Capillary rise between planar surfaces

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Minimization of free energy is used to calculate the equilibrium vertical rise and meniscus shape of a liquid column between two closely spaced, parallel planar surfaces that are inert and immobile. States of minimum free energy are found using standard variational principles, which lead not only to an Euler-Lagrange differential equation for the meniscus shape and elevation, but also to the boundary conditions at the three-phase junction where the liquid meniscus intersects the solid walls. The analysis shows that the classical Young-Dupré equation for the thermodynamic contact angle is valid at the three-phase junction, as already shown for sessile drops with or without the influence of a gravitational field. Integration of the Euler-Lagrange equation shows that a generalized Laplace-Young (LY) equation first proposed by O'Brien, Craig, and Peyton [J. Colloid Interface Sci. **26**, 500 (1968)] gives an exact prediction of the mean elevation of the meniscus at any wall separation, whereas the classical LY equation for the elevation of the midpoint of the meniscus is accurate only when the separation approaches zero or infinity. When both walls are identical, the meniscus is symmetric about the midpoint, and the midpoint elevation is a more traditional and convenient measure of capillary rise than the mean elevation. Therefore, for this symmetric system a different equation is fitted to numerical predictions of the midpoint elevation and is shown to give excellent agreement for contact angles between 15° and 160° and wall separations up to 30 mm. When the walls have dissimilar surface properties, the meniscus generally assumes an asymmetric shape, and significant elevation of the liquid column can occur even when one of the walls has a contact angle significantly greater than 90°. The height of the capillary rise depends on the spacing between the walls and also on the difference in contact angles at the two surfaces. When the contact angle at one wall is greater than 90° but the contact angle at the other wall is less than 90°, the meniscus can have an inflection point separating a region of positive curvature from a region of negative curvature, the inflection point being pinned at zero height. However, this condition arises only when the spacing between the walls exceeds a threshold value that depends on the difference in contact angles.

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I. INTRODUCTION

The spontaneous rise of liquid confined in a capillary is one of the more striking phenomena associated with wetting. Capillary rise occurs because the free energy gained by wetting the internal surfaces of the capillary walls is sufficient to perform the work of raising the liquid mass in a gravitational potential field. Capillary action is responsible for a wide range of natural phenomena and engineering processes, including the movement of water in soils, drainage of tear fluid from the eye, water transport in plants, and the wicking action of absorbent media like concrete, plaster of Paris, sponges, and paper towels.

The theoretical analysis of capillary rise dates back to the seminal work of Laplace [2] and Young [3]. By balancing the postulated upward vertical component of force, exerted by the surface tension of the liquid meniscus at its junction with the wall, with the downward gravitational force exerted by the mass of liquid in the column, they derived the following equation for the height h_b at the base (i.e., the midpoint) of the meniscus of a liquid column in a thin cylindrical tube of diameter D:

$$h_b = \frac{4\gamma_{lv}\cos\theta}{\Delta\rho g D} \tag{1}$$

or between two vertical and parallel plates separated by a narrow distance w:

$$h_b = \frac{2\gamma_{lv}\cos\theta}{\Delta\rho g w}, \tag{2}$$

where h_b is the height of the lowest point on the meniscus above the surface of the liquid reservoir, γ_{lv} is the surface tension of the liquid-vapor meniscus, θ is the contact angle of the meniscus at the wall, using the convention in Fig. 1, $\Delta\rho$ is the difference in density between liquid and the vapor above the meniscus, and g is the gravitational acceleration. It is important to note that both these equations neglect the meniscus shape and the influence of the liquid above the base of the meniscus, which is valid only for very narrow capillaries or plate spacings. Although originally derived using a force balance analysis, these equations and others, such as the Young equation for the contact angle, have been justified by later authors using more rigorous energy balance or energy minimization analyses [1,4–10].

When a liquid is confined between two infinite, rigid, and parallel plates, and when the spacing between the plates is sufficiently small, the influence of gravity on the meniscus shape is negligible, so that the meniscus has a cross section

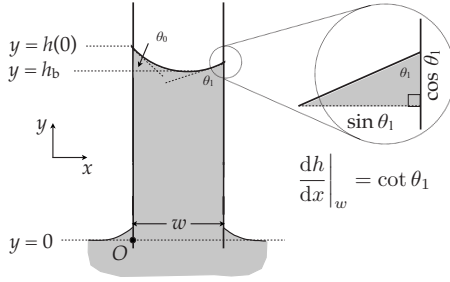---

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FIG. 1. Schematic drawing of a liquid column between vertical parallel plates, showing the convention used to specify the contact angle θ at each wall.

that is a portion of a circle, with the center of curvature lying outside the liquid if $\theta < 90°$ or inside the liquid if $\theta > 90°$. In the latter case, Eq. (2) predicts capillary depression, $h_b < 0$.

