Geometry-induced capillary emptying

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When a capillary is half-filled with liquid and turned to the horizontal, the liquid may flow out of the capillary or remain in it. For lack of a better criterion, the standard assumption is that the liquid will remain in a capillary of narrow cross-section, and will flow out otherwise. Here, we present a precise mathematical criterion that determines which of the two outcomes occurs for capillaries of arbitrary cross-sectional shape, and show that the standard assumption fails for certain simple geometries, leading to very rich and counterintuitive behavior. This opens the possibility of creating very sensitive microfluidic devices that respond readily to small physical changes, for instance, by triggering the sudden displacement of fluid along a capillary without the need of any external pumping.

capillarity | surface tension | contact angle | Young–Laplace equation

The interaction of liquids with solids has been a fertile topic for physicists, chemists, mathematicians, and engineers, providing fundamental insights into the properties of matter, for example, the necessity of attractive molecular forces (1–3), explaining the rich phenomenology of wetting (4–7) and superhydrophobicity (8–11), and leading to the development of modern microfluidic devices (12–15). One of the prototypical examples of this is the capillary rise of a liquid in a vertical tube, where the shape and location of the meniscus (the interface separating the liquid from the gas) are determined by the surface tensions, the geometry of the capillary, and the strength of the gravitational force, as firmly established by comprehensive studies spanning several centuries (16). It is somehow surprising that, in contrast, the simplest question that may be asked when a capillary is turned to the horizontal, namely, "Does the liquid spill out?," has so far remained unanswered. Here, we answer this question providing an appropriate mathematical criterion for spilling, and show that the phenomenology of a horizontally oriented capillary is distinctively richer than that of its vertical counterpart because, in this configuration, the meniscus undergoes an unbound deformation triggered by the effect of gravity that precedes the emptying of the capillary. This effect is absent in previous studies of capillarity in "horizontal" systems, like fibers (17) or grooves (18), where gravity is neglected.

Emptying

It is common experience that when a wide container, like a cylindrical glass, is partially filled with liquid and tilted slowly to the horizontal, the liquid spills out, and the glass inevitably empties. In contrast, if the container is narrow enough, like a drinking straw, the liquid remains in the container even in the horizontal position. For lack of a better criterion, the standard assumption is that the liquid will remain in a capillary of narrow cross-section and will flow out otherwise, but can one provide a definite answer that takes into account the cross-sectional shape of the capillary? To answer this question, we turn to macroscopic thermodynamics, which states that the liquid adopts the shape that minimizes the total free energy. This energy has three terms, each dependent on the shape ℓ of the meniscus:

$$E[\ell]/\gamma = \mathcal{A} - \cos\theta\, \mathcal{S} + \mathcal{G}/a^2. \quad [1]$$

Here, γ is the surface tension of the liquid–gas interface and θ is the contact angle (indicative of the affinity of the liquid toward the solid). The capillary length $a = \sqrt{\gamma/\Delta\rho\, g}$ is defined in terms of the mass density difference between the liquid and the gas $\Delta\rho$, and the gravitational acceleration g; for pure water at room temperature, $a \approx 2.7$ mm. The functional dependence of the free energy on the meniscus shape ℓ enters through three geometrical quantities: the area of the meniscus $\mathcal{A}$, the surface area of the container walls in contact with the liquid $\mathcal{S}$, and the position of the center of mass of the fluid multiplied by its volume $\mathcal{G}$. The equilibrium shape of the fluid can be obtained from minimization of [**1**], which amounts to balancing the three competing terms, subject to a constant volume condition. This can be done formally and leads to the renowned Young–Laplace equation for ℓ, which must be solved requiring the meniscus to touch the container walls at an angle θ. However, obtaining the shape of the liquid meniscus is a very demanding task in practice. Despite enormous efforts (16), hardly any analytical solutions to the Young–Laplace equation are known, except for simple containers without gravity. Here, we concentrate on the solutions to this equation when the container is a horizontal capillary of arbitrary cross-section. These show a number of remarkable features:

i) The Young–Laplace equation may or may not have a solution. The absence of a solution indicates that no meniscus can hold the liquid and, therefore, the liquid must necessarily flow out of the capillary. This contrasts with vertical (or, in general, upward-oriented) capillaries, for which the Young–Laplace equation always has a solution, except in the complete absence of gravity (16). Without gravity, the orientation is clearly irrelevant and therefore both the vertical and horizontal capillaries behave identically.

ii) For a given capillary geometry (cross-sectional shape and orientation), one may identify an emptying line in the (θ, a) plane which corresponds to the values of the parameters for which solutions cease to exist. This line separates two regions, which we refer to as "filled" and "empty."

iii) The emptying line is a critical line. All existing solutions in the filled region disappear when this line is crossed.

