Discontinuous Liquid Rise in Capillaries with Varying Cross-Sections

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We consider theoretically liquid rise against gravity in capillaries with height-dependent cross-sections. For a conical capillary made from a hydrophobic surface and dipped in a liquid reservoir, the equilibrium liquid height depends on the cone-opening angle α, the Young−Dupré contact angle θ, the cone radius at the reservoir's level R_0, and the capillary length κ^{-1}. As α is increased from zero, the meniscus' position changes continuously until, when α attains a critical value, the meniscus jumps to the bottom of the capillary. For hydrophilic surfaces the meniscus jumps to the top. The same liquid height discontinuity can be achieved with electrowetting with no mechanical motion. Essentially the same behavior is found for two tilted surfaces. We further consider capillaries with periodic radius modulations and find that there are few competing minima for the meniscus location. A transition from one to another can be performed by the use of electrowetting. Finite pressure difference between the two sides of the liquids can be incorporated as well, resulting in complicated phase-diagrams in the α−θ plane. The phenomenon discussed here may find uses in microfluidic applications requiring the transport small amounts of water "quanta" (volume < 1 nL) in a regular fashion.

Introduction

The behavior of liquids confined by solid surfaces is important in areas such as microfluidics,[1,2] wetting of porous media,[3] the creation of hydrophobic surfaces,[4,5] oil recovery,[6] and water transport in plants.[7] As the system size is reduced, the interfacial tensions become increasingly important in comparison to bulk energies and are essential in understanding the equilibrium states as well as the system dynamics.

Wetting has been studied for liquids in contact with curved surfaces,[1,8,9,10] wedges,[11,12] cones,[13−15] and topographically[16,17] or chemically modulated substrates.[18−21] However, surprises appear even for very simple geometries of the bounding surfaces. Here we focus on the rise of a liquid in capillaries with nonuniform cross-sections. When a solid capillary is immersed in a bath of liquid, the height of the contact line above the bath level h is given by

$$h = c\kappa^{-2} \cos \theta / R \qquad (1)$$

where $\kappa^{-1} \equiv (\sigma/g\rho)^{1/2}$ is the capillary length, σ is the liquid−gas interfacial tension, ρ is the liquid mass density (gas density neglected), g is the gravitational acceleration, and θ is the Young−Dupré contact angle given by $\cos \theta = (\gamma_{gs} - \gamma_{ls})/\sigma$, where γ_{gs} and γ_{ls} are the gas−solid and liquid−solid interfacial tensions, respectively.[1] The constant c is $c = 2$ for a cylindrical capillary, in which case R is the radius, or $c = 1$ for two parallel and flat surfaces separated at distance $2R$. The liquid is sucked upward if the capillary's surface is hydrophilic ($\theta < {}^1/_2\pi$), and is depressed downwards in the case of a hydrophobic surface ($\theta > {}^1/_2\pi$).[22]

Capillaries with Varying Cross-Sections

Suppose now that the capillary walls are not vertical but rather have some opening angle α as is illustrated in Figure 1. What is the liquid rise then? One can naively expect that if α is small, h changes from eq 1 by a small amount proportional to α; it is not even a priori clear whether h increases or decreases. We restrict ourselves to narrow capillaries, where $\kappa R \ll 1$ is satisfied. In this case, as will be verified below, the height is larger than the radius, $h \gg R$, and the height variations of the meniscus surface are negligible as compared to the total height.

In mechanical equilibrium, at the contact line the Laplace pressure is balanced by the hydrostatic pressure

$$P_0 + \frac{c\sigma}{r} = P_0 - \rho g h \qquad (2)$$

where P_0 is the ambient pressure and r is the inverse curvature and is given by $r(h) = -R(h)/\cos(\theta + \alpha)$.We denote R_0 as the radius at the bath level (see Figure 1) and hence $R(h) = R_0 + h \tan \alpha$.