Systems involving dissimilar solids or solids with variable wetting properties have received much less theoretical attention, but nevertheless have considerable importance in a wide range of applications, including food processing [11], slip casting of ceramic slurries [12], liquid-phase sintering of composite materials [13,14], and the placement and maintenance of dental materials [15,16]. For dissimilar wall geometries, the contact angle θ_0 at one of the walls is generally different from the contact angle θ_1 at the other wall. If one of the contact angles is less than 90° but the other one exceeds 90°, Laplace commented [2] that the liquid may be elevated near the wettable wall and depressed near the nonwettable wall, so that there *may* be a point of inflection between a portion of the meniscus with negative curvature and a portion with positive curvature. Laplace went on to prove, using a balance of forces, that if such an inflection point exists on the meniscus, then that point must be pinned at zero elevation. Laplace did not, however, argue that an inflection point *must* exist whenever one contact angle is less than 90° and the other is greater than 90°, nor did he provide quantitative conditions under which an inflection point is expected. Experimental evidence that an inflection point need not exist under such circumstances was provided by O'Brien, Craig, and Peyton [1], who measured capillary rise of water between two nearly vertical glass planes, one that was glass only and another that was made of glass coated with polytetrafluoroethylene (PTFE). These authors independently measured the contact angle of water drops on the glass and PTFE surfaces and reported values of 14° and 110°, respectively, at a temperature of 27 °C, and they reported that the capillary rise of water between the two plates with spacing w was not zero, but instead fitted their model equation

$$h = \frac{\gamma_{lv}(\cos \theta_0 + \cos \theta_1)}{\rho g w}, \quad (3)$$

where ρ is the density of the liquid. These investigators do not specify whether h refers to the elevation of the lowest part of the meniscus, the highest part, or some average of the two.

We are aware of no prior publication in which strict minimization of free energy is used to predict meniscus shape and

capillary rise between dissimilar surfaces and to compare with force balance [2,3] and energy balance [1,9] analyses. Yet such an analysis seems warranted because of the question of the existence of a meniscus inflection point and, more generally, the influence of a nonwettable surface in close proximity to a wettable one. In this paper, the free energy governing these systems is formulated and variational principles are used to determine free-energy-minimizing states. The analysis makes no *a priori* assumptions about contact angle or the shape of the meniscus. Instead, the variational techniques lead naturally to a functional dependence of contact angle on the various local surface free energies, and also to a differential equation describing the equilibrium shape of the meniscus which is solved by numerical methods. The results of this approach therefore yield a general set of differential equations that can be solved to predict capillary rise and meniscus shape for any liquid and any pair of dissimilar surfaces if the relevant thermodynamic material parameters are known. Numerical solutions of the equations are used to make direct comparison with Eq. (3), and also to estimate the minimum spacing required to observe an inflection point in the meniscus.

II. THEORY

At constant temperature and volumes of the three phases in Fig. 1, the thermodynamic potential G which governs the equilibrium and stability of the system is [17]

$$G = G_b + G_g + \sum_i \gamma_i A_i, \quad (4)$$

where G_b is the energy contribution of the bulk phases in the absence of gravity, G_g is the contribution of gravitational potential energy, A_i is the area of the ith type of surface, and

$$\gamma_i \equiv \left(\frac{\partial G}{\partial A_i} \right)$$

is the surface energy density of the ith type of surface.

When a liquid is bonded to one or more solids that are inert and immobile, and when changes in the areas of the various interfaces are the only source of variation in G, then infinitesimal changes in G can be written in terms of the variations in the areas of contact between the liquid and the other phases with which it is in contact [18],

$$\delta G = \delta G_g + \gamma_{lv} \delta A_{lv} + \sum_i (\gamma_{sl} - \gamma_{sv})_i \delta A_i, \quad (5)$$

where A_{lv} is the surface area between the liquid and vapor, A_i is the area of contact between the liquid and the ith solid surface, and $(\gamma_{sl} - \gamma_{sv})_i$ is the difference between the liquid-solid surface energy and the solid-vapor energy for the ith solid surface.

The gravitational potential energy of the liquid mass in the column is described by an integral over the liquid volume in the column:

$$G_g = -\int_V \rho \vec{g} \cdot \vec{r}(x_1, x_2, x_3) dV, \tag{6}$$

where $\vec{r}$ is the position vector relative to the origin O in Fig. 1, $\vec{g}$ is the acceleration due to gravity, ρ is the density of the liquid, and we hereafter neglect the density of the vapor phase compared to that of the liquid. Using the coordinate system of Fig. 1, the integrated form of Eq. (5) and the gravitational potential energy can be summed to give the relevant thermodynamic potential for the problem at hand,

$$G = \gamma_{lv} S_{lv} L + (\gamma_{sl} - \gamma_{sv})_0 h(0) L + (\gamma_{sl} - \gamma_{sv})_1 h(w) L$$
$$+ \frac{1}{2} L \rho g \int_0^w h^2(x) dx, \tag{7}$$

where L is the length of the meniscus in the direction perpendicular to the cross section shown in Fig. 1, and now $h(x)$ is a function describing the height of the meniscus as a function of distance x from the left plate, and S_{lv} is the total arc length of the cross-section of the meniscus surface. This equation can be transformed to dimensionless form using the following dimensionless groupings of variables:

$$\Gamma = G/(\gamma_{lv} L w), \quad \alpha_0 = (\gamma_{sl} - \gamma_{sv})_0 / \gamma_{lv}, \quad \alpha_1 = (\gamma_{sl} - \gamma_{sv})_1 / \gamma_{lv},$$

$$\eta = h/w, \quad \zeta = x/w, \quad \sigma = \rho g w^2 / \gamma_{lv}. \tag{8}$$

