The wetted solid—A generalization of the Plateau problem and its implications for sintered materials

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A new generalization of the Plateau problem that includes the constraint of enclosing a given region is introduced. Physically, the problem is important insofar as it bears on sintering processes and the structure of wetted porous media. Some primal and dual characterizations of the solutions are offered and aspects of the problem are illustrated in one and two dimensions in order to clarify the combinatorial elements and demonstrate the importance of numerous local minima.

I. THE PROBLEM AND ITS PHYSICAL REALIZATIONS

We present a physically interesting and largely unexplored generalization of the problem of Plateau. Plateau's original problem concerns the surface of least area with a given boundary curve.[1–4] Its solutions, known as minimal surfaces, have zero mean curvature and are usually associated with soap bubbles and wire frames. A well-known generalization is the problem of minimum area with a given boundary and enclosing a given volume.[1,4] The solutions are again surfaces with constant mean curvature and are usually associated with the shape of a liquid–gas interface.

In the present work we introduce still another extension of this classic problem. The extension arises in the analysis of sintering processes and again incorporates a volume constraint while adding the constraint of enclosing a given region.

Problem: Given a region Ω and a positive real number V_Γ, find a region Γ with a smooth boundary $\partial\Gamma$ having the minimum area such that Γ contains Ω and has volume V_Γ.

Physically, this extension represents the problem of the *shape* Γ *of the wetted solid* Ω. Figure 1 illustrates the point. Some problems of this sort have been posed and solved,[5,6] but the general importance of the problem does not seem to have been previously appreciated and the purely geometric formulation given above is new.

The primary raison d'être of this paper rests on the mathematicians' traditional criterion of shedding new light on a classical problem. In addition, we introduce an example which forms the basis of further calculations[7–10] on sintering processes.

We begin by arguing that this problem indeed represents the ideal wetted solid. There are two physical interpretations. In the first, we force the liquid to cover the solid, although perhaps only with an infinitesimal layer. Since the area of the liquid–solid interface is then fixed and the area of the gas–solid interface is zero, the total surface free energy attributable to the shape of the wetted solid is proportional to the total surface area of the liquid, which leads to the conclusion that the shape of Γ minimizes such an area. In this idealization we neglect the effect of layer thickness on the energies.[11]

The second interpretation lies closer to our presently intended applications. We imagine the liquid and the solid to be very similar in their physical properties: In fact, we take them to be identical except for their ability to support a shear stress. Our motivation comes from surface melting models of sintering processes.[12] In such processes the "liquid" merely represents a more mobile form of the solid. Specifically, we assume that the liquid and solid are so similar that the energy per unit area for the gas–solid and gas–liquid interfaces are equal, while the liquid–solid surface tension is negligible, i.e.,

$$\sigma_{gl} = \sigma_{gs}, \quad \sigma_{ls} = 0, \tag{1}$$

where σ_{gl}, σ_{ls}, and σ_{gs} are the respective surface tensions and the subscripts refer to gas, liquid, and solid. Corresponding to a variation in the shape of the total region of liquid and solid Γ, the variation dG in total surface free energy is now the sum

$$dG = \sigma_{gl}\, dA_{gl} + \sigma_{ls}\, dA_{ls} + \sigma_{gs}\, dA_{gs}, \tag{2}$$

where the dA's are variations in the areas of the respective surfaces. Using conditions (1) on the surface tensions, Eq. (2) becomes

$$dG = \sigma_{gl}(dA_{gl} + dA_{gs}) = \sigma_{gl}\, dA_\Gamma, \tag{3}$$

where A_Γ is the area of the outer surface of the condensed phase (solid or liquid) in contact with the gas. Condition

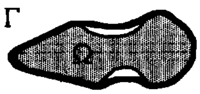

FIG. 1. The shaded solid Ω is wetted with white "liquid" to form the total object Γ, within the heavy outline, which has the given volume V_Γ.

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(3), along with $\sigma_{gl} > 0$, implies that the minimum surface free energy coincides with the minimum area for $\partial\Gamma$, the boundary separating Γ from the gas.