We therefore find that the liquid rise is given by

$$\cos(\theta + \alpha) = f(\bar{h}) \qquad (3)$$

$$f(\bar{h}) = \frac{1}{c}\bar{h}(\bar{R}_0 + \bar{h} \tan \alpha) \qquad (4)$$

where the dimensionless variables $\bar{h} \equiv \kappa h$ and $\bar{R}_0 \equiv \kappa R_0$ have been used. These equations reduce to the familiar form eq 1 in the limit $\alpha \to 0$. Let us concentrate first on the case where α is

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(1) de Gennes, P. G.; Brochard-Wyart, F.; Quéré, D. *Gouttes, Bulles, Perles et Ondes*; Belin: 2002.
(2) de Gennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827.
(3) Marmur, A. *J. Colloid Interface Sci.* **1989**, *129*, 278.
(4) Bico, J.; Marzolin, C.; Quéré, D. *Eur. Phys. Lett.* **1999**, *47*, 220.
(5) Lafuma, A.; Quéré, D. *Nature Mater.* **2003**, *2*, 457.
(6) Morrow, N. R.; Mason, G. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 321.
(7) Zimmermann, M. H. *Sci. Am.* **1963**, *208*, 133.
(8) Quéré, D.; Meglio, J. M. D.; Brochard-Wyart, F. *Science* **1990**, *249*, 1256.
(9) Quéré, D.; Meglio, J. M. D. *Colloid Interface Sci.* **1994**, *48*, 141.
(10) Oron, A.; Davis, S. H.; Bankoff, S. G. *Rev. Mod. Phys.* **1997**, *69*, 931.
(11) Concus, P.; Finn, R. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 292.
(12) Hauge, E. H. *Phys. Rev. A* **1992**, *46*, 4994.
(13) Rejmer, K.; Dietrich, S.; Napiórkowski, M. *Phys. Rev. E* **1999**, *60*, 4027.
(14) Parry, A. O.; Wood, A. J.; Rascon, C. *J. Phys.: Condens. Mater.* **2001**, *13*, 4591.
(15) Parry, A. O.; Wood, A. J.; Rascon, C. *J. Phys.: Condens. Mater.* **2001**, *13*, 4591.
(16) Seemann, R.; Brinkmann, M.; Kramer, E. J.; Lange, F. F.; Lipowsky, R. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 1848.
(17) Shuttleworth, R.; Bailey, G. L. J. *Discuss. Faraday Soc.* **1948**, *3*, 16−22.
(18) Jopp, J.; Grüll, H.; Yerushalmy-Rozen, R. *Langmuir* **2004**, *20*, 10015.
(19) Hartmut, G.; Herminghaus, S.; Lenz, P.; Lipowsky, R. *Science* **1999**, *283*, 46.
(20) Brinkmann, M.; Lipowsky, R. *Appl. Phys.* **2002**, *92*, 4296.
(21) Lipowsky, R. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 40.

(22) Throughout this paper, line tension effects are ignored because the length scales considered are not small enough;[1] these effects can be incorporated as well.[23,24]

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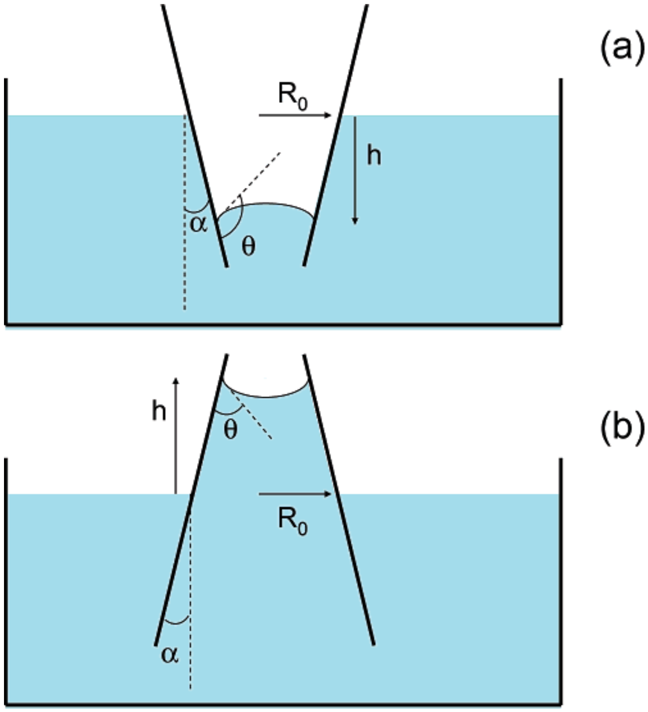

Figure 1. Schematic illustration of cone capillary or two tilted planes and definitions of parameters. Two of the possible cases: (a) hydrophobic surface, cos $\theta < 0$, positive opening angle α, and negative h. (b) hydrophilic surface, cos $\theta > 0$, negative α, and positive h.