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Significance

We present a precise mathematical criterion that determines whether the liquid in a capillary of arbitrary cross-section will remain in it or will flow out when the capillary is at a horizontal position. The rich phenomenology found can be used to construct very sensitive microfluidics devices.

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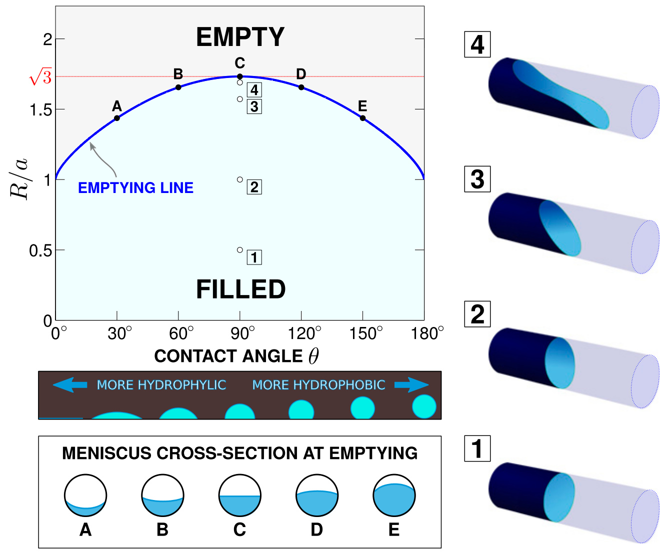

Fig. 1. Emptying line for a cylindrical capillary of radius R as a function of the contact angle θ of the liquid with the walls. The cross-section of a 3D drop of constant volume is included to illustrate the interaction of the liquid with a flat wall for different contact angles, from very hydrophilic ($\theta = 0°$) to very hydrophobic ($\theta = 180°$). The emptying line separates the filled region (where a meniscus exists) from the empty region (where no meniscus exists, which prompts the emptying of the capillary). Plots 1–4 show the deformation of the meniscus for $\theta = 90°$ as the emptying line is approached (by increasing the value of R/a), and the appearance of a liquid tongue before emptying. Plots *A–E* illustrate the cross-section of the (infinitely long) liquid tongue at emptying for five different contact angles.

In general, the meniscus obtained from solving the Young–Laplace equation spreads out progressively along the capillary as this line is approached and, close to it, small changes in the parameters produce large changes in the length of the meniscus, which becomes infinitely (arbitrarily) long when the line is reached. See 1–4 in Fig. 1.

iv) Crucially, there are different mechanisms by which the meniscus spreads out, arising from the competition between gravity (that wants the liquid to be at the lowest point of the capillary) and capillary forces (that prefer the meniscus to be near the points of highest curvature of the capillary). As a consequence, the emptying line can have different sections corresponding to different emptying mechanisms.

Computing the emptying line by the direct numerical determination of 3D menisci is impracticable due to the critical nature of capillary emptying. To avoid this, we have devised an exact reduction of the problem: Instead of minimizing the 3D functional **[1]** subject to a constant volume constraint, we minimize a 2D functional defined for the cross-section of the capillary but with variable volume. Physically, this functional represents the energy cost per unit length of a translationally invariant meniscus that extends along the horizontal capillary (*Supporting Information*). The minimizing 2D shape corresponds to the section of the (arbitrarily long) 3D meniscus that prompts the emptying of the capillary. Mathematically, this method represents a physically motivated generalization of the pioneering work of Finn on capillaries without gravity (16), and is ultimately based on the recent application of generalized Poincaré inequalities to functions of bounded variation (19).

Results

When this method is applied to a capillary with a circular cross-section of radius R, the simple emptying line of Fig. 1 is obtained. From this, we see that any circular capillary, made of any material and containing any liquid, whose radius is larger than $\sqrt{3}\,a$, will empty in the horizontal position. Likewise, any circular capillary whose radius is smaller than a will remain filled in that position, irrespective of the contact angle. Only in a narrow range of sizes $a < R < \sqrt{3}\,a$ does the contact angle θ (i.e., the choice of liquid and capillary material) exert an influence on the final outcome. This is similar to what happens to a liquid confined in a horizontal