Our problem is related to classical capillarity problems.[4,13] The usual condition for the contact angle θ is known as the Young equation:

$$\sigma_{gs} = \sigma_{ls} + \sigma_{gl} \cos \theta. \tag{4}$$

When our assumptions on the surface tensions, Eq. (1), are substituted into Eq. (4), we find that θ should vanish. This is not surprising in light of the fact that Eq. (4) follows from the minimization of the total surface free energy given the relative worths of the areas at the interfaces. Since our formulation counts liquid and solid surfaces equally, the optimal contact angle is zero.

II. STRUCTURE OF THE SOLUTIONS

While existence and regularity are relatively easy to establish for our problem,[14] in the present development we entirely ignore such issues. We assume existence and regularity and focus on other, equally interesting aspects. After deducing some necessary conditions arising from global optimality, we turn to combinatorial aspects which follow from the fact that in general the solutions are far from unique. We show this to be the case by considering the problem first in one and two dimensions.

A. One dimension

In one dimension we are looking for a set Γ which covers (contains) a given set Ω, has given length $L(\Gamma)$, and such that it has the minimum number of endpoints, i.e., such that the cardinality $C = |\partial\Gamma|$ is minimum. While this problem is very easy, it already exhibits highly degenerate solutions with numerous local minima for even moderately complicated Ω. These features introduce the combinatorial considerations which stay with the problem in two and three dimensions. As a concrete one-dimensional example take the following union of intervals [see Fig. 2(a)]:

$$\Omega = [-3, -2] \cup [-1, 0] \cup [0.5, 1] \cup [1.5, 2]. \tag{5}$$

The minimal cardinality C^* as a function of length is

$$C^*(L) = \min|\partial\Gamma| = \begin{cases} \text{undefined}, & \text{if } L < 3, \\ 8, & 3 \leqslant L < 3.5, \\ 6, & 3.5 \leqslant L < 4, \\ 4, & 4 \leqslant L < 5, \\ 2, & 5 \leqslant L, \end{cases} \tag{6}$$

while the number of different ways of achieving C^* is

$$N(C^*(L)) = \begin{cases} 1, & \text{if } \quad L \in \{3,4,5\} \\ 2, & \text{if } \quad L = 3.5 \\ \infty, & \text{if } \quad L \notin \{3,3.5,4,\}. \end{cases} \tag{7}$$

The two possible coverings with length $L = 3.5$ are shown in Fig. 2(b).

One could further resolve the infinite solution set obtained for other values of L by deriving an expression for its volume $V(C^*(L))$. For example, for $L = 4.8$ all solutions are of the form

$$\Gamma = [-3 - x_1, -2 + x_2] \cup [-1 - x_3, 2 + x_4], \tag{8}$$

with $x_i \geqslant 0$ for $i = 1, 2, 3, 4$ and $\Sigma_i x_i = 0.8$, as illustrated in Fig. 2(c). Generalizing, we see that with the parametrization (8), the solution set for the given L is always a simplex $x_i \geqslant 0$ for $i = 1, \ldots, C^*(L)$ and $\Sigma_i x_i = L - L^*$, where $L^* = \min L$ with the given C^*. This simplex has the volume

$$V(C^*(L)) = (L - L^*)^{C^*} \sqrt{C^*}/(C^* - 1). \tag{9}$$

Fixing C at some value above C^*, the solution sets become more complicated, at least in part due to the appearance of local minima. As an example, consider $L = 4$ and $C = 6$; one "locally optimal" solution is given by $\Gamma = [-3, 0] \cup [0.5, 1] \cup [1.5, 2]$, as shown in Fig. 2(d).