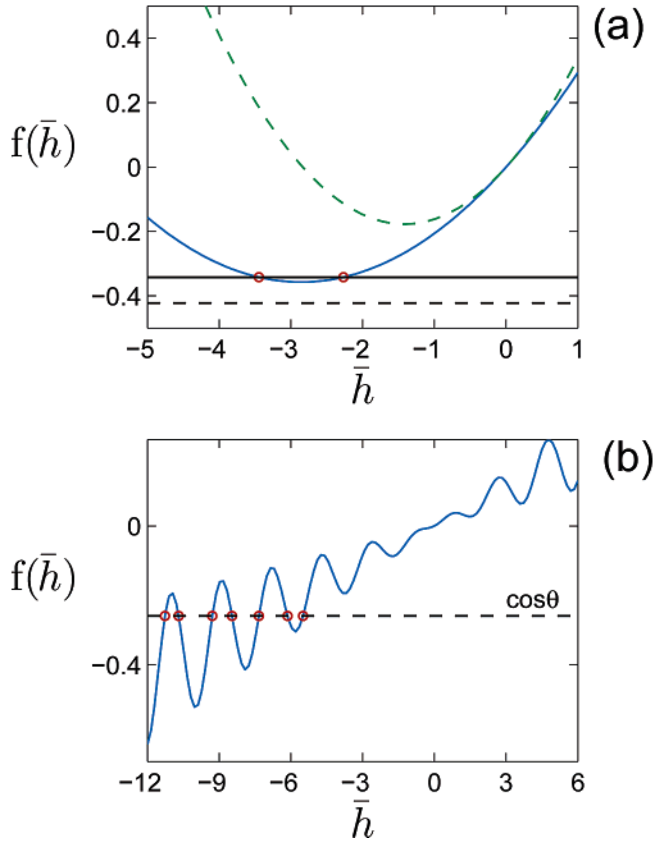

Figure 2. (a) Solid curved line is a plot of $f(\bar{h})$ from eq 4, and solid horizontal line is $\cos(\theta + \alpha)$. Their intersection occurs at two points $\bar{h}_1$ (the meniscus location) and $\bar{h}_2 < \bar{h}_1$ marked with circles. $\bar{R}_0 = 0.5$, $c = 2$, and $\alpha = 0.087$ (5°). Dashed lines are the same, but α is twice as large, $\alpha = 0.174$ (10°) above the critical angle. In this case there is no solution to eq 3, and the meniscus jumps down to the bottom of the capillary. (b) Plot of $f(\bar{h})$ in the case of periodically modulated capillary (eq 8). The horizontal dashed line is cos θ, and the multiple intersections give the possible meniscus locations. $c = 2$, $\bar{R}_0 = 0.07$, $\bar{R}_m = \bar{R}_0/2$, and $\mu = 3$.

positive and the surface is hydrophobic, cos $\theta < 0$ (see Figure 1a); the results for $\alpha < 0$ follow immediately.The left hand-side of eq 3 is then negative for small enough values of α, and the quadratic form of $f(\bar{h})$ means that the two solutions $h_1$and h_2 are negative (see Figure 2a). The stable solution is h_1 while $h_2 < h_1$ is unstable.

If the opening angle α is too large, however, the minimum of $f(\bar{h})$, attained at $\bar{h}^* = -\bar{R}_0/(2 \tan \alpha)$, is $f(\bar{h}^*) = -\bar{R}_0^2/(4c \tan \alpha) > \cos(\theta + \alpha)$, and there is no solution. Hence, for a given value of contact angle θ, the critical value of the opening angle α_c is given by the condition $f(\bar{h}^*) = \cos(\theta + \alpha_c)$. As α is increased past α_c, the meniscus "jumps" all the way to the bottom of the capillary; in the case of a nearly closed capillary this occurs at $\bar{h} = 2\,\bar{h}^*$.

When the surface is hydrophilic and both θ and α are small, then there is always a positive solution for $\bar{h}$. However, if $\theta < {}^1/_2\pi$ but $\theta + \alpha > {}^1/_2\pi$, the liquid height is negative and the jump again is possible. In essense the capillary behaves as a hydrophobic surface.

