

Supporting Information

Geometry Induced Capillary Emptying

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1 Equation for the Emptying Line

1.1 The Young-Laplace Equation

The free-energy of a liquid droplet in a capillary can be written as the following functional of the meniscus shape ℓ

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

Here, γ is the liquid-gas surface tension, θ is the contact angle of the liquid with the capillary material, and $a = \sqrt{\gamma/\Delta\rho g}$ is the capillary length, defined in terms of the mass density difference between the liquid and the gas $\Delta\rho$, and the gravitational acceleration g . 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} .

In turn, the equilibrium shape of the liquid drop is obtained from minimization of $E[\ell]$, subject to the condition that the liquid volume \mathcal{V} is fixed. Therefore, the functional to be minimized is:

$$F[\ell] = \mathcal{A} - \cos \theta \mathcal{S} + \mathcal{G}/a^2 + \lambda \mathcal{V} \quad (2)$$

where λ is the Lagrange multiplier. With an appropriate choice of coordinates (see Fig. 1), the meniscus can be represented as a function $\ell(x, y)$ and the above terms can be written for a horizontal capillary:

$$\begin{aligned} \mathcal{A} &= \int_{\Omega} dx dy \sqrt{1 + (\nabla \ell)^2} \\ \mathcal{S} &= \oint_{\partial\Omega} ds \ell \\ \mathcal{G} &= \int_{\Omega} dx dy (x \sin \phi + y \cos \phi) \ell \\ \mathcal{V} &= \int_{\Omega} dx dy \ell \end{aligned} \quad (3)$$

where Ω represents the cross-section of the capillary, and $\partial\Omega$ its perimeter. A formal minimization of (2) produces the Young-Laplace equation:

$$\nabla \cdot \left(\frac{\nabla \ell}{\sqrt{1 + (\nabla \ell)^2}} \right) = \frac{1}{a^2} (x \sin \phi + y \cos \phi) + \lambda \quad (4)$$

together with the boundary condition that the angle formed by the meniscus with the capillary walls must be θ at all points. In physical terms, the left side of this equation is (twice) the mean curvature of the meniscus at each point which, in the absence of gravity ($a \rightarrow \infty$), needs to be a constant.

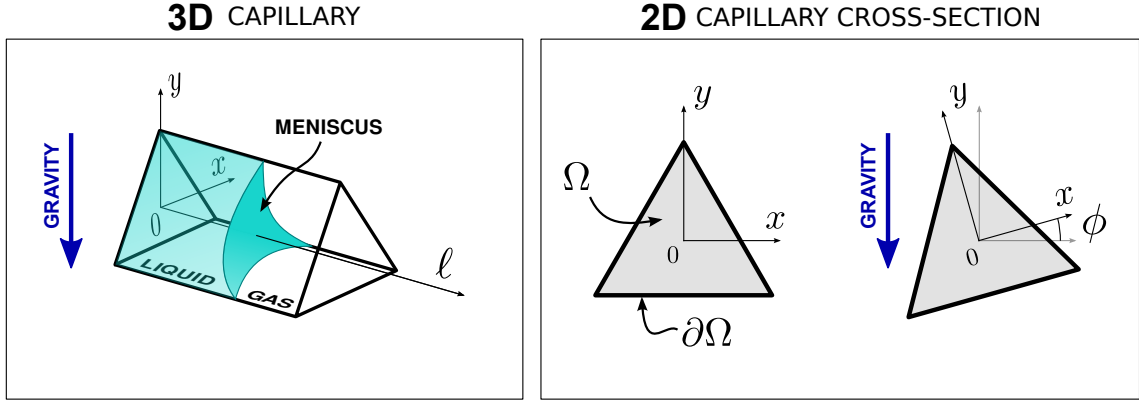


Figure 1: Schematic drawing of a capillary and its cross-section, indicating the choice of coordinates. The variable ϕ represents the rotation angle of the capillary around its longitudinal axis.