B. Two dimensions

The problem in two dimensions is richer. Since a globally optimal solution is also locally optimal, we examine a portion of an optimal configuration for which we may choose a Cartesian coordinate system in which a suitable portion of the boundary $\partial\Gamma$ is given by a smooth curve $f(x)$ on an interval $[x_1, x_2]$, with Γ locally defined by $Y \leqslant f(x)$. We further divide the interval $[x_1, x_2]$ into subintervals according to whether f can have one- or two-sided variations, i.e., according to whether $f(x)$ does or does not coincide with the boundary of Ω.[15] On intervals where two-sided variations are available, the local problem is just the classic isoperimetric problem[1,4,16–18] of minimizing the length

$$L(f) = \int_{x_1}^{x_2} \sqrt{1 + f'^2}\, dx \tag{10}$$

subject to a given area

$$V = \int_{x_1}^{x_2} f(x)\, dx \tag{11}$$

and given endpoints. The classical results assure us that the solutions must be pieces of circles with radius $R = 1/\lambda$, where λ is the Lagrange multiplier from the Lagrangian $L = \sqrt{1 + f'^2} + \lambda f$. Since λ is the Lagrange multiplier corresponding to the area constraint, it must also equal the rate at which perimeter increases per unit change in area.[16–18] From this we can see that a necessary condition for global optimality is that *all such circular arcs have the same radius*! Note that this follows from the sign of the first variation, which transfers some area from one interval to another. While our

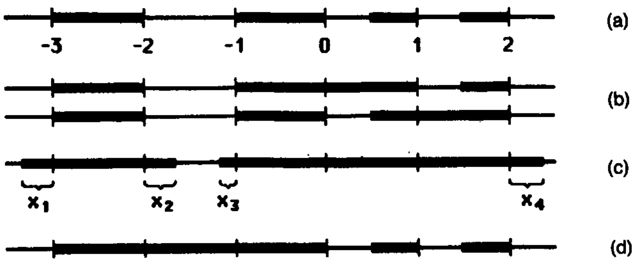

FIG. 2. (a) The one-dimensional region Ω given in Eq. (5). (b) Two possible coverings with length $L = 3.5$. (c) A generic element from the simplex of coverings with $L = 4.8$. (d) A covering with $L = 4$, which represents only a local minimum.

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arguments are local, they may be applied to any portion of $\partial\Gamma$; thus we conclude that this boundary is the union of pieces of $\partial\Omega$ and pieces of circles. We see that such circles must be tangent to $\partial\Omega$ by another local argument. Again consider a Cartesian coordinate system and an interval $[x_1,x_2]$, where the boundary $\partial\Omega$ is given by a function $Y_\Omega(x)$ and $\partial\Gamma$ makes contact with the $\partial\Omega$ in the interval. The inclusion of Ω in Γ is then expressed by the inequality

$$f(x) \geqslant Y_\Omega(x). \qquad (12)$$

Classical arguments on corner conditions with one-sided variations[19] assure us that f is tangent to $Y_\Omega(x)$ since $L_{f'f'}$ cannot vanish.

As a final global condition, we find that the curvature of the circular arcs on the "wet" portion of $\partial\Gamma$ (i.e., on the portion where it is distinct from $\partial\Omega$) must be less than the curvature of the dry portion where $\partial\Gamma$ and $\partial\Omega$ coincide. This follows from the same first variation argument we used to conclude that the circular arcs all had to have the same radii. This tempts us to attempt the construction of an optimal family of solutions for a given Ω and progressively larger areas V_Γ by "growing" the solutions along the segments of minimum curvature. While this construction gives locally optimal shapes, it can fail to take advantage of topological changes which could improve the objective, i.e., decrease total perimeter (see Fig. 3).

In fact, the physically realized state for a wetted porous medium depends in detail on the fill–drain history of the sample. Accordingly, it is of as much interest to give the density of states at a certain energy and volume as to give the shape which realizes the absolute minimum of the energy at the volume.