A different approach, potentially useful in applications, is that of electrowetting. In the experimental setup the opening angle α is fixed, but the contact angle may be changed with an external potential V imposed on the walls: $\theta = \theta(V)$. The change to cos θ is $\epsilon V^2/(2\sigma\lambda_D) \sim 0.3\, V^2$ and thus can be quite large (we took the dielectric constant of water and the Debye screening length $\lambda_D = 10$ nm and V is in volt).[25−27] At a fixed value of α, an increase in θ lowers the liquid height until θ reaches θ_c given by

$$\theta_c = \arccos(-\bar{R}_0^{\,2}/(4c \tan \alpha)) - \alpha \qquad (5)$$

At all $\theta > \theta_c$ the meniscus jumps again to the bottom of the capillary. However, if $\alpha < \alpha^*$, where α^* is given by

$$\sin \alpha^* = \bar{R}_0^{\,2}/4c \qquad (6)$$

the liquid height is a continuous function of θ at all θ. The threshold angle α^* is quite small; if $\bar{R}_0 = 0.1$, we find $\alpha^* = 1.25{\cdot}10^{-3}$ (0.07°).

Figure 3a is a phase-diagram in the $\alpha-\theta$ plane. In the region marked "continuous" and for positive α, $\bar{h}(\alpha, \theta)$ changes continuously. Across the critical line $\theta_c(\alpha)$ (eq 5), $\bar{h}$ changes discontinuously (meniscus is at the bottom of the capillary). Figure 3b shows the height $\bar{h}$ as a function of θ at fixed value of α. The meniscus height $\bar{h}$ decreases below zero until, at the critical value of θ, its height jumps from $\bar{h}^*$ to the capillary bottom (at $2\bar{h}^*$ if the capillary is nearly closed). Further increase of θ does not change the meniscus' location.

The liquid behavior in capillaries with negative α (Figure 1b) follows from the symmetry of the problem: the transformation $\alpha \to -\alpha$ and $\theta \to \pi - \theta$ leaves eqs 3 and 4 unchanged if $\bar{h} \to -\bar{h}$. For negative values of α, a decrease of θ from large values to small ones past θ_c leads to a jump of the meniscus to the top of the capillary.

The above insight can be used to exploring different capillaries, and we briefly mention a capillary with periodic width modulations,[28,29] namely, $R(h) = R_0 + R_m \sin(qh)$, where R_m is the

(23) Lin, F. Y. H.; Lib, D. *Colloid Surf. A* **1994**, *87*, 93.
(24) Jensen, W. C.; Li, D. Q. *Colloid Surf. A* **1999**, *156*, 519.
(25) Quilliet, C.; Berge, B. *Eur. Phys. Lett.* **2002**, *60*, 99.
(26) Quilliet, C.; Berge, B. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 34.
(27) Mugele, F.; Baret, J.-C. *J. Phys.: Condens. Matter.* **2005**, *17*, R705.
(28) Borhan, A.; Rungta, K. K. *J. Colloid Interface Sci.* **1993**, *155*, 438.