Equation (7) is thereby transformed to

$$\Gamma(\eta, \dot{\eta}) = \int_0^1 \left(\frac{\sigma}{2} \eta^2(\zeta) + \sqrt{1 + \dot{\eta}^2(\zeta)} \right) d\zeta + \alpha_0 \eta(0) + \alpha_1 \eta(1), \tag{9}$$

where $\dot{\eta}(\zeta)$ is the first derivative of η with respect to ζ. The first term in the integrand is the contribution of gravitational potential energy, and the second term, the differential arc length element, is the contribution of the liquid-vapor surface energy. The task at hand is to find the function $\eta(\zeta)$ that leads to an absolute minimum value of Γ. The variational procedure closely follows that required for calculating equilibrium shapes of sessile liquid drops on immobile substrates, and the details are provided elsewhere [7,19]. Briefly, we assume that $H(\zeta)$ is the minimizing function, and we examine small perturbations of the meniscus of the form

$$\mathbb{H}(\zeta) = H(\zeta) + \epsilon_1 p_1(\zeta) + \epsilon_2 p_2(\zeta),$$

where p_1, p_2 are arbitrary functions with continuous first derivatives, and $\epsilon_1, \epsilon_2 \ll 1$. Substituting $\mathbb{H}(\zeta)$ into Eq. (9) and setting the gradient of Γ equal to zero as a necessary condition of equilibrium leads to three differential equations that must be satisfied [19]:

$$\frac{\partial \Gamma}{\partial H} - \frac{d}{d\zeta} \frac{\partial \Gamma}{\partial \dot{H}} = 0, \quad \zeta \in (0,1), \tag{10}$$

$$\alpha_0 - \left. \frac{\partial \Gamma}{\partial \dot{H}} \right|_{\zeta=0} = 0, \tag{11}$$

$$\alpha_1 + \left. \frac{\partial \Gamma}{\partial \dot{H}} \right|_{\zeta=1} = 0. \tag{12}$$

Equations (11) and (12) are the boundary conditions that must be satisfied at $\zeta=0$ and 1, respectively. Inspection of Eq. (9) with $\eta=H$ and $\dot{\eta}=\dot{H}$ shows that

$$\frac{\partial \Gamma}{\partial \dot{H}} = \frac{\dot{H}}{\sqrt{1 + \dot{H}^2}}$$

The boundary conditions are then seen to be

$$\alpha_0 = \frac{\dot{H}(0)}{\sqrt{1 + \dot{H}^2(0)}} = -\cos \theta_0 \tag{13}$$

$$\alpha_1 = \frac{-\dot{H}(1)}{\sqrt{1 + \dot{H}^2(1)}} = -\cos \theta_1 \tag{14}$$

where the second equality in each case arises from the fact that $\dot{H}(0) = -\cot(\theta_0)$ and $\dot{H}(1) = \cot(\theta_1)$ as shown Fig. 1. Since $\alpha_i = (\gamma_{sl} - \gamma_{sv})_i / \gamma_{lv}$, these two boundary conditions are identical to the classical Young-Dupré equation for contact angle [3]. The validity of the Young-Dupré equation for the contact angle of sessile drops on flat substrates has been scrutinized by a number of investigators [5,20–22]. The more rigorous theoretical studies based on free energy minimization seem to have settled the issue for sessile drops on deformable substrates in the absence of gravity [5] and on rigid flat substrates in the presence of gravity [22]. Although the equality of the contact angle for sessile liquid drops on a solid and in capillaries of the same solid has never been questioned, the present analysis confirms the Young-Dupré equation for capillaries.

Turning now to the Euler-Lagrange equation (10), substituting the expressions for the derivatives of Eq. (9) produces the following equivalent form,

$$\sigma H = \frac{\ddot{H}}{(1 + \dot{H}^2)^{3/2}} \tag{15}$$

To see the physical meaning of Eq. (15) more clearly, we rewrite it in terms of the physical parameters:

$$\rho g h = \frac{\gamma_{lv} \ddot{h}}{(1 + \dot{h}^2)^{3/2}} \equiv -\gamma_{lv} \kappa \tag{16}$$

where $\kappa \equiv -\ddot{h}/(1 + \dot{h}^2)^{3/2}$ is the local mean curvature of the meniscus.[1] The left side of Eq. (16) is the specific gravitational potential energy of liquid with density ρ and height h, and the right side is the increase in specific chemical potential in a liquid, over the specific chemical potential per unit volume of the surrounding vapor, when the liquid and vapor

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[1]We use the convention, common in the theory of capillary phenomena, of denoting by the term "mean curvature" a property of surfaces that is actually twice the mean curvature as it is defined in differential geometry.

are separated by an interface with mean curvature κ. Therefore, the governing differential equation for meniscus shape expresses the principle that the gravitational and capillary pressures are balanced at each point along the meniscus. A consequence of this is that any portion of the meniscus above $h=0$ must have a negative mean curvature (i.e. center of curvature outside the liquid) and, conversely, any portion of the meniscus below $h=0$ must have a positive mean curvature, thereby confirming Laplace's inference that an inflection point on the meniscus surface, if it exists, must be pinned at $h=0$.