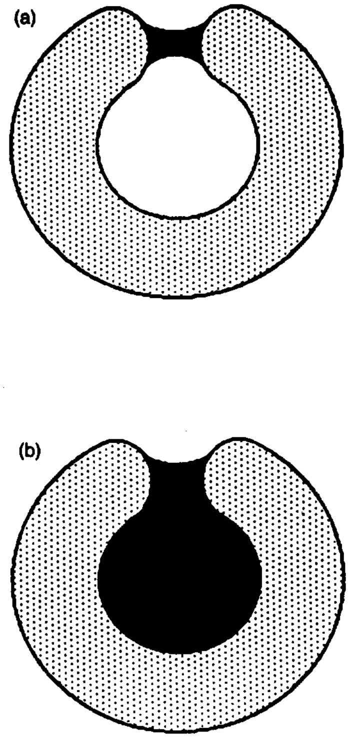

FIG. 3. The shaded solid is wetted by black "liquid" of the same mean curvature in both panels, but the difference in liquid volume is due to the past history of the system: dry in panel (a) and wet in panel (b).

C. Three dimensions

The situation in three dimensions is very similar. We again turn first to the local problem, which has been well studied and for which standard arguments guarantee existence and regularity.[1,4] Using a coordinate system, we focus on a portion of $\partial\Gamma$ such that this boundary is defined by a function $z = f(x,y)$ and Γ is locally defined by $z \leqslant f(x,y)$ for (x,y) in an interval $I = [x_1,x_2] \times [y_1,y_2]$. On this interval the problem becomes the well-known obstacle problem with a constraint. We again divide into subregions according to whether or not f coincides with $\partial\Omega$. On subregions where f is distinct from $\partial\Omega$, we are allowed two-sided variations. The problem is then one of minimizing

$$A(f) = \int_I \sqrt{1 + f_x^2 + f_y^2}\, dx\, dy \qquad (13)$$

subject to the constraint of the given volume

$$V_\Gamma = \int_I f(x,y)\, dx\, dy, \qquad (14)$$

where f_x and f_y are partial derivatives of f with respect to x and y. This gives the Lagrangian

$$L = \sqrt{1 + f_x^2 + f_y^2} + \lambda f, \qquad (15)$$

whose extremals are surfaces with constant mean curvature:

$$\bar{\kappa} = (1/R_1 + 1/R_2)/2 = \lambda, \qquad (16)$$

where R_1 and R_2 are the radii of curvature in two conjugate directions and λ is again the Lagrange multiplier corresponding to the volume constraint. As before, λ represents the rate at which surface area must increase per unit increase in volume; thus the global solution must consist of pieces of $\partial\Omega$ and pieces that are surfaces of constant mean curvature tangent to $\partial\Omega$. By the same first-order variational argument employed above, we find that the mean curvature of all these pieces must be the same and it must be greater than the mean curvature anywhere on the portion of $\partial\Gamma$ which coincides with $\partial\Omega$. The tangency of f where it again meets $\partial\Omega$ follows by standard results on one-sided variations.

Physically, we can understand the solutions as puddles forming on the solid skeleton provided by Ω. The fact that all the puddles have the same mean curvature results from the familiar equation[20,21]

$$p_1 - p_2 = 2\sigma\bar{\kappa}, \qquad (17)$$

which relates the pressure drop $p_1 - p_2$ across an elastic surface to the surface tension σ and mean curvature $\bar{\kappa}$ of the surface. The constancy of $\bar{\kappa}$ then follows from the equilibrium condition that the liquid pressure be the same in all the puddles.

To gain further physical insight, we introduce a dual realization of our problem. We again consider Ω to be the solid skeleton, but rather than covering Ω with a given volume $V_\Gamma - V_\Omega$ of liquid which wets the surface, we cover it with an elastic skin with constant surface energy density σ and envision pumping a gas at a given pressure p_2 into the compartment between Ω and the skin while fixing the exter-

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nal pressure at a level p_1 which is sufficiently large to guarantee that the elastic skin is everywhere pressed firmly against the solid when $p_2 = 0$. We will refer to this problem as the bean-in-a-bag or "Christo" problem. It is clear from this model, which involves pockets of gas, that the separation of the elastic skin will occur first from points of large mean curvature $\bar{\kappa}$, thereby reducing the surface area the most. In fact, the Christo problem helps by providing a physical realization of a dual in which the givens are Ω and $\kappa_{\min}$. In this dual formulation, the problem is to find the region Γ with the minimum volume which contains Ω and whose mean curvature is everywhere greater than or equal to $\kappa_{\min}$. Achieving a given $\kappa_{\min}$ requires pumping the gas under the elastic skin with a given pressure $p_2 = p_1 - 2\sigma\kappa_{\min}$. We could also characterize the problem by asking for the smooth surface containing Ω and volume V_Γ which has the largest value of the minimum mean curvature.