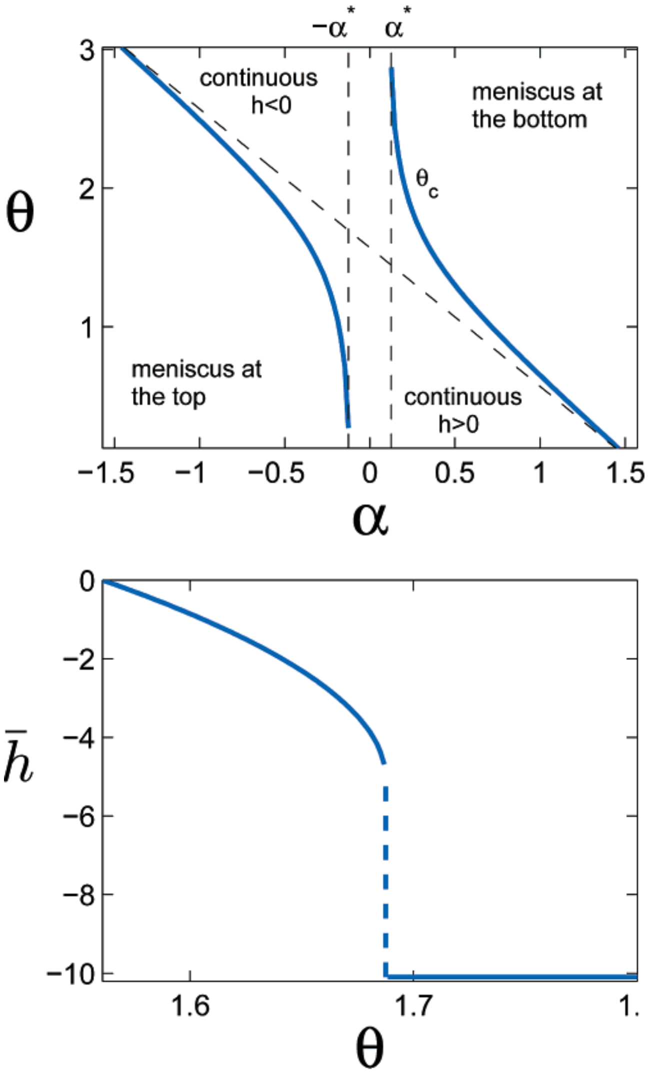

Figure 3. (a) Phase-diagram in the opening angle-contact angle ($\alpha-\theta$) plane. For positive α, solid line is $\theta_c(\alpha)$ from eq 5, separating two regions: below it, the meniscus height $\bar{h}$ changes continuously as a function of α and θ. $\bar{h}$ is positive if $^1/_2\pi - \alpha > \theta$, negative if $^1/_2\pi - \alpha < \theta < \theta_c$, and zero when $\theta + \alpha = {}^1/_2\,\pi$ (dashed diagonal line). At a given opening angle α, increase of θ past θ_c leads to a jump down of the meniscus from $\bar{h} = \bar{h}^* < 0$ to the bottom of the capillary. Above the critical line the meniscus is at the bottom. For all angles $\alpha < \alpha^*$ (see text) the behavior is continuous. The phase-diagram is symmetric with respect to $\alpha \rightarrow -\alpha$, $\theta \rightarrow \pi - \theta$ and $\bar{h} \rightarrow -\bar{h}$. Parameters are $\bar{R}_0 = 1$ and $c = 2$. (b) Meniscus location $\bar{h}$ as a function of the contact angle θ at fixed $\alpha = 0.01$, $c = 2$, and $\bar{R}_0 = 0.1$.

modulation amplitude and q its wavenumber (see Figure 4). We restrict ourselves to the long wavelength regime, where $qR_m \ll 1$. In this case it can be shown that the governing equations replacing eqs 3 and 4 are

$$\cos\theta = f(\bar{h}) \tag{7}$$

$$f(\bar{h}) = \frac{1}{c}\bar{h}(\bar{R}_0 + \bar{R}_m \sin(\mu\bar{h})) \tag{8}$$

where $\bar{R}_m \equiv \kappa R_m$ and $\mu = q/\kappa$. It is clear from Figure 2b that there are multiple solutions, half of which are maxima and the other half are minima.

(29) Sharma, R.; Ross, D. S. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 619.
(30) Levine, S.; Lowndes, J.; Reed, P. *J. Colloid Interface Sci.* **1980**, *77*, 253.

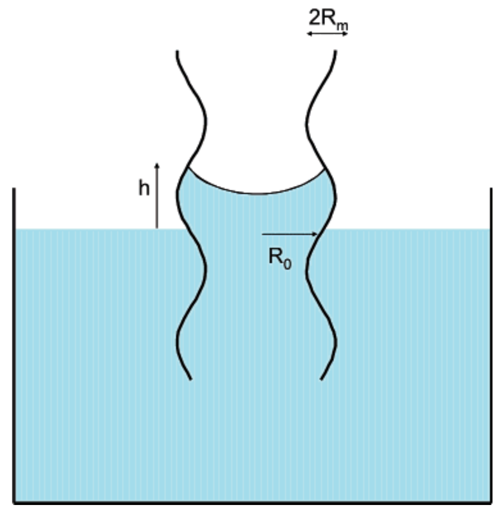

Figure 4. Schematic illustration of a capillary with sinusoidal modulations of the radius.

