

Final state of a perturbed liquid film inside a container under the effect of solid-liquid molecular forces and gravity

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(Received 19 November 2013; published 9 April 2014)

We investigate theoretically the possible final stationary configurations that can be reached by a laterally confined uniform liquid film inside a container. The liquid is under the action of gravity, surface tension, and the molecular interaction with the solid substrate. We study the case when the container is in an upright position as well as when it is turned upside down. The governing parameters of the problem are the initial thickness of the film, the size of the recipient that contains the liquid, and a dimensionless number that quantifies the relative strength of gravity with respect to the molecular interaction. The uniform film is always a possible final state and depending on the value of the parameters, up to three different additional final states may exist, each one consisting in a droplet surrounded by a thin film. We derive analytical expressions for the energy of these possible final configurations and from these we analyze which state is indeed reached. A uniform thin film may show three different behaviors after a perturbation: The system recovers its initial shape after any perturbation, the fluid evolves towards a drop (if more than one is possible, it tends toward that with the thinnest precursor film) for any perturbation, or the system ends as a uniform film or a drop depending on the details of the perturbation.

DOI: [10.1103/PhysRevE.89.043010](https://doi.org/10.1103/PhysRevE.89.043010)

PACS number(s): 47.15.gm, 47.54.-r, 68.15.+e, 68.18.Fg

I. INTRODUCTION

The coverage of a solid surface with a liquid and the eventual emergence of stationary patterns are intensive areas of theoretical study due to their technological applications as much as for modeling certain natural processes. For example, we can mention the industrial coating processes [1,2], the liquid lining of pulmonary alveoli and ocular surfaces by polymeric solutions [3,4], and the pattern formation in dewetting of liquids [5,6]. The final morphology adopted by the fluid is the result of the competition among the different forces and effects involved in each problem such as surface tension, evaporation, condensation, centrifugation, molecular interaction with the substrate, gravity, chemical and/or physical inhomogeneities of the substrate and/or the liquid, and stresses applied on the surface of the fluid (for reviews see [7–10]). A successful theoretical approach employed to study the evolution of thin films is the lubrication or long-wave approximation. The fundamental assumptions are that the liquid surface has smooth variations so that the longitudinal scale of the liquid layer is much larger than its thickness and that the inertial effects are negligible.

For horizontal substrates, typical stationary thickness profiles are a uniform liquid film or a droplet. In Ref. [8], the authors presented a review of the stability of a film under different combination of forces, including the case of hanging films. There are also many papers studying the morphology of droplets [11–19], however, few of them give analytical solutions that relate the macroscopic and microscopic parameters of the droplets when a pair of attractive and repulsive molecular forces is considered. More recently, an analytical expression

for two-dimensional drops mounted on a thin film under the action of surface tension and the intermolecular interaction between the liquid and the substrate was found in [20]. This work was generalized in [21], incorporating gravity, which in fact allows us to consider sitting droplets as well as hanging droplets. In addition, given that gravity is considered in [21], a different kind of drop, called pancake in the literature, is included in the analysis. This pancake drop is much wider than it is high (this structure can be seen as a uniform film surrounded by a thinner uniform film). In [21] the authors analyzed the necessary conditions for a drop to exist, although nothing is said about its stability.

The works mentioned in the previous paragraphs assumed that the solid substrate is infinite. In a more realistic situation, an additional factor involved in the selection of the possible patterns is the size of the recipient that contains the liquid. The finiteness of the container has two effects. On the one hand, an unstable configuration may become stable if the wavelength of the shortest unstable mode does not fit in the container. On the other hand, the volume of the liquid will also be finite. This point was addressed in Refs. [22–25] for the two-dimensional (2D) case and more recently for the three-dimensional case in Ref. [26]. Here we analyze theoretically the possible final 2D state of an initially uniform liquid film inside a container with finite width after perturbation. We consider the effects of surface tension, intermolecular interaction between the liquid and the bottom of the recipient, and gravity, when the container is in an upright position and the liquid is over the substrate as well as when the container is turned upside down and the liquid is below the substrate. The results from [21] allow us to do this work without heavy numerical calculations and to obtain some analytical results.

This article is organized as follows. In Sec. II the problem is stated. We show how many final configurations are possible, depending on the governing parameters of the problem in

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Sec. III. Section IV is devoted to the derivation of the energy of a liquid layer and of a droplet inside a container. In Sec. V we show how to determine which is indeed the chosen final configuration between the possible final states. In Sec. VI we discuss our results and conclusions are given. Since this article makes intensive use of the results of [21], some of them are listed in the Appendix.

II. PROBLEM STATEMENT

Let us consider an initially uniform film of fluid within a horizontal vessel. The aim of the work is to predict analytically what the final stable distribution of the fluid will be after the film is perturbed. The thickness of the fluid is $\hat{h} \equiv \hat{h}(\hat{x}, \hat{t})$, where the dimensional coordinate \hat{x} runs along the bottom of the container and \hat{t} is the time. The fluid is under the action of molecular interaction with the substrate, by means of a disjoining-conjoining potential [27], and gravity.