The generalized form of the Laplace-Young equation can be obtained by integrating both sides of Eq. (15):

$$\sigma \int_0^1 H \, d\zeta = \int_0^1 \frac{\ddot{H}}{(1+\dot{H}^2)^{3/2}} d\zeta. \tag{17}$$

The integral on the left is the mean height of the meniscus, $\langle H \rangle$. Also, it is readily demonstrated that the antiderivative of the integrand of the second integral is $\dot{H}/\sqrt{1+\dot{H}^2}$. Therefore, Eq. (17) becomes

$$\sigma \langle H \rangle = \frac{\dot{H}(1)}{\sqrt{1+\dot{H}(1)^2}} - \frac{\dot{H}(0)}{\sqrt{1+\dot{H}(0)^2}}. \tag{18}$$

The two terms on the right side are given by the boundary conditions in Eqs. (13) and (14). Therefore, again substituting the physical parameters for the dimensionless ones, Eq. (18) can be rewritten as

$$\langle h \rangle = \frac{\gamma_{lv}(\cos\theta_0 + \cos\theta_1)}{\rho g w}. \tag{19}$$

Therefore, the equation proposed by O'Brien, Craig, and Peyton [1], Eq. (3), is actually an exact result *at any spacing* if the elevation is identified as the mean height of the meniscus instead of the height of the minimum point of the meniscus. When $\theta_0 = \theta_1$, Eq. (19) reduces to the Laplace-Young equation which, again, is exact at any spacing with the proviso that the relevant measure of capillary rise is the mean meniscus elevation. Recently, Roura re-derived the Laplace-Young equation (1) for narrow cylindrical capillaries using a virtual work argument [9]. He also gave an indication of how that derivation would need to be modified to account for the potential energy of the mass of liquid above the base of the meniscus in wide capillaries. The present derivation has the advantage that the Euler-Lagrange equation for the meniscus shape not only accounts for the mass of liquid above the base of the meniscus, but it also can be solved numerically to give the detailed meniscus shape at any spacing and for walls made of identical or dissimilar materials, as shown in the next section.

III. RESULTS AND DISCUSSION

The remaining task is to solve the Euler-Lagrange equation (15) subject to the boundary conditions given in Eqs. (13) and (14). Due to the nonlinear nature of Eq. (15), a computer program for solving two-point boundary value
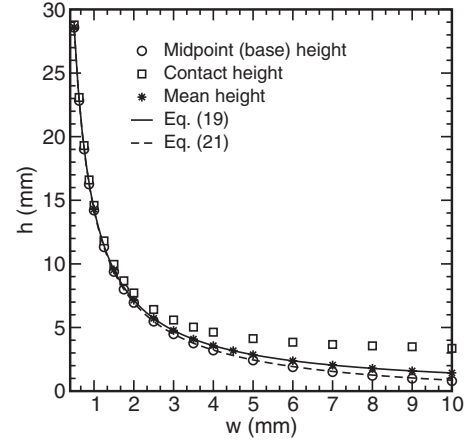

FIG. 2. Elevation of the meniscus at the midpoint between plates, at the contact line with the plate, and the mean meniscus elevation, calculated by numerical solution of Eq. (15) as a function of separation w. The solid curve is Eq. (19) for the mean elevation. The dashed curve is a plot of Eq. (21). Calculations were made with $\gamma_{lv}=72.2$ mJ/m^2, $\rho=1000$ kg/m^3, $\theta_0=\theta_1=14°$, and $g=9.8$ m/s^2.

problems using iterated deferred corrections [23–26] is used to produce particular solutions corresponding to different sets of the three input parameters $\{\sigma, \theta_0, \theta_1\}$.

Figure 2 compares the numerical solution of Eq. (15) to the Laplace-Young equation (2), as a function of the plate separation w. The figure was plotted using input parameters appropriate for pure water between two clean glass plates: $\gamma_{lv}=72.2$ mJ/m^2, $\rho=1000$ kg/m^3, $\theta_0=\theta_1=14°$, and $g=9.8$ m/s^2. These properties correspond to $\sigma=0.1357w^2$ in Eq. (8). The figure shows the calculated heights both of the base of the meniscus and of the meniscus contact with the wall. At all widths, the height predicted by the Laplace-Young equation falls between these two calculated heights, although it lies closer to the calculated base height of the meniscus. The difference between the base and contact heights of the meniscus increases with increasing separation, which is expected because, at infinite separation, the liquid still wets the glass wall but the meniscus height decreases to zero with distance from the wall. The calculated symmetric meniscus shapes are shown for glass plate separations of 0.5, 2.5, and 10 mm in Fig. 3.

The classical equations (1) and (2) are expressions for the elevation of the minimum point, or base, of the meniscus in a cylinder or between vertical plates, respectively [2]. Laplace recognized that these equations should be valid only for very narrow capillaries for which the volume of liquid above the base of the meniscus is negligible. At wider spacings, the potential energy of the liquid mass above the meniscus base becomes an increasingly important contribution to the free energy. The classical equations neglect this liquid mass above the base, and they are known to become increasingly inaccurate at wider spacings. Nevertheless, Eq. (19), plotted as star-shaped points in Fig. 2, is exact for any spacing.