The Lagrange multiplier λ is itself determined by the constant volume condition. However, for capillaries (containers with a constant cross-section), λ is independent of the volume of liquid, provided the meniscus does not touch the end cap. This follows immediately from integration of (4) over Ω , yielding:

$$\lambda = \frac{\partial\Omega_0 \cos \theta}{\Omega_0} \quad (5)$$

where Ω_0 is the area of the capillary cross-section, and $\partial\Omega_0$ the length of its perimeter. In writing (5), we have assumed that the origin of the coordinates x and y lies along the line of the center of mass of Ω ; this choice means that λ does not depend on the turning angle ϕ . The independence of the Lagrange multiplier on volume implies that the meniscus *shape* is also independent of the volume of liquid, which is in accord with experience. In the following, we assume that the length of the capillary and volume of liquid are effectively infinite, which prevents the uninteresting influence of finite size effects in our results.

1.2 Emptying Tongue

On approaching any point on the emptying line from the filled region, the meniscus will, in general, develop a tongue of length L which diverges when the emptying line is reached (see Fig. 2). Note that, since the total energy of the meniscus, given by (1), is finite, the energy cost *per unit length* of this (in that limit, infinitely long) tongue must necessarily be zero. In other words, the emptying line must correspond to the condition that there is a translationally invariant solution to (4) with zero energy. This applies *even if no tongue develops*. To see this, note that if there exists any translationally invariant solution to (4) with negative energy, the total energy of the system, which must attain the minimum possible value, would *decrease* unboundedly by simply making a meniscus tongue with the shape of that solution progressively longer; if the total energy is negatively unbound, no meniscus shape exists that can hold the liquid in the capillary, and this must empty.

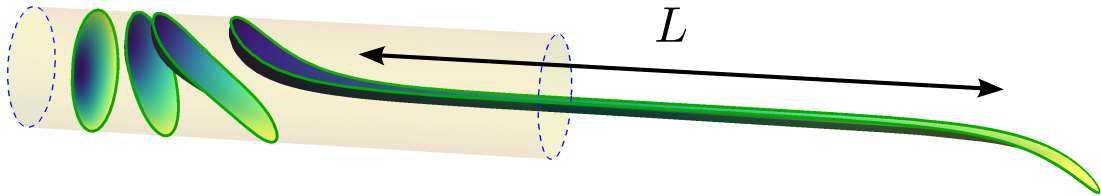


Figure 2: Schematic drawing of menisci in a horizontal capillary approaching the emptying line as the capillary length a is decreased progressively (from left to right). When the emptying line is reached (for a particular value of a), the length L diverges. Although the liquid volume is conserved, the menisci have been shifted along the capillary to facilitate representation.

1.3 Emptying Line

The existence of a translationally invariant solution to (4) with zero energy, may be formulated as

$$\min_{\eta} E^{2D}[\eta] = 0 \quad (6)$$

where E^{2D} is a two dimensional reduction of the functional (2):

$$E^{2D}[\eta] = \mathcal{A}^{2D} - \cos \theta \mathcal{S}^{2D} + \mathcal{G}^{2D}/a^2 + \lambda \mathcal{V}^{2D} \quad (7)$$

This functional represents the energy of a 2D drop of liquid η placed inside the cross-section Ω , in the grand canonical ensemble. The 2D drop η corresponds to the cross-section of the translationally invariant meniscus tongue, which is assumed to be of infinite length. In expression (7), λ is still given by Eq. (5) and, therefore, does not impose a constraint on the volume \mathcal{V}^{2D} . In fact, in this interpretation, (5) is a generalised Kelvin equation [25], and the value of λ is essentially the pressure at which there is thermodynamic coexistence between two phases: capillary liquid (a completely full capillary) and capillary gas (a completely empty capillary).

The physical argument of section 1.2 implies that no solution to Eq. (4) can exist whenever the functional (7) attains negative values. It is, therefore, a *sufficient* condition for the non-existence of solutions. The fact that it is also a *necessary* condition has been proved recently in the more mathematical context of functions of bounded variation by Obersnel *et al.* [19]. In consequence, equation (6) corresponds to the line that separates the regions of existence and non-existence of solutions to the Young-Laplace equation (4) and is, therefore, the mathematical expression of the emptying line for all capillaries with arbitrary cross-sections. Note that, in fact, cross-sections are required to be Lipschitz [19]. Broadly speaking, this means that the boundary Ω needs to be piecewise smooth, and is allowed to have kinks but not cusps; this includes most, if not all, physically relevant geometries.