In order to simplify the analysis and be able to use previous results, it is convenient to employ the dimensionless variables h , x , and t that were defined in Ref. [21],

$$h = \hat{h}/h_0, \quad x = \hat{x}/x_0, \quad t = \hat{t}/t_0, \quad u = \hat{u}t_0/x_0. \quad (1)$$

The scales are h_0 , which is the thickness for which the disjoining-conjoining pressure vanishes, $x_0 \equiv (\gamma h_0/\kappa)^{1/2}$, and $t_0 \equiv 3\mu\gamma/h_0\kappa^2$. Here γ is the surface tension, μ is the viscosity of the fluid, and the constant κ quantifies the strength of the conjoining-disjoining pressure and is proportional to the Hamaker constant (interested readers can find the relationship between κ and the Hamaker constant in the Appendix of Ref. [20]).

Figure 1 shows a sketch of the problem. The dimensionless half-width of the container is ℓ , the initial thickness is H , and in order to keep the problem simple we assume that the contact angle between the fluid and the vertical walls of the recipient is $\pi/2$.

Within the framework of the lubrication approximation, the evolution of the thickness profile is described by the following dimensionless equation [21]:

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial x} \left\{ h^3 \frac{\partial}{\partial x} \left[\frac{\partial^2 h}{\partial x^2} + \left(\frac{1}{h^3} - \frac{1}{h^2} \right) - dh \right] \right\}. \quad (2)$$

The first term in square brackets represents the action of surface tension. The second one is the disjoining-conjoining pressure that takes into account the molecular forces of the substrate on the liquid [5,28]. Among the different approximations found in the literature, we choose a two-term approximation for the disjoining-conjoining pressure that is frequently employed to represent the action of two antagonistic molecular forces and also to model partial wetting conditions, which is our

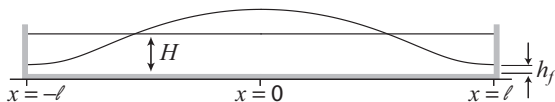


FIG. 1. An amount of fluid with an initially uniform thickness H inside a rectangular recipient with width 2ℓ . The system may remain in the initial configuration or evolve towards a final state with the shape of a drop with precursor film h_f .

interest here. The theoretical foundation of each term has been discussed elsewhere [29–31]. In particular, the exponents (3 and 2) take into account the effect of London–van der Waals molecular and ionic-electrostatic interactions. It has been successfully applied to model different partial wetting phenomena, such as the analysis of hysteretic effects in droplet motion [32], the formation of dewetting patterns [5], the growth of contact line instabilities [28], and flow at nanopores [33]. The last term is the gravity term, in which d is a dimensionless number that measures the strength of gravity relative to the conjoining-disjoining pressure, which is defined as

$$d \equiv \rho g h_0 / \kappa, \quad (3)$$

where ρ is the density and g is the acceleration of gravity. If the container is in an upright position we have $d > 0$; when the container is turned upside down we have $d < 0$. In what follows we will employ $d = 0.02$, except in cases specifically indicated otherwise. Despite this value being high by a factor of 1000 for terrestrial gravity and simple liquids such as water on silica at room temperature, it allows us to speed up the simulations without affecting the generality of the results. The use of smaller values of d only introduces slight quantitative changes with no qualitative modifications. It is important to have in mind that the stationary solutions for Eq. (2) that describe a drop surrounded by a uniform film that is laterally *unconfined* can be found in Ref. [21].

Witelski and co-workers largely studied the evolution of thin films in infinite domains and found that nonsteady configurations evolve to a single droplet surrounded by a thin film [14,17]. Based on their results, we assume that if a liquid film with uniform thickness H inside the container is perturbed, there are only two possible ways in which the system may evolve: (a) The system returns to the initial configuration and remains at rest with $h = H$ forever or (b) after a transient period the liquid finally adopts the shape of a single droplet surrounded by a thin film with thickness h_f (with $h_f < H$). In case (b), if the width of the drop is sufficiently smaller than 2ℓ , or equivalently $h(\ell) = h(-\ell) \approx h_f$, then the shape of the droplet is well described by an implicit expression $x = x(h)$ given in Eq. (A3). As shown in Ref. [21], the thickness h_f of the precursor film is bounded and verifies $h_{f,\min} < h_f < h_{f,\max}$. The analytical expressions for $h_{f,\min}$ and $h_{f,\max}$ are reproduced in Eqs. (A4) and (A5), respectively [21].

For given values of ℓ and H the possible drop is characterized by the thickness of its precursor film h_f . From the conservation of mass the value of h_f must satisfy

$$H = h_f + \frac{1}{2\ell} a, \quad (4)$$

where

$$a = \int_{-\ell}^{\ell} (h - h_f) dx \quad (5)$$

is the area of the drop above h_f . Once again, assuming that $h(\ell) = h(-\ell) \approx h_f$, the area a can be calculated as

$$a = \int_{-\infty}^{\infty} (h - h_f) dx, \quad (6)$$

whose analytical expression is reproduced in the Appendix. A noticeable result is that for a given value of d , there is a one-to-

one relationship between a and h_f , as shown in Eq. (A7). It is also convenient to have in mind that for $h_f \rightarrow h_{f,\max}$, $a \rightarrow 0$ and then $H \rightarrow h_{f,\max}$ [21].