For a system prepared in a given minimum, increasing θ by the use of electrowetting decreases $\cos\theta$. Thus, the liquid location changes $-h$ decreases. When the liquid height overlaps with a minimum of $f(\bar{h})$, further increase of θ leads to a jump in the liquid height to the next "branch" of $f(\bar{h})$. In this way one "quantum" of liquid is depleted from the capillary; if θ is decreased, at each step one liquid unit is sucked into the capillary. The unit volume can be estimated to be $v \sim R_0^2/q$; for a capillary width of $R_0 = 100\ \mu$m and wavenumber $q = 10^3\ \mathrm{m}^{-1}$, we find $v = 10$ nL, whereas reducing the sizes to $R_0 = 10\ \mu$m and $q = 10^4\ \mathrm{m}^{-1}$ gives $v = 10^{-2}$ nL.

Nonzero Pressure Difference

It is instructive to look at situations where the pressure inside the capillary is higher than the ambient pressure p_0 at the liquid level by amount Δp, as may be relevant in many cases (e.g., micropipet). For simplicity, we derive results only for the cone and wedge capillaries. Following a straightforward procedure, we obtain the equation for the liquid height:

$$\cos(\alpha + \theta) = f(\bar{h}) \tag{9}$$

$$f(\bar{h}) = \frac{1}{c}\bar{R}_0\Delta\bar{p} + \frac{1}{c}(\bar{R}_0 + \Delta\bar{p}\tan\alpha)\bar{h} + \frac{1}{c}\tan\alpha\,\bar{h}^2 \tag{10}$$

where the dimensionless pressure is $\Delta\bar{p} \equiv \Delta p/(\kappa\sigma)$. For a positive opening angle α and $\theta > {}^1/_2\pi$, the minimum of $f(\bar{h})$ occurs at $\bar{h}^* = -(\bar{R}_0 + \Delta\bar{p}\tan\alpha)/2\tan\alpha$, and the meniscus is at a negative position if $f(\bar{h}^*) = -(\bar{R}_0 - \Delta\bar{p}\tan\alpha)^2/(4c\tan\alpha)$ is smaller than $\cos(\alpha + \theta)$. The meniscus jumps to the bottom of the capillary if $f(\bar{h}^*)$ is larger than $\cos(\alpha + \theta)$. The expression for the critical angle θ_c generalizing eq 5 is

$$\theta_c = \arccos\left(-\frac{1}{4c}\frac{(\bar{R}_0 - \Delta\bar{p}\tan\alpha)^2}{\tan\alpha}\right) - \alpha \tag{11}$$

Conversely, an increase of $\Delta\bar{p}$ from zero past a critical pressure $\Delta\bar{p}_c$ leads to a jump of the meniscus to the bottom of the capillary. $\Delta\bar{p}_c$ is given by

$$\Delta\bar{p}_c = (\bar{R}_0 - (-4c\tan\alpha\cos(\alpha + \theta))^{1/2})/\tan\alpha \tag{12}$$

In the limit $\alpha \rightarrow 0$, we find $\Delta\bar{p}_c = R_0/\alpha$, or expressed in physical units, $\Delta p_c = \bar{R}_0\kappa^2\sigma/\alpha$. An estimate using capillary radius of $R_0 = 1$ mm, $\alpha = 0.01$, $\kappa = 10^{-3}\ \mathrm{m}^{-1}$, and $\sigma = 0.1$ N/m, leads to $\Delta p_c = 10^{-1}$ atm.

The phase-diagram is shown in Figure 5 for several values of the pressure: $\Delta\bar{p} = 0.5$, 1.2, and 1.9. There are three regions:

