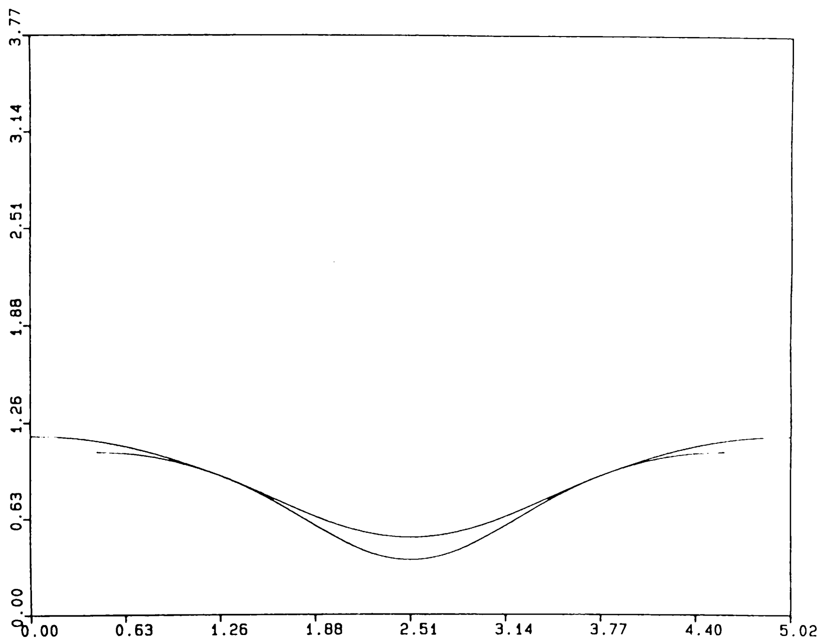

FIG. 4(c). Delaunay curve y_c of positive mean curvature λ for the wetting of Delaunay surface y_s with positive mean curvature λ_s. $\lambda > 0$.

V. Conclusions. We demonstrated the role played by Delaunay curves and associated Delaunay surfaces in the description of the wetting of axisymmetric solids. We derived analytic conditions restricting the pieces of a Delaunay curve to be used in a wetting problem. These conditions play a central role in any numerical effort aimed at finding solid-liquid configurations with minimum area. We presented several important examples that demonstrate many of the typical situations encountered in the wetting of axisymmetric bodies generated by rotating a piecewise continuous function $g(x)$.

In order to keep the discussion manageable, we have foregone a detailed treatment of the global optimization aspects of the problem, but it is obvious that, even in these rather simple examples, questions of global optimality determine the choice of the right combination of Delaunay curves. Thus it becomes even more imperative to understand the properties of these curves, since knowledge of the locally optimal solutions is necessary for the determination of the global optimum. We plan to discuss these global questions in a forthcoming publication.

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VII. Appendix. The purpose of this appendix is to justify our interpretation of the mean curvature κ as the local value of the rate of change of surface area per unit volume. While this interpretation fails for a general surface, it is nonetheless valid for the types of surfaces (and allowed variations) that we consider in this paper.

Recall that our surfaces are necessarily interfaces between condensed phases and vapor. By assumption, these surfaces represent the possible shapes of optimally wetted solids and are therefore a patchwork of solid regions and liquid regions. The liquid regions have constant mean curvature and can experience two-sided variations, while the solid regions can only undergo one-sided variations since by becoming wetted they can grow only outwards. Due to this distinction, the reasoning leading to the interpretation

$$\kappa = dA/dV \tag{A.1}$$

is slightly different in the two cases.

To keep the present exposition short we restrict ourselves to showing that equation (A.1) holds everywhere on the surface except perhaps on a set of measure zero. Notably we omit the arguments for creases in the surface (where κ becomes discontinuous) and for the points on the boundary between liquid and solid regions.

Mathematically, we consider a C^0 surface S in R^3 whose mean curvature κ is piecewise continuous. Consider a point P in the surface such that κ is continuous at P. Since the surface is a manifold, it can be locally represented in the form $z = f(x, y)$ by a suitable choice of coordinates [22, 23]. The results are based on the following well-known lemma.

LEMMA. For all variations $\eta(x, y)$ of a surface $z = f(x, y)$ with continuous mean curvature $\kappa(x, y)$, the first variation of the area and the volume are given respectively by

$$\begin{aligned} \delta A &= \int \kappa \eta \, dx \, dy, \\ \delta V &= \int \eta \, dx \, dy. \end{aligned} \tag{A.2}$$

Proof. Both expressions follow directly from the definition of A, V, and κ [23].

Since we are interested only in local variations of the surface, it is sufficient to limit ourselves to variations η such that the support of η is restricted to a small neighborhood of P. Formally, we define *a variation of S at P* to mean a one-parameter family of variations η_t such that $P \in \operatorname{supp}(\eta_t)$ for all t, while $\operatorname{diameter}(\operatorname{supp}(\eta_t)) \to 0$ as $t \to \infty$. Our two cases then simply follow as corollaries.

COROLLARY 1 (liquid surface). Consider P such that the mean curvature κ is constant on some neighborhood of P. Then, for all variations η_t at P, there exists $N > 0$ such that

$$\delta A(\eta_t) = \kappa \delta V(\eta_t) \quad \text{for } t > N. \tag{A.3}$$

Proof. The corollary follows by choosing N sufficiently large so that κ is constant on the support of η_t for $t > N$ and by using the expressions for δA and δV given in the lemma.

COROLLARY 2 (solid surface). If the variations η_t are everywhere nonnegative, then

$$\lim_{t\to\infty} \frac{\delta A(\eta_t)}{\delta V(\eta_t)} = \kappa. \tag{A.4}$$

Proof. Since the variations $\eta_t \geq 0$, the mean value theorem allows us to conclude that

$$\inf_{\mathrm{supp}(\eta_t)} (\kappa) \int \eta_t \, dx \, dy \leq \delta A(\eta_t) \leq \sup_{\mathrm{supp}(\eta_t)} (\kappa) \int \eta_t \, dx \, dy . \tag{A.5}$$

The result follows since κ is continuous and $\mathrm{diam}(\mathrm{supp}(\eta_t)) \to 0$.

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