III. POSSIBLE FINAL STATES

In this section the possible final states will be identified based solely on the ability of the system to satisfy the mass conservation condition (4), without any reference to the values of energy (this will be the subject of the next section). Since a is only a function of h_f and d [21], for fixed values of H , ℓ , and d Eq. (4) gives the allowed value or values for h_f . A stationary solution of Eq. (2) describing a drop is completely characterized by the values of d and h_f (see the Appendix). Then, for given values of H , d , and ℓ there is a possible single-drop stationary solution for each real value of h_f that satisfies the mass conservation (4). On the contrary, if Eq. (4) does not provide a real value of h_f a drop cannot be a final state. Figure 2 shows the mass conservation presented in Eq. (4) for $d = 0.02$ and different values of ℓ . Here we can determine the existence and number of possible drop solutions for any value of H by counting the number of times the line $H = H_0 = \text{const}$ crosses a curve for a given ℓ .

It can be observed that for any ℓ there is an absolute minimum for H , which we call H_m , such that if $H < H_m$ there is no possible drop and only the uniform film with thickness H is possible. For example, for $\ell = 115$ the absolute minimum is $H_m = 1.41$ and for $\ell = 15$, $H_m = 1.56$. Notice that for $H > H_m$ and depending on ℓ , there are up to three different final stages, all of them consisting in a droplet surrounded by a thin film.

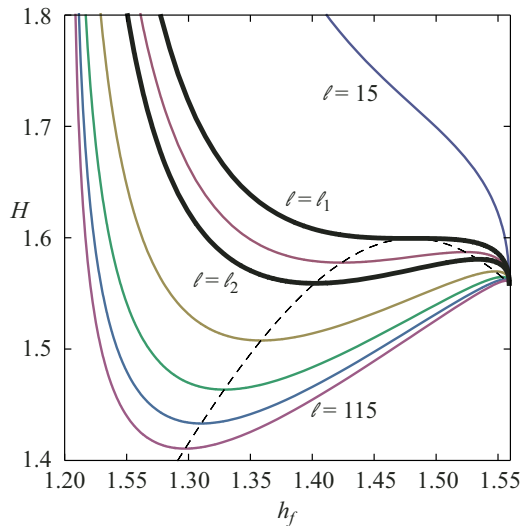


FIG. 2. (Color online) Thickness H of the initial uniform film vs the thickness h_f of the surrounding film of the possible drop for $d = 0.02$. Thin lines correspond to equally spaced values of ℓ from 15 to 115. Thick lines correspond to $\ell = \ell_1 = 30.132$ and $\ell = \ell_2 = 39.427$. The dashed line is the locus of the critical points of the curves, whose ordinates are H_1 for the minimum and H_2 for the maximum. The minimum and maximum values of h_f are $h_{f,\min} \approx 1.205$ and $h_{f,\max} \approx 1.559$.

The topography of the curves H vs h_f , which depends on ℓ , is what determines how many solutions (if any) exist. For each value of d there are two characteristic values of ℓ , which we denote by ℓ_1 and ℓ_2 with $\ell_1 < \ell_2$ (black solid lines in Fig. 2). The shape of the curve is different for each of the following ranges of ℓ . For $\ell < \ell_1$ the curve H vs h_f is monotonically decreasing. For $\ell > \ell_1$ there is a local minimum H_1 and a local maximum H_2 . In particular, for $\ell_1 < \ell < \ell_2$ the absolute minimum $H_m = h_{f,\max} \neq H_1$. Finally, if $\ell > \ell_2$ it is verified that $H_m = H_1$ and $H = h_{f,\max}$ is just a local minimum.

The procedure to calculate ℓ_1 and ℓ_2 is the following. Given d , one must find $\ell_c(h_f)$, which is obtained by solving for ℓ the equation $\partial H(h_f, \ell) / \partial h_f = 0$. Then ℓ_1 is the minimum of $\ell_c(h_f)$. To calculate ℓ_2 we first define $H_c(h_f) \equiv H(h_f, \ell_c(h_f))$ and find an $h_{f,0}$ that satisfies $H_c(h_{f,0}) = h_{f,\max}$ (notice that the dashed line in Fig. 2 is the plot of H_c vs h_f). Finally, $\ell_2 = \ell_c(h_{f,0})$. Only for $d = 0$ can the exact values of ℓ_1 and ℓ_2 be obtained.

Now it is possible to assert the final solutions for the steady problem as follows (the number in parentheses is the total number of solutions).

(a) If $\ell < \ell_1$ and (a1) $H < H_m = h_{f,\max}$, a uniform film results (1) or (a2) $H_m < H$, a uniform film or a drop results (2).

(b) If $\ell_1 < \ell < \ell_2$ and (b1) $H < H_m = h_{f,\max}$, a uniform film results (1); (b2) $H_m < H < H_1$, a uniform film or a drop results (2); (b3) $H_1 < H < H_2$, a uniform film or three different drops result (4); or (b4) $H_2 < H$, a uniform film or a drop results (2).

(c) If $\ell_2 < \ell$ and (c1) $H < H_m = H_1$, a uniform film results (1); (c2) $H_m < H < h_{f,\max}$, a uniform film and two different drops result (3); (c3) $h_{f,\max} < H < H_2$, a uniform film and three different drops result (4); or (c4) $H_2 < H$, a uniform film and a single drop results (2).