D. Two properties

We conclude this section with two general and yet powerful properties of the class of solutions. We will refer to the first of these as the *layering property*: Let Γ be a solution to the problem given Ω_0 and V and let $\Omega_0 \subset \Omega_1 \subset \Gamma$; then Γ is also a solution to the problem given Ω_1 and V.

The proof is immediate. The layering property derives from the fact that when some of the liquid covering a wetted solid freezes, its freezing does not affect the shape of the liquid above it, i.e., of the new wetted solid (assuming that the liquid does not change its volume upon freezing).

The layering property hints at a universality of structure among solutions to the problem which we pursue a little further here. To see this we define an equivalence relation on the family of solid skeletons. Formally, we say that Ω_1 is equivalent to Ω_2 at volume V and write

$$\Omega_1 = {}_V\Omega_2, \tag{18}$$

provided that there exists a region Γ which solves the wetted solid problem with Ω_1, V as data and, also, the problem with Ω_2, V as data. That is to say that by the time we have covered up Ω_1 or Ω_2 to a level V, their distinctive jagged features have been covered over by the puddles. This leads to something resembling ultrametricity among the set of states containing a skeleton Ω_0 and having a given volume. The associated "distance" can be thought of as the total fill–drain volume needed to reach Ω_1 from Ω_2.

As the final property, we mention *scale invariance*. Specifically, let Γ be a solution of the problem for Ω and V and let μ be a scale factor for the map sending (x,y,z) to $(\mu x,\mu y,\mu z)$ in some coordinate frame. Then the region $\mu\Gamma$ solves the problem for given $\mu\Omega$ and $\mu^3 V$.

III. APPLICATIONS

Because of its relation to porous media and sintered materials, the case where Ω is a lattice of packed spheres is of great interest.[5–10] For values of V_Γ near V_Ω, solving the problem is equivalent to locating the puddles in the necks surrounding the points of tangency between spheres. Puddling grows until the liquid or mobile "phase" attains a volume $V_1 = V_\Gamma - V_\Omega$ at which these puddles first come into contact. For a lattice of identical spheres, the "liquid" layer becomes connected at this stage, while patches of solid $\partial\Omega$ still show through. In the next stage, Γ has a surface of constant mean curvature with the topology of a three-dimensional lattice: We may suppose for the present that it belongs to the recently announced class of periodic complete surfaces of constant mean curvature.[22] Once the given volume V_Γ increases considerably beyond this value, the solution Γ begins to include filled pockets delineated by four spheres in mutual contact. Note that the Christo representation no longer works in the regime where pockets become filled. While there are many equivalent ways of filling such pockets for identical spheres, the order in which the pores are filled in a real porous material can make small differences and create many local optima. Finding the global optimum is then a problem of the modern "programming" sort and probably best attacked by methods such as simulated annealing.[23] Since the state of the real physical system is to a large extent dependent on its fill–drain history rather than on the true minimum of the free energy, the global optimum is again of secondary interest to counting the number of states at a certain level of suboptimality.