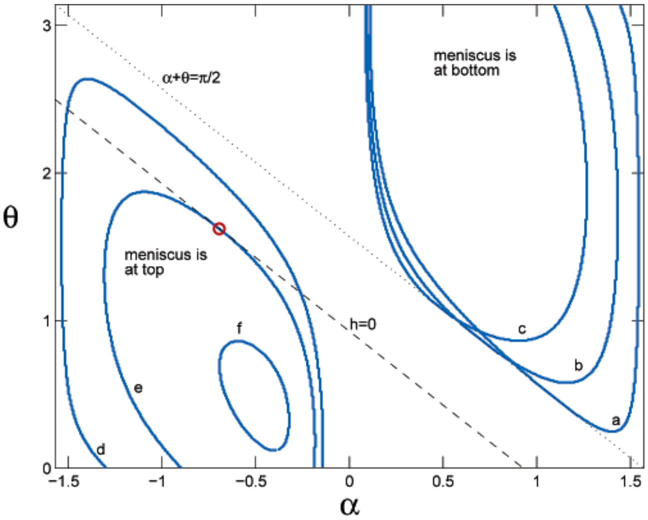

Figure 5. Phase-diagram in the ($\alpha - \theta$) plane, similar to Figure 3a but with finite pressure difference calculate for three different dimensionless pressures $\Delta\bar{p}$. At the pressure $\Delta\bar{p} = 0.5$, inside loop "a" at the right-top of the diagram, the meniscus is at the bottom of the capillary, and inside loop "d" in the left-bottom region of the diagram, the meniscus is at the capillary's top. Outside these regions the meniscus height h is a continuous function of α and θ. Curves "b" and "e" correspond to $\Delta\bar{p} = 1.2$, while curves "c" and "f" correspond to $\Delta\bar{p} = 1.9$. Dotted diagonal line is $\alpha + \theta = {}^1/_2\pi$, tangent to all loops "a", "b", and "c". Lower dashed diagonal line marks the line where $h = 0$ for the case where $\Delta\bar{p} = 1.2$ and is tangent to loop "e" at the point marked with circle (see text). We took $\bar{R}_0 = 1$ and $c = 2$.

in the first region, inside the loops "a", "b" and "c" (top-right of diagram), the meniscus is found at the bottom of the capillary. In the second region, inside the loops "d", "e" and "f" (bottom-left part), the meniscus is at the top. Outside these loops the meniscus location changes continuously as a function of α and θ. The loops "a", "b" and "c" are all tangent to the line $\alpha + \theta = {}^1/_2\pi$. At a given pressure difference $\Delta\bar{p}$, there is a line in the phase diagram where the meniscus height is zero: $\bar{h} = 0$. This line is readily found to be satisfied by

$$\alpha + \theta = \arccos(\bar{R}_0\Delta\bar{p}/c) \qquad (13)$$

This line is tangent to the loop bounding the region where the meniscus is at the top. For example, the line $\bar{h} = 0$ corresponding to $\Delta\bar{p} = 1.2$ appears tangent to the loop marked "e". If $\bar{R}_0\Delta\bar{p}/c > 1$ there is never zero liquid height $\bar{h} = 0$, and the loop at bottom-left completely disappears.

The location of the tangent point (marked with a circle) is given by two conditions for α and θ:

$$\cos(\alpha + \theta) = \frac{1}{c}\bar{R}_0\Delta\bar{p} \qquad (14)$$

$$\bar{R}_0 + \Delta\bar{p}\tan\alpha = 0 \qquad (15)$$

The first condition states that $\bar{h} = 0$ is a solution of eqs 9 and 10, and the second condition means that the solution $\bar{h} = 0$ is also a maximum of $f(\bar{h})$. Thus, as we decrease θ across the loop "e" at the tangent point (fixed values of α and $\Delta\bar{p}$), the meniscus jumps from $\bar{h} = 0$ to the capillary's top.

Conclusions

We have shown that the liquid height in capillaries with nonuniform cross-sections is a discontinuous function of the geometrical variables and the external pressure. This peculiar phase-transition is important for the understanding of liquids confined to small environments, as capillaries in practice rarely have uniform cross-sections. Indeed, since α^* can be extremely small, if the surfaces of the capillary are super-hydrophobic, very small deviations of α around $\alpha = 0$ are expected to yield discontinuous liquid heights. The current treaties is different from refs 14, 15, and 17 in that (i) it takes into account gravity forces and pressure differences and (ii) the liquid layer on top of the solid surface is connected to a big reservoir underneath the solid.

It may be beneficial to exploit the dependence of the water level on the contact angle or the pressure in, for example, microfluidic applications where it is desired to accurately control small volumes of liquid. The setup of Figure 1 could possibly be used as a switch to prevent or allow a flow of liquid or electrical current in the direction perpendicular to the plane of the paper, while the setup of Figure 4 permits it to "suck" known quantities of fluids.

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