It is appropriate to note that when h_f is close to $h_{f,\max}$ the drops have a value of h_f very similar to H , so these drops are extremely flat and in fact they are not discernible from the uniform film. In addition, when h_f tends to $h_{f,\min}$ the width of a drop diverges for $d \geq 0$ and the contact angle tends to $\pi/2$ for $d < 0$, so the region $h_f \rightarrow h_{f,\min}$ should be disregarded in the analysis for any d .

IV. ENERGY OF FLAT FILMS AND DROPS

The energy of the liquid inside the container is given by

$$\varepsilon = \int_{-\ell}^{\ell} (u_g + u_{\pi} + u_{\gamma} + A) dx, \quad (7)$$

where

$$u_g = \frac{1}{2} dh^2, \quad (8)$$

$$u_{\pi} = \frac{1}{2h^2} - \frac{1}{h}, \quad (9)$$

$$u_{\gamma} = \frac{1}{2} \left(\frac{dh}{dx} \right)^2, \quad (10)$$

and A is a constant. For a vertical column of fluid with height h and width dx , u_g , u_{π} , and u_{γ} are the gravitational energy, the energy from the molecular interaction with the substrate, and

the energy from surface tension, respectively. It was chosen $A = (1 - d)/2$ so that $\varepsilon = 0$ for all ℓ when $h = 1$.

The energy ε_f of a liquid film with thickness H inside a recipient whose width is 2ℓ is then easily calculated

$$\varepsilon_f = \frac{\ell}{H^2}(H - 1)(dH^3 + dH^2 + H - 1).$$

Similarly, an analytical expression for the energy ε_d of a drop is obtained after heavy algebraical manipulations. The energy ε defined by Eq. (7) can be calculated for a drop, noting that the energy due to surface tension can be written down by substituting (A1) in (10) as

$$u_\gamma = \frac{1}{2} \frac{(h - h_f)^2}{h^2 h_f^3} [dh^2 h_f^3 - 2(h_f - 1)h + h_f]. \quad (11)$$

$$\begin{aligned} \varepsilon_d = & \frac{\ell}{h_f^2} (h_f - 1)(dh_f^3 + dh_f^2 + h_f - 1) - \frac{1}{d} \sqrt{d - d_m} (\sqrt{d_M} + dh_f^2) \\ & + \frac{1}{d^{3/2} h_f^2} [d(3 - 4h_f) - d_M] \ln \left[\frac{\sqrt{d_M} - \sqrt{d}(\sqrt{d} + \sqrt{d - d_m}) h_f^2}{\sqrt{d_M} - d} \right] \\ & + 2 \ln \left\{ \frac{\sqrt{d_M} - dh_f^2 (1 - h_f + \sqrt{d_M - dh_f^2})}{[2 + h_f(\sqrt{d - d_m} h_f - 1)][1 + h_f(\sqrt{d_M} - dh_f - 1)]} \right\}, \end{aligned} \quad (14)$$

where d_m and d_M are defined in Eq. (A3b).

In Figs. 3, 4, and 5 we plot the energy ε_d of a drop minus the energy ε_f of the uniform film for $\ell = 25 < \ell_1$, $\ell_1 < \ell = 35 < \ell_2$, and $\ell = 55 > \ell_2$, respectively, and $d = 0.02$. It can be noticed that, except for those values of H slightly larger than H_m , the energy of a drop is less than the energy of the uniform film. This is not true for larger values of H , but in this region the results are in doubt because the width of the drop is comparable to the size of the recipient and the condition $h(\pm\ell) \approx h_f$ is not verified. In the three figures a bold dot marks the point where $[h(\ell) - h_f]/(h_m - h_f) = 0.001$, which

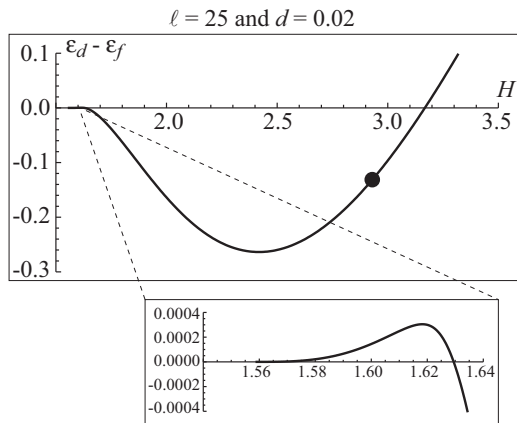


FIG. 3. Energy ε_d of a drop minus the energy ε_f of a film vs the thickness H for $\ell = 25$ and $d = 0.02$. In this case (due to $\ell < \ell_1$) there is only one possible drop as the final state. The bold dot denotes the value of H for which $[h(\ell) - h_f]/(h_m - h_f) = 10^{-3}$. The lower plot is a zoom of of the region $H \gtrsim H_m$.

Then the integral in (7) can be transformed in an integral in h :

$$\int_{-\ell}^{\ell} (u_g + u_\pi + u_\gamma) dx = 2 \int_{h_m}^{h(\ell)} (u_g + u_\pi + u_\gamma) \frac{dx}{dh} dh. \quad (12)$$

Assuming again that $h(\ell) \simeq h_f$, the integral involved in the calculation of the energy of a drop is

$$\int_{h_m}^{h_f} (u_g + u_\pi + u_\gamma) \frac{dx}{dh} dh, \quad (13)$$

where u_g , u_π , u_γ , and $\frac{dx}{dh}$ are given by Eqs. (8), (9), (11), and (A1), respectively. This integral can be analytically performed and the energy of a drop inside a rectangular recipient with width 2ℓ is

is the arbitrary limit we choose for the validity of our analysis. When there are two or three drop solutions, only the one with the smallest h_f satisfies $\varepsilon_d - \varepsilon_f < 0$ (corresponding to the branch to the left of the dashed line for each curve H vs h_f in Fig. 2). Furthermore, there are segments of the curves where $\varepsilon_d - \varepsilon_f \approx 0$, which is so because in those parts $h_f \rightarrow h_{f,\max}$ and thus the drops are so flat that they are indistinguishable from the film.