While we have referred to our problem as the problem of the wetted solid, it is important to note that our "liquid" merely represents mobile pools of material which can be redistributed along the surface of the solid. Realizations of interest include sintered materials, wetted porous media, and precipitates from saturated solutions. Nonetheless, in pursuing the example of the structure of a wetted collection of packed spheres, it is convenient to make intuitive arguments which treat the material that has been transported to the "necks" as though it were a liquid. That is not to say that this pool of material *is* a liquid; it is only to say that it is able to respond to surface tension forces (surface free energy differences) faster than the rate at which new material is supplied or transported to the mobile pool. This is certainly valid for sufficiently small neck sizes. It is also an excellent approximation even for large neck sizes for materials that respond quickly to local surface tension. One case in which this is likely is precisely that of a liquid surface.[24] Searching for conditions that give rise to surface melting was in fact the original motivation for investigating this class of problems. The possibility of a solid skeleton coated by a liquid that is identical to the solid in all ways except for its ability to support a shear stress was instrumental in the isolation of the zero-contact-angle case of the classical theory for the distribution of liquids on a solid.

Applications typically involve a one-parameter family of such problems. For the case of sintering, Ω evolves as sintering progresses. For another class of problems, the family of solutions is indeed well parametrized with Ω as the solid matrix which does not change as V_Γ increases and decreases. This could represent the growing together of precipitated particles immersed in a saturated solution which fills the pore spaces or the equilibrium structure of a liquid which wets a porous medium.

IV. TWO IDENTICAL SPHERES—AN EXAMPLE

We illustrate the above discussions with an example involving two identical spheres in point contact. This example

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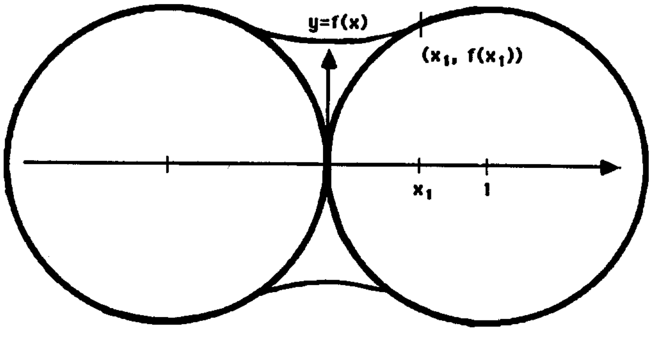

FIG. 4. Notation used for the example of two touching unit spheres, with a small amount of "liquid" filling the neck between them.

is the building block for treating a lattice of spheres in the regime before the puddles in the different necks touch each other. The rotational symmetry of the example allows the problem to be characterized using surfaces of revolution, thus reducing the associated partial differential equations to ordinary differential equations. Rotationally symmetric surfaces of constant mean curvature are known as Delaunay surfaces and have been extensively studied.[25,1,2,4] The problem of fitting them to enclose a given volume around an evolving skeleton Ω represents a new twist appropriate to applications of sintering processes. The one-parameter family of Ω's we consider is where the spheres gradually get smaller, releasing progressively more volume into the mobile pool.

By the scaling property, it is sufficient to solve the problem of two unit spheres in point contact and then scale the results. By symmetry, we may limit our view to the first quadrant. We use the notation of Fig. 4 for the curve $y = f(x)$, which is the generator for the surface in the region of the neck, and let

$$y = y_\Omega(x) \equiv \sqrt{1-(x-1)^2} \tag{19}$$

for y on the circle which defines $\partial\Omega$.

To find the shape of the fluid, we set up the calculus of variations problem to minimize the surface area subject to a fixed volume constraint. Formally, we ask for f, which minimizes the surface area

$$A = 2\pi\int_0^{x_1} f\sqrt{1+f'^2}\,dx + 2\pi\int_{x_1}^2 y_\Omega\,\sqrt{1+y_\Omega'^2}\,dx \tag{20}$$

subject to constrained total volume

$$V = \pi\int_0^{x_1} f^2\,dx + \pi\int_{x_1}^2 y_\Omega^2\,dx \tag{21}$$

with $f'(0) = 0$. The conditions for the point x_1, where the boundaries $\partial\Gamma$ and $\partial\Omega$ join, are $f(x_1) = y_\Omega(x_1)$ and $f'(x_1) = y_\Omega'(x_1)$. This yields the Lagrangian