Note that, owing to the symmetries of Eq. (1), the emptying line is always symmetric about $\theta = 90^\circ$ for capillary cross-sections invariant under a 180° rotation (e.g. ellipses, rectangles...), and for any up-down symmetric configuration (e.g. an equilateral triangle with a vertical side).

2 Numerical Method

In order to obtain the emptying line for a given capillary geometry (Ω and ϕ), we must solve equation (6) for each value of the contact angle θ . To do this, we find first the minimum of (7) for a given a value of the capillary length a , and compute its energy. The emptying line corresponds to the value of a for which this energy is zero. This is a deceptively difficult task for two main reasons:

- A) A formal minimization of the functional (7) yields the differential equation of a 2D drop inside the capillary cross-section under gravity, with the anticipated boundary condition that the drop must touch the capillary walls with the contact angle θ . In Cartesian coordinates, this equation reads

$$\frac{\eta''(x)}{(1 + \eta'(x)^2)^{3/2}} = \pm \frac{1}{a^2} (x \sin \phi + \eta \cos \phi) + \lambda \quad (8)$$

where the sign refers to the liquid being below (+) or above (−) the gas at the point $(x, \eta(x))$. In general, the presence of gravity precludes any analytical solution, and numerical methods must be adopted. Additionally, this equation is known to exhibit **multiple solutions** [26]. The emptying line corresponds to the smallest value of the gravity acceleration (the largest value of a) for which equation (6) is verified. If the energies of two different solutions vanish for the same value of a , this means that there exist two equivalent (yet different) emptying mechanisms for the capillary.

- B) In addition to their shape, the **location** of the drops (the starting point of integration) is not known *a priori*, which increases the complexity of the problem.

To solve these problems, we parametrize the perimeter of the capillary cross-section $\partial\Omega$ with a variable t . Each value of the parameter $t \in [-\pi, \pi)$ refers to a unique point in the perimeter $(x_{\partial\Omega}(t), y_{\partial\Omega}(t))$. Next, we define a function $\Psi(t)$, as the value of (7) that is obtained from integration of the drop equation starting at the point $(x_{\partial\Omega}(t), y_{\partial\Omega}(t))$ making the correct angle θ with the capillary wall. As the initial point of integration and the derivative are known, the integration can be performed, akin to a shooting method, ending when the drop reaches another point on the wall. In general, the contact angle condition is not verified at this second point of contact. However, since the parameter t spans the entire perimeter, all drops satisfying the contact angle condition at both points of contact are necessarily included, and occur at specific values of t . These drops correspond to the stationary points of the functional $E^{2D}[\eta]$, and appear as extrema of the function $\Psi(t)$. Note, however, that not every extremum of $\Psi(t)$ corresponds necessarily to a stationary point of $E^{2D}[\eta]$, with the exception of the global minimum of $\Psi(t)$, which is a guaranteed minimizer of $E^{2D}[\eta]$ and, indeed, its global minimum.

What makes the phenomena of capillary emptying so rich is that solutions to the Young-Laplace equation may disappear abruptly, as pointed out by Finn [26]. This means that the function $\Psi(t)$ is discontinuous, and displays an extraordinary sensitivity to the capillary geometry and to changes of the variables θ and a . This is illustrated in Fig. 3, where the two global minima of $\Psi(t)$ represent different emptying mechanisms.