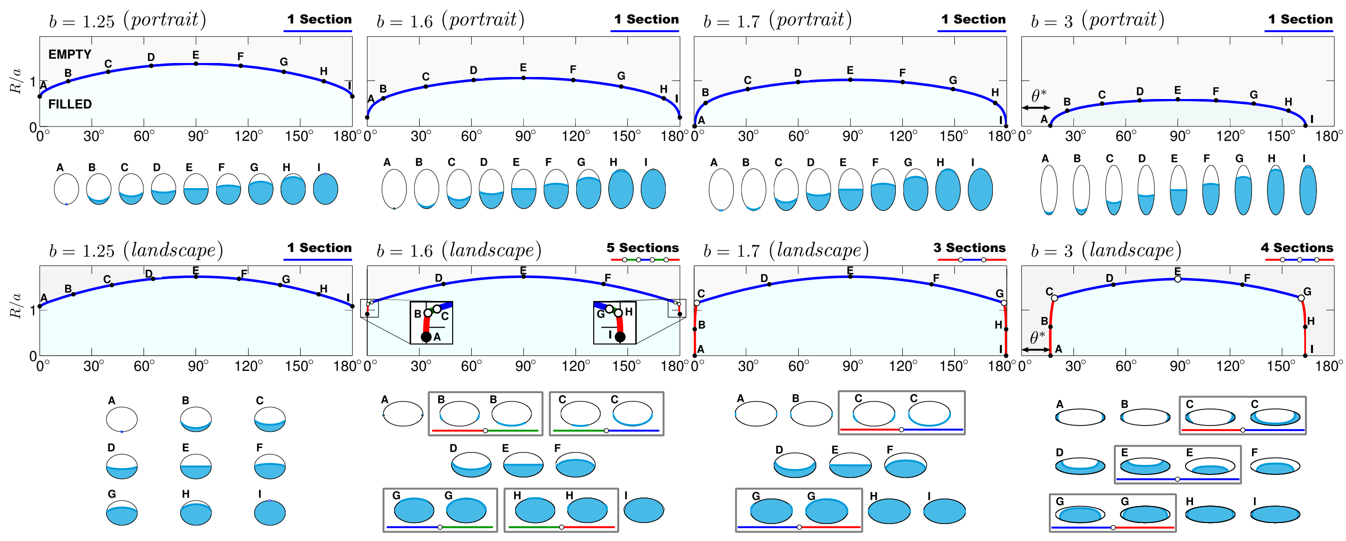

Fig. 2. Emptying line as a function of the contact angle θ for a capillary with an elliptical cross-section of semiaxes R and bR in two different orientations: portrait (*Top*) and landscape (*Bottom*). The meniscus cross-section at different points of the emptying line (circles) is shown under each diagram (*A–I*). In the portrait orientation, the emptying line lowers as b increases, and touches the line $R = 0$ for $b \geq b^* \approx 1.635$. This creates gaps of width $\theta^*(b)$ at both ends of the diagrams (not visible for $b = 1.7$, but apparent for $b = 3$) representing values of the contact angle for which the capillary empties for any size R. In the landscape orientation, gravity and capillary forces compete to place the liquid, respectively, at the lowest position or near the point of highest curvature of the capillary. This competition causes the emptying line to break into sections, each corresponding to a different emptying mechanism, including those with unconnected interfaces (red lines). At the common point of two sections (white circles), two different emptying mechanisms coexist (represented in a common box under the diagrams). The number of sections of the emptying line depends strongly on the geometry, and does not follow a simple pattern.