$$\mathbb{L} = f\sqrt{1+f'^2} + \lambda f^2. \tag{22}$$

Letting

$$H = \mathbb{L} - f'\frac{\partial\mathbb{L}}{\partial f'} = \text{const}, \tag{23}$$

we have the Euler–Lagrange equation[16–18]

$$f' = \frac{df}{dx} = \pm\sqrt{\frac{f^2}{(H+\lambda f^2)^2} - 1}, \tag{24}$$

where H and λ are constants which must be determined from the boundary conditions. While Eq. (24) can be integrated to give f in terms of elliptic functions,[26] the evaluation of f corresponding to a situation of interest is more easily achieved numerically. Useful methods for calculation are discussed in Ref. 8. Here we mention only that the family of solutions is obtained most conveniently in terms of x_1 and that it necessitates some shooting method[27] for most ways of specifying the data for the problem. A solution with unit radius can be scaled to radius R to give $f_R(x) = Rf(x/R)$, which satisfies Eq. (24) with $H_R = RH$ and $\lambda_R = \lambda/R$ and leads naturally to $x_{1R} = RX_1$ and volume $V_{\Gamma R} = R^3 V_\Gamma$.

Note that the Euler–Lagrange equation (24) is completely independent of y_Ω. The solution depends on Ω only through the boundary conditions and in fact, it is satisfied for any solid of revolution with constant mean curvature, i.e., any Delaunay surface. The fact that the Lagrange multiplier λ coincides with the mean curvature $\overline{\kappa}$ can be seen by applying the formula for the mean curvature of a surface of revolution generated by $y = f(x)$ revolved about the x axis[28]:

$$\overline{\kappa} = \frac{1}{2\sqrt{1+f'^2}}\left[\frac{f''}{1+f'^2} - \frac{1}{f}\right]. \tag{25}$$

By inserting Eq. (24), Eq. (25) becomes $\overline{\kappa} = \lambda$.

It is interesting to note that the importance of Delauney surfaces have not been previously recognized in sintering studies, although an instance of them can be found in a previous study of porous media.[5]

The building block of two hard spheres in the small neck regime can be used to treat random or close packed arrays of spheres with known distributions of radii. The new aspects are again combinatorial.

V. CONCLUSIONS

In this paper we have introduced a new modification of the problem of Plateau. Assuming existence and regularity, we used standard results concerning the local version of the problem to deduce new global conditions. While these conditions become obvious after some reflection, they are sufficient to assemble global solutions for many physically interesting examples. We also sketched a method for obtaining the solution in a radially symmetric example important for sintering processes.

Our approach provides a realistic model of wetted porous media and is of particular importance for the understanding of sintered materials. To invoke the present solutions for a wetted solid, we have to ignore the nonideality in the form of a thickness-dependent free energy responsible for the disjoining pressure of Deryaguin.[29,30] Ours is a particularly appropriate model for the sintering processes in which some sort of enhanced surface mobility or surface melting occurs, but the formation of the melted layer is the slow variable. The present model should work very well under such conditions. In particular, it is a much better approximation to reality than the traditional models such as the circle approximation for $f(x)$ advanced by Kuczynski[31] in the

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1950's and used widely since. Our model differs by as much as 200% relative error (for small neck sizes!) and agrees better with experiment.[7,10]

The present approach stresses the importance of combinatorial methods, local minima, and density of solutions, rather than the absolute minimum. Work in this area has drifted away from an interest in the detailed shape of the surface to models for the value of the thermodynamic potential of the liquid covering Ω.[5,6,30] There remains important information to be gained from microscopic details which can supplement macroscopic phenomenology, including models of thermodynamic potentials.

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[11]This is in contradistinction to the approach taken in Refs. 29 and 30, where the effect of layer thickness on energy is assumed to be dominant.

[12]Surface melting[20,21] is a phenomenon whereby the surface of a solid melts at a lower temperature than the bulk. Sintering is the process when packed powdered material is heated (and/or pressed) to promote partial cohesion of the powder.

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