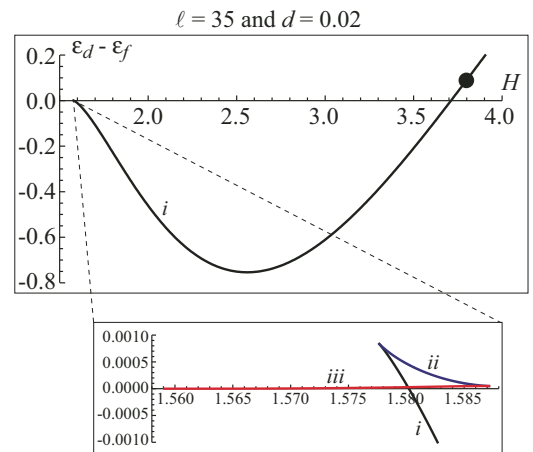


FIG. 4. (Color online) Energy ε_d of a drop minus the energy ε_f of a film vs the thickness H for $\ell = 35$ and $d = 0.02$. In this case ($\ell_1 < \ell < \ell_2$) there are one or three possible drops as the final different states, depending on the value of H . The bold dot denotes the value of H for which $[h(\ell) - h_f]/(h_m - h_f) = 10^{-3}$. In the lower plot we show the details of the graph for $H \gtrsim H_m$. The segments *i* (black line), *ii* (blue line), and *iii* (red line) correspond to the drop with the lowest, intermediate, and largest h_f , respectively.

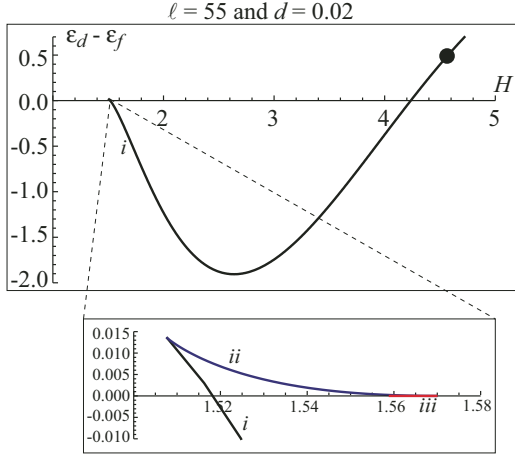


FIG. 5. (Color online) Energy ε_d of a drop minus the energy ε_f of a film vs the thickness H for $\ell = 55$ and $d = 0.02$. In this case ($\ell_2 < \ell$) there are one, two, or three possible drops as the final different states, depending on the value of H . The bold dot denotes the value of H for which $[h(\ell) - h_f]/(h_m - h_f) = 10^{-3}$. In the lower plot we show the details of the graph for $H \gtrsim H_m$. The segments *i* (black line), *ii* (blue line), and *iii* (red line) correspond to the drop with the lowest, intermediate, and largest h_f , respectively.

V. FINAL STAGE

At this point, the question about what the final configuration is seems to be definitely answered: The final state must correspond to the solution, film or droplet, with the lowest energy. This criterion explains why slightly perturbed films evolve to the solution predicted by (A3), such as the case with $d = 0.02$, $H = 3$, and $\ell = 35$. Nevertheless, for some other set of parameters, the solution with the lowest energy is not always reached. For example, let us consider the case of a thin film of thickness $H = 1.582$, $\ell = 35$, and $d = 0.02$. From Fig. 4, the lowest-energy solution correspond to the droplet with the smallest h_f (segment *i*). However, as shown in Fig. 6(a), the flat film profile is recovered after imposing a small initial perturbation of the form $P \cos(\pi x/\ell)$, with $P = 0.1$. [Details of the numerical procedure employed to solve Eq. (2) can be found elsewhere [20,34].] Only when the amplitude of the perturbation is high enough does the system evolve to the solution with the lowest energy, as shown in Figs. 6(b) and 6(c).