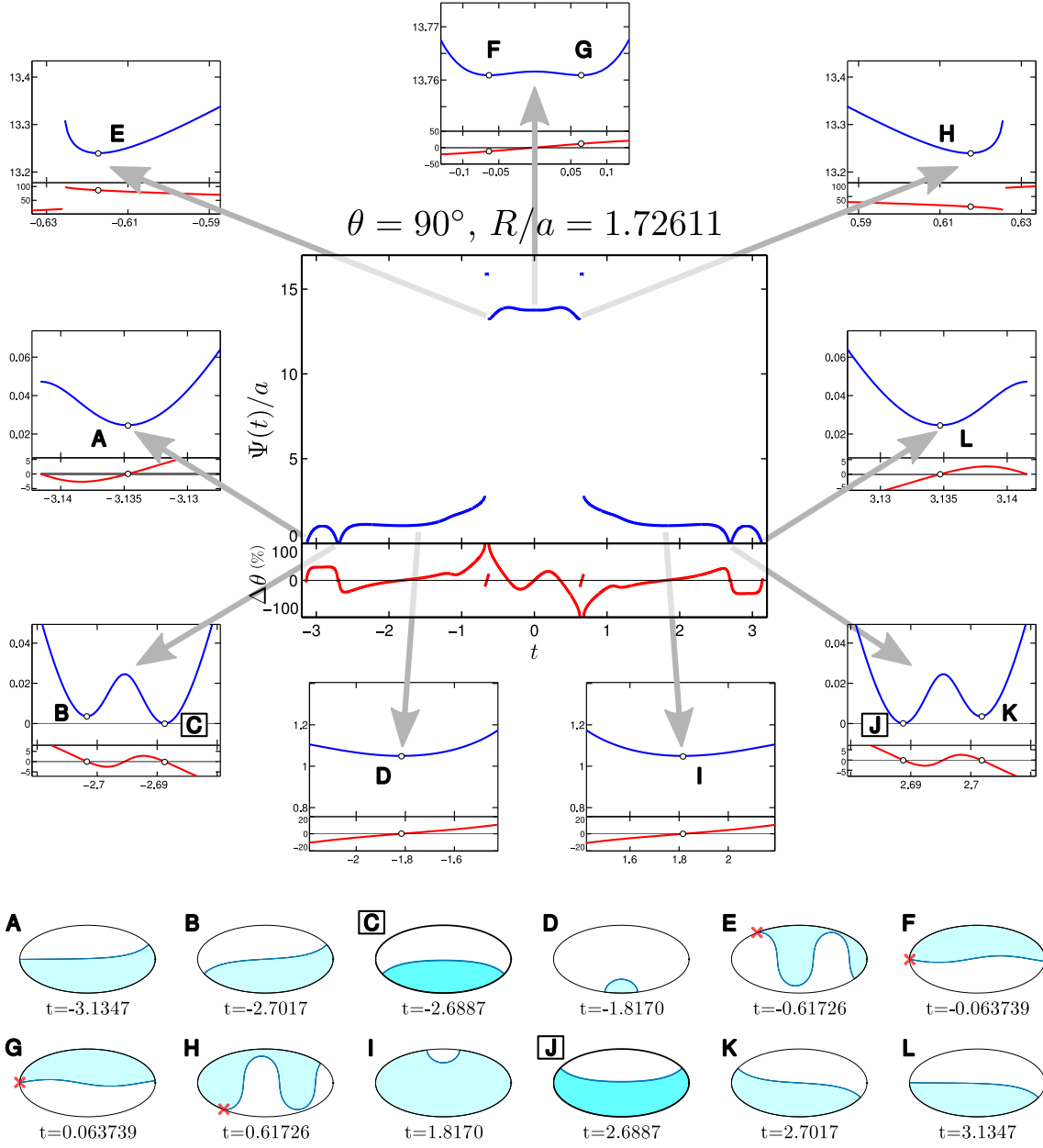


Figure 3: **Blue Line:** Function $\Psi(t)$ for the point $(\theta = 90^\circ, R = 1.72611a)$ on the emptying line of a horizontal capillary with an elliptical cross-section $(x_{\partial\Omega}^2 + \frac{1}{4}y_{\partial\Omega}^2 = R^2)$ oriented at an angle $\phi = 90^\circ$. **Red Line:** Relative error in the contact angle condition $\Delta\theta$ at the second point of contact (Check the definition of $\Psi(t)$ in the text). This error vanishes at all stationary points of the functional (7). **Blowups:** Details of $\Psi(t)$ and $\Delta\theta$ for all minima of the function $\Psi(t)$. **Plots A-L:** Drop shapes corresponding to each of the minima of $\Psi(t)$. Drops C and J correspond to the absolute minima of $\Psi(t)$ and, hence, of the functional (7); as $\Psi(t)$ vanishes at these two minima, they verify Eq. (6) and, therefore, represent equivalent (yet different) cross-sections of the (infinitely long) meniscus at capillary emptying. Drops A, B, D, I, K and L are stationary points of the functional (7); they do not represent emptying mechanisms, as their value of Ψ is positive. Drops E, F, G and H are minima of $\Psi(t)$ but not stationary points of (7), since the second point of contact of these drops with the capillary walls (red crosses) does not display the correct contact angle.