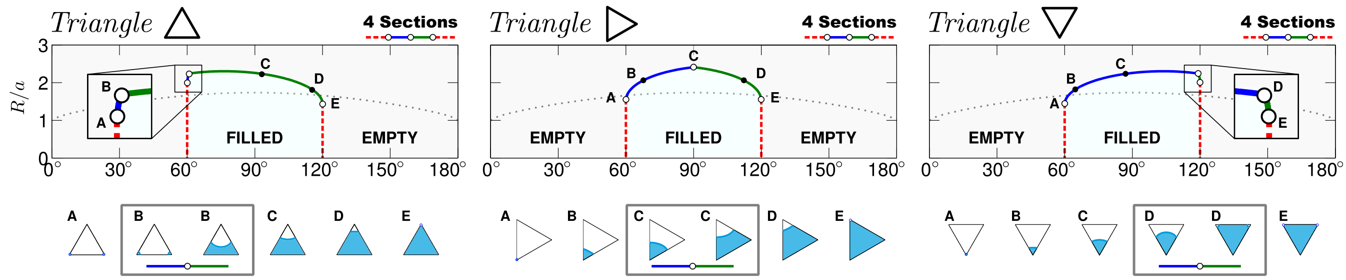

Fig. 3. Emptying line for a capillary of triangular cross-section inscribed in a circle of radius R in three different orientations as a function of the contact angle θ. The meniscus cross-section at different points of the emptying line (circles) is shown under each diagram (*A*–*E*). The existence of corners in the cross-section creates a gap in the emptying line, for which the capillary empties for any size R, similar to that of very eccentric elliptical capillaries of Fig. 2. However, unlike this latter case, the emptying line rises vertically from $R/a=0$ (dashed red lines) and, upon approaching this line from the filled region, no tongue is formed in the meniscus. The emptying line of a circular capillary of radius R is included for comparison (dotted line).

capillary slit made of two parallel walls, which is essentially a 2D phenomenon (20). Although these results roughly confirm the intuitive idea that wide capillaries empty and narrow capillaries remain filled when turned to the horizontal, the reality is very different for capillaries with noncircular cross-sections. For example, Fig. 2 shows the emptying line for capillaries whose cross-sections are ellipses of semiaxes R and bR. The emptying line is computed for progressively more eccentric ellipses and for two different orientations (portrait and landscape-like), which illustrate the extremely sensitive interplay between the different energetic contributions in [**1**]. Two features emerge that are worth emphasizing: (*i*) For sufficiently eccentric capillaries ($b>b^*\approx 1.635$), the emptying line touches the line $R/a=0$ at contact angles $\theta^*(b)$ and $180°-\theta^*(b)$. This means that, contrary to intuition, those capillaries will empty if the contact angle θ is smaller than $\theta^*(b)$ or larger than $180°-\theta^*(b)$, no matter how small they are. The line $R/a=0$ also represents the limit of vanishing gravity and, therefore, any result for that line is necessarily independent of the orientation of the capillary. (*ii*) For landscape-like elliptical cross-sections (Fig. 2), the emptying line is divided into sections corresponding to different emptying mechanisms with distinct meniscus shapes, including those that spread along the sides of the capillary rather than its bottom. At the common point of two adjacent sections, two different (yet equivalent) emptying mechanisms coexist. These common points need to be the starting points of lines of coexisting solutions in the filled region, which the present 2D-reduction approach cannot describe. All these features represent a radical departure from the simple case of the circular capillary, where emptying is essentially determined by the size R (wide or narrow containers), and there is only a single emptying mechanism.

Additional features also emerge when capillary cross-sections with edges are considered. For example, Fig. 3 shows the emptying lines of a horizontal capillary of triangular cross-section. The presence of an opening angle β in the cross-section of the capillary gives rise to a distinct emptying mechanism that takes place close to the corner. Any capillary with such an angle will empty for $\theta<(180°-\beta)/2$ and $\theta>(180°+\beta)/2$, no matter how small the cross-section is. Although this phenomenon, closely related to wedge filling (21), has already been described in the absence of gravity (22), we see here that, quite unexpectedly, it extends unaltered to appreciable values of the gravitational field (dashed red lines) that depend on the geometrical details of the capillary. Approaching these vertical sections of the emptying line, the meniscus does not develop a tongue. This is consistent with the vanishing of the meniscus cross-section on approaching the points "*A*" in Fig. 3 along the (blue) emptying line. In practice, upon crossing these vertical sections of the emptying line, the capillary will simply empty because all of the liquid in the capped end will flow out along the wedge. This has been observed in experiments at zero gravity (corresponding to $R/a=0$) (16). Note also that, as the cross-section of this triangular capillary lacks symmetry under 180° rotations, the emptying line is no longer symmetric about $\theta=90°$, as it was in the previous examples.

With the exception of the vertical sections of the emptying line that appear in capillaries with edges, the 3D meniscus develops a tongue that grows in size whenever an emptying line is approached from the filled region. This can be achieved in a number of ways: changing the contact angle [for instance, varying the temperature or using electrowetting (18, 23)], changing the gravitational acceleration (24), or simply rotating the capillary around its axis. In this way, a number of microfluidic devices can be constructed (including, for instance, those with immiscible fluids or other coexisting phases that could play the role of liquid and gas) that exploit the sharp change in the meniscus shape in response to very small physical changes, for instance, by triggering the sudden displacement of fluid along the capillary without the need of any external pressure, or by increasing the meniscus area for catalytic purposes. As we focus here only on equilibrium properties, contact angle hysteresis has not been addressed. However, earlier experimental studies in zero gravity indicate that even in the presence of large contact angle hysteresis, the meniscus behavior is consistent with the discontinuities predicted by the mathematical solution of the idealized Young–Laplace theory (24). Regarding the dynamics of capillary emptying, note that, in the growth of the tongue, the front and rear of the meniscus will be characterized by the advancing and receding contact angles, respectively. Further consequences of capillary emptying could also be envisaged for the localization of fluids in porous media.