To understand this behavior, we must consider the stability of the initial condition. Making a standard linear stability analysis of a uniform infinite liquid film, it is possible to demonstrate that the film with thickness H is stable if $d > \frac{2H-3}{H^4}$. This implies that the thin film is linearly stable in any of the following cases: (i) $d > 1/16$, (ii) $H < h_{f,\max}$ or $H > h_{f,\max 2}$ and $0 \leq d < 1/16$ [$h_{f,\max 2}$ is calculated as $h_{f,\max}$ but replacing $-$ by $+$ just before the square root in Eq. (A5)], and (iii) $H < h_{f,\max}$ and $d < 0$. The shortest wavelength of an unstable mode is

$$\lambda = \frac{2\pi H^2}{\sqrt{2H-3-dH^4}},$$

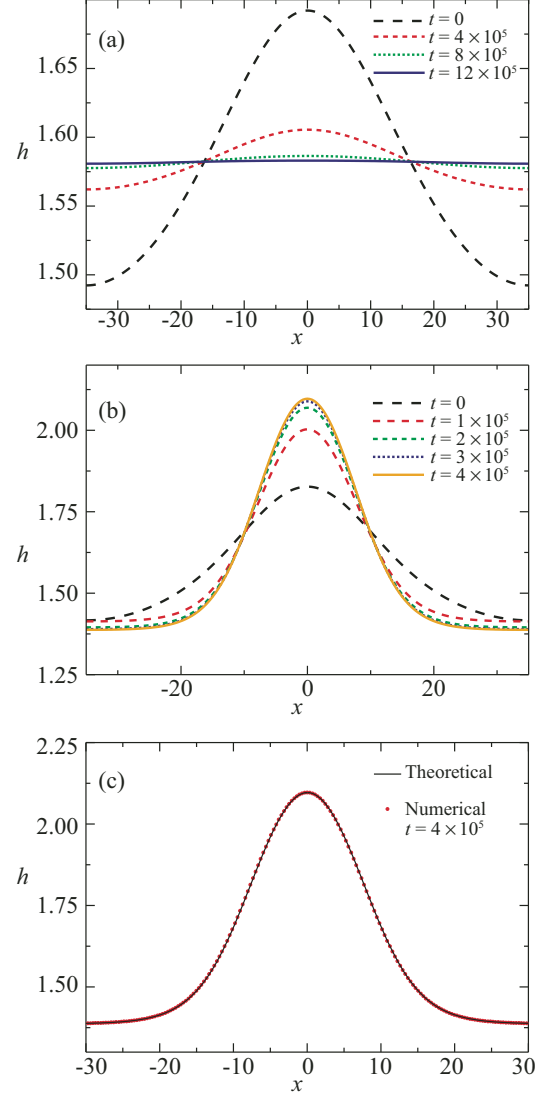


FIG. 6. (Color online) Numerical solution of the evolution of a perturbation $P \cos(\pi x/\ell)$ on a film with thickness $H = 1.582$ for $\ell = 35$ and $d = 0.02$: (a) $P = 0.1$, (b) $P = 0.2$, and (c) comparison of the final profile for the case (b) with the closed-form expression given by Eq. (A3) with $h_f = 1.38586$.

so a uniform film inside a recipient with width 2ℓ is stable when $\lambda > 2\ell$, which finally leads to

$$d > \frac{2H-3}{H^4} - \frac{\pi^2}{\ell^2}. \quad (15)$$

Notice that this implies that if $\ell \leq \ell_{\min} \equiv 4\pi/\sqrt{1-16d}$, a uniform film with any thickness is linearly stable.

This stability analysis adds clarity to our problem. Returning to our example, if $\ell = 35$ and $d = 0.02$, according to Eq. (15) a uniform film is linearly stable if $H < 1.58956$ or $H > 3.42067$. In addition, $\varepsilon_d - \varepsilon_f < 0$ if $1.58023 < H < 3.7112$. Then, if $H \in (1.58023, 1.58956) \cup (3.42067, 3.7112)$ the film is stable but its energy is not the lowest one. Thus, a relatively strong perturbation is needed for the system to escape from this linearly stable state.

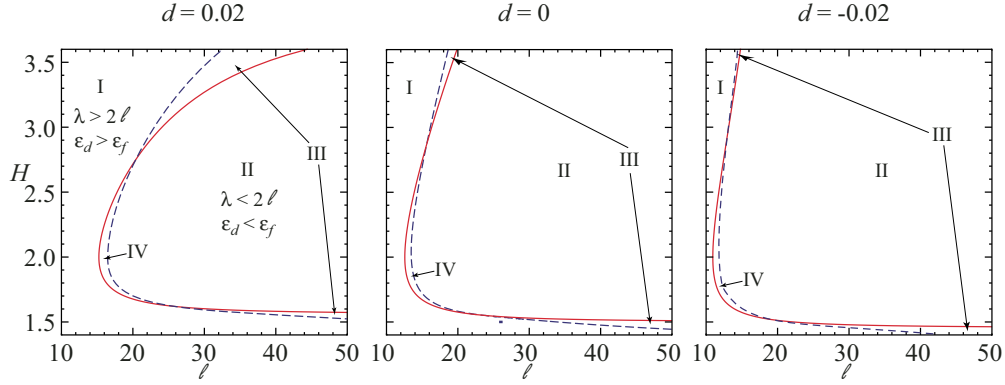


FIG. 7. (Color online) To the left (right) of the solid red line a uniform film is stable (unstable) and to the left (right) of the dashed blue line a uniform film has less (more) energy than a drop. In region I a uniform film is the final state, while in region II a drop is the final state. The final state in region III is either a film or a drop, depending on the perturbation. In region IV the state with the least energy is a half drop, as discussed in the text.