Despite being the correct measure of capillary rise at any spacing, the mean elevation of the meniscus, $\langle h \rangle$, is more difficult to measure experimentally than the elevation at the
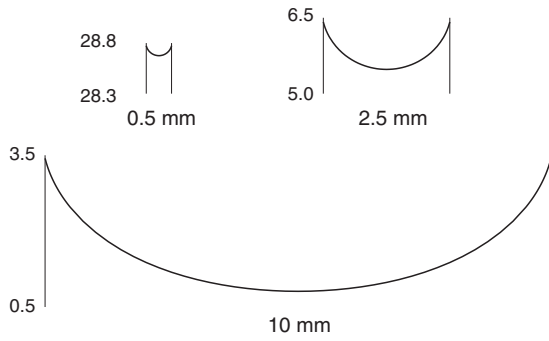
FIG. 3. Calculated meniscus shapes for water confined between two vertical glass plates with spacing of 0.5 mm (base height 28.6 mm), 2.5 mm (base height 5.5 mm), and 10 mm (base height 0.81 mm). Numbers to the left of each plot indicate the heights at the bottom and top of the vertical lines, in millimeters. Input properties are the same as for Fig. 2.
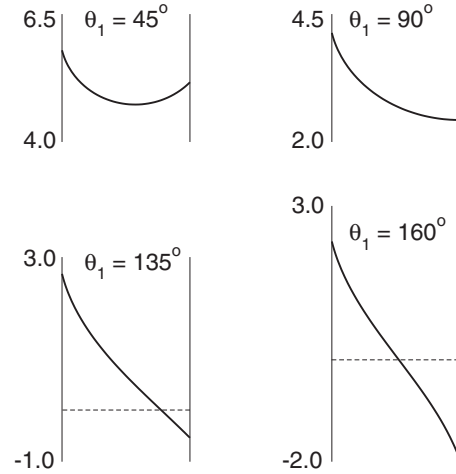

FIG. 4. Calculated meniscus shapes for water confined between two dissimilar vertical walls spaced 2.5 mm apart, showing the effect of different contact angles at the right wall. In each case, the contact angle at the left wall is assumed to be $\theta_0 = 14°$. Other input properties are the same as in Fig. 3. Numbers at the left wall of each plot indicate the heights at the bottom and top of the vertical lines in millimeters. The horizontal dashed lines indicate zero elevation.

midpoint (or base). Therefore, it is desirable to find an equation that adds a correction to Eq. (19) so that it predicts the base elevation up to wider spacings. Laplace himself indicated that the correction to Eq. (2) should be first order in w [2]. For capillary rise of water in large glass cylindrical tubes of diameter D, in which the contact angle is very small, Richards and Coombs [27] fitted their experimental data using a first-order correction to Eq. (1),

$$h_b = \frac{4\gamma_{lv}\cos\theta}{\Delta\rho g D} - \frac{D}{6}. \tag{20}$$

One also could derive a linear correction term to Eq. (2) for capillary rise between vertical plates. However, these kinds of first-order corrections must have a limited value because, as $w \to \infty$, the correction becomes arbitrarily large while the primary term becomes arbitrarily small, leading to the absurd conclusion that $h_b \to -\infty$ as $w \to \infty$. Similarly, for contact angles approaching 90° from below, the primary term becomes arbitrarily small, but the correction term remains finite, again leading to the absurd conclusion that $h_b < 0$ when $\theta \to 90°$ from below. A more satisfying correction term not only should converge to zero as $w \to 0$, but also should converge to zero as $w \to \infty$. Based on these requirements, we propose the following equation for the elevation of the meniscus base, in which the lead term is Eq. (19) with $\theta_0 = \theta_1 = \theta$, and which in dimensionless form is

$$H_b = \frac{2\cos\theta}{\sigma} - f(\theta)g(\sigma)e^{-4.48\sigma^{1/8}}, \tag{21}$$

where

$$f(\theta) = 9.24\cos\theta + 2.13\cos^3\theta,$$

$$g(\sigma) = 0.834\sqrt{\sigma} - 0.024\sigma.$$

In the correction term $f(\theta) \to 0$ as $\theta \to 90°$, which is necessary because no capillary rise occurs for $\theta = 90°$ at any spacing. In addition, $g(\sigma) \to 0$ as $w \to 0$ and the exponential term ensures that the correction term converges to zero as $w \to \infty$. The numerical coefficients were obtained by a least-squares

nonlinear multiparameter fit using DATAPLOT [28], a graphical analysis software package developed at NIST. The coefficients were fitted to the numerical calculations of the base elevation using 598 combinations of θ and σ, where θ varied from 15° to 160° and σ varied from 0.03 to 870. The residual standard deviation of the fit was 0.0024. To give an idea of the quality of this correction term, for all 598 combinations of θ and σ that were investigated, the largest absolute difference between Eq. (21) and the numerical results was $\Delta H_b = 0.004$, which occurred at $\theta = 15°$ and $\sigma = 55$. For water between two glass plates, this corresponds to an absolute difference of $\Delta h_b = 0.1$ mm at a spacing of 30 mm. Equation (21) is shown as a dashed line in Fig. 2, which is seen to closely fit the numerical results for the midpoint elevation of the meniscus.

Figure 4 shows some calculated meniscus profiles for a liquid between dissimilar plates, when the spacing between plates is 2.5 mm. The figure shows the influence of the contact angle θ_1 when the contact angle θ_0 at the left wall is fixed at 14°, a typical value measured for water drops on glass substrates [1]. The meniscus profiles are asymmetric, as expected, and the height of liquid in the column decreases as θ_1 increases. For the profiles with $\theta_1 = 135°$ and $\theta_1 = 160°$, the liquid is elevated near the left wall and is depressed near the right wall; an inflection point, pinned at zero height, separates the regions of positive and negative mean curvature. This behavior was anticipated by Laplace [2]. Bikerman [20] also discusses this kind of capillary behavior for dissimilar plates, and seems to suggest as a general fact that an inflection point can be expected whenever one contact angle exceeds 90°.