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1. Young T (1805) An essay on the cohesion of fluids. *Philos Trans R Soc Lond* 95:65.
2. Laplace PS (1878) Traité de Mécanique Céleste. Suppléments au Livre X, 1805 and 1806, respectively. *Œuvres Complètes* (Gauthier-Villars, Paris), Vol 4. French.
3. Rowlinson JS, Widom B (1982) *Molecular Theory of Capillarity* (Clarendon, Oxford).
4. Dietrich S (1988) Wetting phenomena. *Phase Transitions and Critical Phenomena*, eds Domb C, Lebowitz JL (Academic, London), Vol 12, pp 1–218.
5. Pompe T, Herminghaus S (2000) Three-phase contact line energetics from nanoscale liquid surface topographies. *Phys Rev Lett* 85(9):1930–1933.
6. Rascón C, Parry AO (2000) Geometry-dominated fluid adsorption on sculpted solid substrates. *Nature* 407(6807):986–989.
7. Bonn D, Eggers J, Indekeu JO, Meunier J, Rolley E (2009) Wetting and spreading. *Rev Mod Phys* 81(2):739–805.
8. Quere D (2008) Wetting and roughness. *Annu Rev Mater Res* 38:71–99.
9. Tuteja A, Choi W, Mabry JM, McKinley GH, Cohen RE (2008) Robust omniphobic surfaces. *Proc Natl Acad Sci USA* 105(47):18200–18205.
10. Blow ML, Yeomans JM (2010) Superhydrophobicity on hairy surfaces. *Langmuir* 26(20):16071–16083.
11. Checco A, et al. (2014) Collapse and reversibility of the superhydrophobic state on nanotextured surfaces. *Phys Rev Lett* 112(21):216101.
12. Teh SY, Lin R, Hung LH, Lee AP (2008) Droplet microfluidics. *Lab Chip* 8(2):198–220.

13. Vogel MJ, Steen PH (2010) Capillarity-based switchable adhesion. *Proc Natl Acad Sci USA* 107(8):3377–3381.
14. Seemann R, Brinkmann M, Pfohl T, Herminghaus S (2012) Droplet based microfluidics. *Rep Prog Phys* 75(1):016601.
15. Tani M, Kawano R, Kamiya K, Okumura K (2015) Towards combinatorial mixing devices without any pumps by open-capillary channels: Fundamentals and applications. *Sci Rep* 5:10263.
16. Finn R (1986) Equilibrium capillary surfaces. *Grundlehren der Mathematischen Wissenschaften* (Springer, New York), Vol 284.
17. Princen HM (1970) Capillary phenomena in assemblies of parallel cylinders III. Liquid columns between horizontal parallel cylinders. *J Colloid Interface Sci* 30:359.
18. Seemann R, Brinkmann M, Kramer EJ, Lange FF, Lipowsky R (2005) Wetting morphologies at microstructured surfaces. *Proc Natl Acad Sci USA* 102(6):1848–1852.
19. Obersnel F, Omari P, Rivetti S (2014) Asymmetric Poincaré inequalities and solvability of capillarity problems. *J Funct Anal* 267:842.
20. Parry AO, Rascón C, Jamie EAG, Aarts DGAL (2012) Capillary emptying and short-range wetting. *Phys Rev Lett* 108(24):246101.
21. Parry AO, Rascón C, Wood AJ (2000) Critical effects at 3D wedge wetting. *Phys Rev Lett* 85(2):345–348.
22. Concus P, Finn R (1969) On the behavior of a capillary surface in a wedge. *Proc Natl Acad Sci USA* 63(2):292–299.
23. Mugele F, Baret JC (2005) Electrowetting: From basics to applications. *J Phys Condens Matter* 17:R705–R774.
24. Concus P, Finn R, Weislogel M (2000) Measurement of critical contact angle in a microgravity space experiment. *Exp Fluids* 28:197.
25. Evans R (1990) Fluids adsorbed in narrow pores: Phase-equilibria and structure. *J Phys Condens Matter* 46:8989–9007.
26. Finn R (2002) Eight remarkable properties of capillary surfaces. *Math Intell* 24:21–33.