Now we have the elements to determine whether a uniform film or a drop will be the final state. In Fig. 7 we plot in the plane l - H the curves where $\lambda = 2\ell$ and $\varepsilon_d = \varepsilon_f$. These curves define four regions. The region to the left of both curves, indicated in the figure as I, is the place where $\lambda > 2\ell$ (the shorter unstable wavelength is larger than the size of the container) and $\varepsilon_d > \varepsilon_f$. Thus, in this region, a uniform film will be the final state. Region II is to the right of both curves and thus it is the place where a drop will be the final state. In region III the uniform film is stable but has a higher energy than the drop solution, so the final configuration would be either the uniform film or the drop, depending on the characteristics of the perturbation, as it was previously explained.

Finally, in region IV a uniform film is unstable and has less energy than the drop, so the final state is neither of these two possibilities. Then the question is what the final state is in region IV. Although we accept that, under the physical assumptions of this work, a uniform film and a drop are the two unique possible final states, from a mathematical point of view there is another possibility: a half drop with its maximum at one of the vertical walls of the container ($x = -\ell$ or $x = \ell$). This is in indeed the final state reached by our numerical simulations when the parameters are chosen inside region IV. For this half drop the thickness h_f of the precursor film is determined by Eq. (4) but replacing a by $a/2$. However, this state can be ignored because, unlike the film or the centered drop solutions, the existence of the half-drop state strongly depends on the boundary conditions. Here we have assumed for simplicity that the contact angle between the liquid and the lateral walls is 90° . If we would assume, for example, a contact angle of 10° , the film and centered drop solutions will be slightly modified by a meniscus at each lateral wall. Nevertheless, we cannot assume the same for a half-drop configuration because a small contact angle at the boundary will severely modify the profile. We note that there is another possible final state: a depression that is obtained if a drop is broken at $x = 0$ and each half drop is located with its maximum at a lateral wall. This state has the same energy as a drop, but can be ignored for the same reasons as the half drop.

VI. DISCUSSION AND CONCLUSIONS

Here we analyzed theoretically the possible 2D final shape that a uniform film of liquid confined inside a container adopts after a perturbation. The problem is governed by three parameters: the initial thickness H of fluid, the half-width ℓ of the recipient, and d , which quantifies the gravity with respect to the molecular interaction of the fluid with the bottom of the container. We showed that, depending on the values of these parameters, the possible final states are a flat film or up to three different drops (although one of them is so flat that it is in fact almost a uniform film). We derived analytical expressions for the energies of a film and a drop and we determined which state is the one with less energy. The results presented here are consistent with those for the 3D case [26] and they are generalizations in the sense that gravity is included.

The system may show three different behaviors after the perturbation: It recovers unavoidably the uniform thickness it had before the perturbation, it adopts unavoidably the shape of a droplet surrounded by a thin film, or it ends as a uniform film or a drop, depending on the details of the perturbation. For a given value of H , the containers with $\ell < \ell_{\min}$ have a uniform liquid film as the only possible final state; ℓ_{\min} increases with gravity for upright containers ($d > 0$) and decreases for containers turned upside down ($d < 0$).

For very wide recipients, that is, for $\ell \rightarrow \infty$, and for those values of H for which a drop is the final state, the value of h_f will be very close to $h_{f,\min}$, as shown in Fig. 2. In Ref. [21] it was shown that for $d > 0$ the limit $h_f \rightarrow h_{f,\min}$ corresponds to drops with finite height and divergent area and width. When the recipient is wide and in the upright position the drop solutions are of the pancake type. Figure 8 shows one of these profiles for $\ell = 400$.

For $d > 0$ and constant $\ell > \ell_{\min}$ a film will be the final configuration for small and large values of the initial thickness H and a drop will be the final state for intermediate values of H . For $d < 0$ the uniform layer of liquid is the final state for small values of H . From Fig. 7 we can infer that for a container in an upright position the effect of gravity is to increase the size of region I, where the film is the final state, reducing the

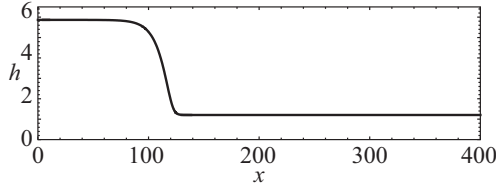


FIG. 8. The final configuration for large values of ℓ is a pancake-shaped drop. Here $\ell = 400$, $d = 0.02$, and $H = 2.5$. With these values replaced in Eq. (4) one obtains $h_f = 1.206$.

possibility of obtaining a drop as the final configuration (region II) and also reducing the size of region III where both a film and a drop are possible. On the contrary, for the case of a container turned upside down, the effect of gravity is to expand region II, where a droplet is the final state, at the expense of reducing the possibility of getting a uniform layer as the final configuration.

Imagine now a recipient such that one of its vertical walls may be smoothly displaced laterally and thus the width 2ℓ may be modified slowly, but the amount of liquid inside the container is held constant. Our results allow us to predict the evolution of the free surface of the liquid (assuming that ℓ varies slowly enough such that the surface evolves through a succession of stationary states). To do this it is necessary to plot the hyperbola $2\ell H = \mathcal{A} = \text{const}$ (where \mathcal{A} denotes area) in Fig. 7 (for the corresponding d). For those points of the hyperbola inside region I the final state of the system is a uniform film, for those inside region II the final state is a drop, and for those in region III, where both a drop and a uniform film are possible final stages, the shape of the surface cannot be predicted because it depends on the details of the perturbation induced by the movement of the vertical wall. Nevertheless, if we move very slowly (so that the perturbation is tiny) from region I to a given point Q within region III we will finally get a uniform film, but if we move on the same hyperbola from region II to Q the final state will be a drop. In this example, the system has a memory of the initial condition under which it enter region III, although this memory is fragile because it will be lost with a sufficiently strong perturbation.