The present calculations indicate that the question of the presence or absence of an inflection point in the meniscus is decided not only by the difference in contact angles, but also by the spacing between the plates. Figure 5 shows, for $\theta_0 = 14°$ and $\theta_1 = 135°$, the calculated meniscus profile when w
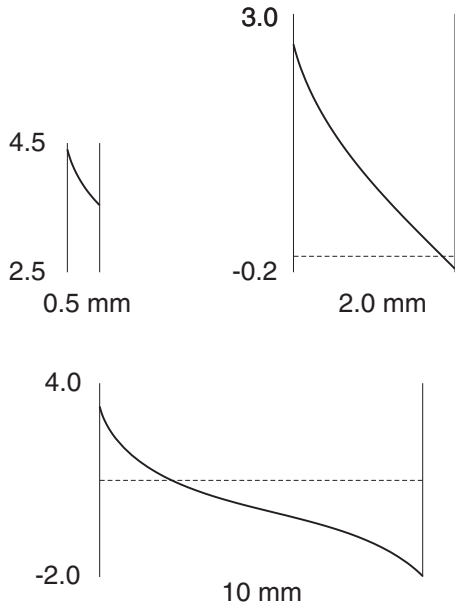
FIG. 5. Calculated meniscus shapes for water confined between two dissimilar vertical walls, shown for wall spacings of 0.5, 2.0, and 10 mm. In all three plots, $\theta_0 = 14°$, $\theta_1 = 135°$, and all other input properties are the same as in Fig. 3. In each plot, the horizontal scale is equal to the vertical scale, but the overall scale of the 10 mm plot has been reduced relative to the other two. Numbers to the left of each plot indicate the minimum and maximum heights of the vertical lines in millimeters, and the horizontal dashed lines indicate zero height.

=0.5, 2, and 10 mm. At the two wider spacings, an inflection point pinned at zero height is predicted, but when w =0.5 mm, there is no inflection point and the liquid is elevated to 3.6 mm at the less wettable wall. In fact, elevation is predicted at a wall for when $\theta_1 = 135°$ as long as σ ≤ 0.455; for water in Earth's gravity, this corresponds to a separation of $w = 1.83$ mm.

More generally, for any pair of contact angles $\{\theta_0, \theta_1\}$, for which $\theta_0 < 90°$ and $\theta_1 > 90°$, a critical value of σ can be found above which an inflection point should be observed on the meniscus. Figure 6 shows a plot of the critical value σ^* as a function of θ_1 for several different values of θ_0. The curves in this figure each can be thought of as a cut through a two-dimensional surface describing $\sigma^*(\theta_0, \theta_1)$. This surface increases without bound as one or the other of the contact angles approaches 90° from above. Clearly, σ^* is undefined when the contact angles are either both less than 90° or both greater than 90°, in which case capillary rise or depression, respectively, occurs at all spacings.

In 1968, O'Brien, Craig, and Peyton (OCP) [1] reported measurements of the elevation of water between vertical walls of dissimilar solids with various spacings up to about 1 mm, and in the same paper they proposed Eq. (3) as a modification of the Laplace-Young equation for such systems. As shown by Eq. (19), the relation they proposed is exact as long as the mean meniscus elevation is the measure of capillary rise. Reference [1] also reported careful, independent measurements of the contact angle of sessile water droplets on tilted plates of the same materials. The greatest
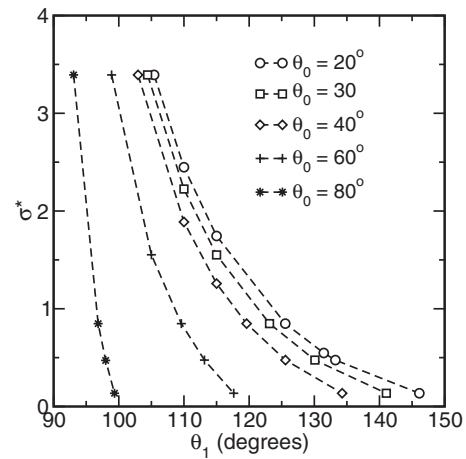

FIG. 6. Critical values of $\sigma = \rho g w^2 / \gamma_{lv}$. For a given pair of contact angles (θ_0, θ_1), σ^* is the value of σ above which an inflection point, pinned at height zero, will be present on the meniscus.

difference in down-slope contact angles they measured was between glass ($\theta = 14°$) and PTFE ($\theta = 110°$). Over the range of spacings that OCP investigated, Fig. 7 compares their measured heights to those predicted by Eq. (19) with this pair of contact angles. In addition, the minimum and maximum height of the meniscus at each width, predicted by numerical solution of Eq. (15), is also shown for the same pair of contact angles. The measured heights in the figure (stars) were obtained by linear interpolation from a digital scan of Fig. 5 in Ref. [1]. The uncertainty in the interpolation procedure is estimated to be less than 1 mm at each point. At least up to a spacing of 0.5 mm, Eq. (19) agrees reasonably well with the experimental measurements, although the measured values are systematically lower than prediction. OCP made their measurements of meniscus height using the hyperbola method, by which the two vertical plates are clamped together with a shim on one side, forming a small wedge geometry. This configuration enabled those investiga-
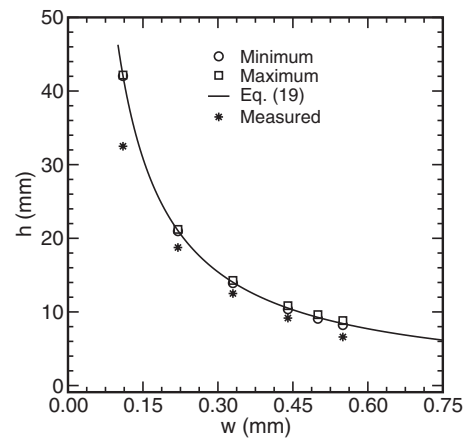

FIG. 7. Comparison of calculated meniscus elevations to experimentally measured values of capillary rise of water between a glass plate ($\theta_0 = 14°$) and a glass plate coated with PTFE ($\theta_1 = 110°$) reported in Ref. [1]. Minimum and maximum elevations at any width are calculated from numerical solutions of Eq. (15), and the mean elevation is given by Eq. (19).
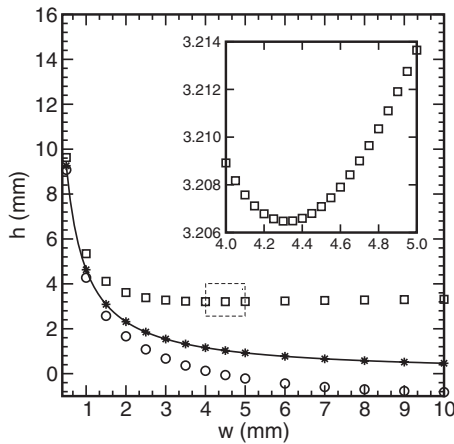
FIG. 8. Comparison of numerical solution of Eq. (15) to the OCP equation (19) (the solid curve) for capillary rise as a function of separation w when $\theta_0 = 14°$ and $\theta_1 = 110°$. Squares and circles indicate the maximum and minimum elevations of the meniscus, respectively. Other input properties are the same as in Fig. 2.

tors to access a continuous range of approximately parallel spacings between 0.1 and 0.5 mm in one experiment, but it also could lead to systematic differences in the height measured for any particular spacing due to the fact that the plates are not exactly parallel. Alternatively, it is possible that one or both contact angles at the vertical walls were greater than the advancing contact angles of sessile water drops that they measured. OCP did not attempt to measure the actual contact angles at either wall during the experiment, so it is difficult to assess the likelihood of this second possibility.

OCP did not report measurements at spacings greater than 0.5 mm, but Fig. 8 shows the prediction of Eq. (19) for spacings up to 10 mm, using the same pair of contact angles and liquid properties as in Fig. 7. The star-shaped points are the calculated mean elevation of the meniscus, calculated from the numerical solution of Eq. (15). The extrema in the meniscus elevation at each width was also obtained from the numerical solutions and are shown in Fig. 8 for comparison. As expected, the meniscus always obtains its maximum elevation at the glass wall and always obtains its minimum elevation at the PTFE wall.

In systems with one wall having $\theta > 90°$ and the other wall having $\theta < 90°$, an interesting phenomenon can occur: at the wall with $\theta < 90°$, the elevation of the meniscus may initially decrease with increasing spacing (as expected), but then reach a minimum at some intermediate spacing above which the elevation increases and converges to its asymptotic value as $w \to \infty$. This phenomenon is evident in the inset to Fig. 8. This minimum cannot occur for capillary rise between identical walls, for which the meniscus elevation decreases monotonically with increasing wall separations as shown in Fig. 2. But with dissimilar walls, the elevation at the wall with $\theta < 90°$ is influenced both by the work required to lift the liquid column against gravity and by the work required to cover a portion of wall with $\theta > 90°$. At very narrow separations, the elevation can be large, despite the proximity of the wall with $\theta > 90°$, because the work required to lift the narrow column against the gravitational field is small. At infinite

wall separation, the wall with $\theta > 90°$ has no influence on the meniscus shape near the wall with $\theta < 90°$, and the meniscus elevation at that wall therefore has a well-defined value determined by a balance of the work required to lift the liquid and the work supplied by wetting that wall. At intermediate separations, however, both gravity and the proximity of the wall with $\theta > 90°$ act to reduce the elevation. The combination of the two influences can lead to a minimum in the elevation at the wall with $\theta < 90°$.

Our analysis in this paper has been restricted to the simple two-dimensional geometry of parallel plates. However, the same procedure can be readily applied to axisymmetric cylindrical geometries and the qualitative results are expected to be the same as found here for identical parallel plates. For example, the Laplace-Young equation (1) for cylinders should be valid for any diameter with the proviso that the capillary rise is measured by the mean elevation of the meniscus. For three-dimensional geometries involving dissimilar surfaces, the analysis generally would become more complicated because of the discontinuities that arise when dissimilar surfaces intersect. One of us has addressed the wetting of fluids in small rectangular cavities for which the floor and walls have different wetting properties, which is important in the manufacture of patterned circuits by electroplating [29]. But that analysis used some simplifying assumptions about the shape of the liquid-vapor surface, and it is not immediately clear how the more rigorous treatment presented in this paper could be applied to those kinds of situations.