It is important to emphasize the double effect of lateral confinement. On the one hand, the confinement implies that the volume of the fluid is finite, which provide a link between H and h_f [expressed by Eq. (4)] that selects the possible attained drops only based on the constancy of the volume of fluid. On the other hand, any unstable mode whose wavelength is longer than the size of the container cannot exist inside it, which increases the chances that a uniform film is stable. In fact, if the container is sufficiently small ($\ell < \ell_{\min}$) any uniform film is linearly stable.

Here it was assumed just for simplicity that the contact angle of the liquid with the vertical walls of the container is $\pi/2$. However, the results reported here are still valid if the contact angle takes a different value (assuming that ℓ is large enough such that the droplet and each meniscus are separated by a flat film). To see this, one has to realize that if the fluid wets the lateral walls of the recipient it is necessary to add (to subtract if the liquid does not wet the walls) the area of the meniscus on both sides of Eq. (4) and thus this equation remains unchanged.

It is possible to speculate about the existence of a final state with two or more drops. Let us first consider a state composed of two drops. The pressure inside the highest one is smaller than the pressure inside the other drop and this pressure difference will generate a flow towards the highest droplet through the thin film connecting the drops, which in turns increases the pressure difference. Thus, the highest droplet grows at the expense of the smallest drop, until this is completely absorbed. Now let us consider a state with n identical drops (this problem is equivalent to considering only one drop inside a container with width $2\ell/n$) so that there is no pressure difference between the drops. However, this state is unstable because if any little difference between the drops appears, the mechanism just described is started. A deep analysis on how a system with n droplets coalesce in one drop can be found in Refs. [14,17].

ACKNOWLEDGMENTS

C.A.P., J.R.M.I., and J.M.G. acknowledge Grants No. PIP 299 and No. PIP 356 from Consejo Nacional de Investigaciones Científicas y Técnicas and Grant No. PICT 1707 from Agencia Nacional de Promoción Científica y Técnica.

APPENDIX: EQUATIONS FOR A DROP

Assuming that the flow is slow and the surface of the liquid is a gentle slope, the lubrication theory can be applied and Eq. (2) is derived. Then, looking for a stationary solution that satisfies that $h \rightarrow h_f$ if $x \rightarrow \pm\infty$, one arrives at an equation for the profile h of a drop

$$\left(\frac{dh}{dx}\right)^2 = \frac{(h - h_f)^2}{h^2 h_f^3} [dh^2 h_f^3 - 2(h_f - 1)h + h_f]. \quad (\text{A1})$$

From here the maximum thickness h_m is obtained

$$h_m = \frac{h_f - 1 - \sqrt{(h_f - 1)^2 - dh_f^4}}{dh_f^3}. \quad (\text{A2})$$

Equation (A1) has an implicit solution that describes any sessile or pendant two-dimensional drop centered at $x = 0$ and is given by

$$x = -\frac{1}{\sqrt{d}} \ln \left(\frac{s_1 - s\sqrt{d}}{h_f \sqrt{d_M - d}} \right) + \frac{1}{\sqrt{d - d_m}} \times \ln \left(\frac{s_2 + s\sqrt{d - d_m}}{(h - h_f)\sqrt{d_M - d}} \right), \quad (\text{A3a})$$

where

$$\begin{aligned} s &= \sqrt{h_f(2h + h_f - 2hh_f + dh_f^3)}, \\ s_1 &= 1 - (1 + dhh_f^3)/h_f, \\ s_2 &= -1 + (h + 2h_f - hh_f + dh_f^4)/h_f^2, \\ d_m &= (2h_f - 3)/h_f^4, \\ d_M &= (h_f - 1)^2/h_f^4. \end{aligned} \quad (\text{A3b})$$

For a given value of d the thickness of the precursor film h_f must verify $h_{f,\min} \leq h_f \leq h_{f,\max}$, where

$$h_{f,\min} = \begin{cases} 0 & \text{if } d < 0 \\ \frac{2}{1+\sqrt{1-4\sqrt{d}}} & \text{if } d \geq 0 \end{cases} \quad (\text{A4})$$

and

$$h_{f,\max} = \frac{D}{2} \left(\sqrt{r} - \sqrt{-r + D \frac{4}{d\sqrt{r}}} \right). \quad (\text{A5})$$

Here $D \equiv \text{sgn}(d)$ and r is given by

$$r \equiv \frac{2^{5/3}d + 2^{1/3}(d + \sqrt{d^2 - 16d^3})^{2/3}}{d(d + \sqrt{d^2 - 16d^3})^{1/3}}. \quad (\text{A6})$$

Finally, the dimensionless area over the precursor film a defined in Eq. (6) can be calculated from Eqs. (A3),

$$a = -\frac{2}{d} \sqrt{d - d_m} h_f + \frac{2}{h_f^2 d^{3/2}} \left(\frac{1}{h_f} - 1 \right) \times \ln \left[\frac{h_f - 1 - dh_f^4 - \sqrt{d(d - d_m)} h_f^4}{\sqrt{d_M - d} h_f^2} \right]. \quad (\text{A7})$$

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