IV. SUMMARY

Free energy minimization has been used to formulate the differential equation and boundary conditions describing the liquid meniscus shape for capillary rise or depression between vertical plates. The equations were derived with no *a priori* assumptions about the contact angle at either liquid-solid-vapor junction, but the variational principles nevertheless lead to the mathematical requirement that the free energy can be minimized only if the classical Young-Dupré equation for contact angle is satisfied at each wall. A generalized, exact form of the Laplace-Young equation, Eq. (19) has been derived that is applicable at any capillary spacing as long as the mean meniscus elevation is used as the measure of capillary rise. At very narrow capillary spacings, the mean elevation and the base elevation are nearly identical, but the differences become appreciable at wider spacings. Nevertheless, the base meniscus elevation is a more convenient practical measurement, especially when the walls are identical and the meniscus is symmetric about a midpoint. A relatively simple correction to the classical Laplace-Young equation, consistent with physical expectations, has been proposed and demonstrated to greatly improve the Laplace-Young predictions of the *base* elevation between identical walls at wider spacings.

When the walls each have a different contact angle with the liquid meniscus, the meniscus assumes an asymmetric shape. Liquid elevation occurs at all wall spacings when both contact angles are less than 90°, and depression occurs at all

wall spacings when both contact angles exceed 90°. However, when only one contact angle exceeds 90°, capillary elevation is still predicted, even at the nonwettable wall, as long as the dimensionless quantity $\sigma = \rho g w^2 / \gamma_{lv}$ is less than a critical value that depends on the difference in contact angles. When σ exceeds the critical value, capillary elevation still occurs near the wettable wall, but the liquid is depressed near the nonwettable wall and an inflection point pinned at zero height separates regions of positive and negative mean curvature on the meniscus. Equation (3) gives excellent agreement with the numerical solutions over the range of

separations investigated here, but again, it must refer to the average elevation $\langle h \rangle$ of the meniscus.

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[1] W. J. O'Brien, R. G. Craig, and F. A. Peyton, J. Colloid Interface Sci. **26**, 500 (1968).

[2] P. S. Laplace, *Mécanique Céleste* (Little and Brown, Boston, MA, 1839), Vol. 4, Supplements 1 (1806) and 2 (1807).

[3] T. Young, in *Miscellaneous Works of the Late Thomas Young*, edited by G. Peacock (John Murray, London, 1855), Vol. 1.

[4] R. E. Collins and J. C. E. Cooke, Trans. Faraday Soc. **55**, 1602 (1959).

[5] M. E. R. Shanahan, J. Chim. Phys. Phys.-Chim. Biol. **84**, 459 (1987).

[6] W. C. Carter, Acta Metall. **36**, 2283 (1988).

[7] J. W. Bullard and M. Menon, J. Colloid Interface Sci. **219**, 320 (1999).

[8] P. Roura and J. Fort, J. Colloid Interface Sci. **272**, 420 (2004).

[9] P. Roura, Eur. J. Phys. **28**, L27 (2007).

[10] J. W. Bullard, NIST Interagency Report No. 7272, U.S. Department of Commerce, 2005 (unpublished).

[11] Y. Fang, C. Selomulya, and X. D. Chen, Drying Technol. **26**, 3 (2008).

[12] J. S. Reed, *Introduction to the Principles of Ceramic Processing* (Wiley-Interscience, New York, 1988).

[13] M. Ahmadian, D. Wexler, T. Chandra, and A. Calka, Int. J. Mod. Phys. B **22**, 3296 (2008).

[14] M. H. Maneshian and A. Simchi, J. Alloys Compd. **463**, 153 (2008).

[15] R. J. Craig and T. K. Wang, J. Oral Rehabil. **7**, 361 (1980).

[16] M. Abourass and F. J. Patonai, Oral Surg., Oral Med., Oral Pathol. **53**, 524 (1982).

[17] J. W. Gibbs, *Thermodynamics*, The Collected Works of J. Willard Gibbs Vol. 1 (Yale University Press, New Haven, CT, 1928).

[18] A. W. Searcy, Scr. Mater. **40**, 979 (1999).

[19] J. W. Bullard and P. E. Stutzman, Cem. Concr. Res. **36**, 1548 (2006).

[20] J. J. Bikerman, *Physical Surfaces* (Academic Press, New York, 1970).

[21] B. A. Pethica, J. Colloid Interface Sci. **62**, 567 (1977).

[22] E. M. Blokhuis, Y. Shilkrot, and B. Widom, Mol. Phys. **86**, 891 (1995).

[23] J. R. Cash and M. H. Wright, *User's Guide for TWPBVP: A Code for Solving Two-Point Boundary Value Problems* (Imperial College, London, 1998).

[24] J. R. Cash, Comput. Math. Appl. **12**, 1029 (1986).

[25] J. R. Cash, SIAM (Soc. Ind. Appl. Math.) J. Numer. Anal. **25**, 862 (1988).

[26] J. R. Cash and M. H. Wright, SIAM (Soc. Ind. Appl. Math.) J. Sci. Stat. Comput. **12**, 971 (1991).

[27] T. W. Richards and L. B. Coombs, J. Am. Chem. Soc. **37**, 1656 (1915).

[28] J. J. Filliben, NBS Special Publication No. 667, U.S. Department of Commerce, 1984 (unpublished).

[29] J. W. Bullard, J. Colloid Interface Sci. **276**, 188 (2004).