



HAL
open science

Equilibrium thickness of large liquid lenses spreading over another liquid surface

Julien Sebilliau

► **To cite this version:**

Julien Sebilliau. Equilibrium thickness of large liquid lenses spreading over another liquid surface. Langmuir, 2013, 29 (39), pp.12118-12128. 10.1021/la402509n . hal-03524842

HAL Id: hal-03524842

<https://hal.science/hal-03524842>

Submitted on 13 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 9796

To link to this article : DOI:10.1021/la402509n
URL : <http://dx.doi.org/10.1021/la402509n>

To cite this version : Sebilleau, Julien. *Equilibrium thickness of large liquid lenses spreading over another liquid surface*. (2013) Langmuir, vol. 29 (n° 39). pp. 12118-12128. ISSN 0743-7463

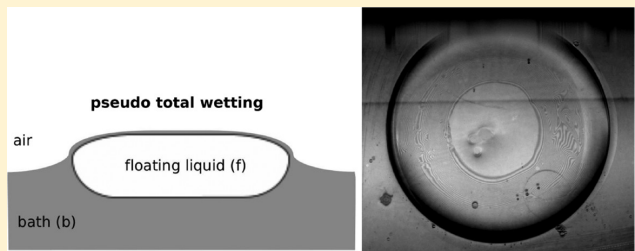
Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Equilibrium Thickness of Large Liquid Lenses Spreading over Another Liquid Surface

Julien Sebilliau*

Université de Toulouse, INPT, UPS, CNRS, IMFT (Institut de Mécanique des Fluides de Toulouse), Allée Camille Soula, F-31400 Toulouse, France

ABSTRACT: This article discusses the equilibrium states and more particularly the equilibrium thickness of large lenses of a liquid spread over the surface of a denser liquid. Both liquids are supposed to be nonvolatile and immiscible. Taking into account the effect of intermolecular forces in addition to the sign of the spreading parameters leads to four possible states. The three first are similar to the states of equilibrium of a liquid spread on a solid surface: total wetting where the floating liquid spreads until it reaches an equilibrium thickness on the order of the molecular size, partial wetting where the floating liquid forms a lens of macroscopic thickness in equilibrium with a “dry” bath, and pseudopartial wetting where the floating liquid spreads as a lens of macroscopic thickness in equilibrium with a thin film covering the bath. The last regime, called pseudototal wetting, consists of a macroscopic lens of the floating liquid covered with a thin film of the bath. These four regimes are described through a free-energy minimization, and their equilibrium thicknesses are predicted. A comparison of this model with experimental results available in the literature and dedicated experiments for the pseudototal wetting state are reported.



INTRODUCTION

Wetting phenomena are ubiquitous in both nature and technology. Thus, they have been intensively studied in past decades.^{1–8} Most of the studies addressed the problem of a liquid spreading on a solid substrate,^{3–5,7,8} and the problem of a liquid spreading on the surface of another one has been less investigated.^{1,2,6,9–18} Since the pioneering work of Harkins and Feldman on the spreading parameter⁹ and of Langmuir on oil lenses on water,¹⁰ most studies have focused on the spreading regimes of viscous liquid on a denser bath,^{1,2,11–15,18–20} on the equilibrium shape of the lens,^{11,21} on the line tension,^{22–26} on the wetting transition,^{6,27–29} on the inertial dynamics of the contact line under partial wetting conditions,^{16,17} or on complex situations involving evaporation, solubility, and surfactant effects.^{30–32}

For a liquid spreading over a solid substrate, the equilibrium state of the puddle depends on both the spreading parameter S and the disjoining pressure Π_d .^{4,7,33} It arises that, for nonvolatile liquids, three equilibrium states exist: the total wetting regime where the liquid spreads as a “pancake” reaching an equilibrium thickness on the order of the molecular size, the partial regime where the liquid spreads as a droplet making a finite contact angle on the “dry” substrate, and the pseudopartial wetting regime where the equilibrium state is a large droplet (of macroscopic thickness) surrounded by a thin film of thickness on the order of a few molecular sizes. These three wetting regimes have also been observed for a liquid substrate in studies on the wetting transition.^{6,27–29} In these studies, the equilibrium of volatile linear alkanes on water or brine is studied and the transitions between partial and pseudopartial and between pseudopartial and total wetting

occur when one varies the surface tensions and intermolecular forces by changing the temperature or surfactant concentration. The aim of the present work is to carry out an analysis similar to that proposed by Brochard-Wyart et al.³³ in the case of the spreading of a liquid (called the floating liquid and denoted by the subscript “f”) on the surface of a denser fluid (called the bath and denoted by the subscript “b”). These two liquids are supposed to be nonvolatile, immiscible, and uncharged. In addition to the three previous equilibrium states—total, partial, and pseudopartial wetting (Figure 1)—it arises from this analysis that a fourth regime can be obtained. This last regime, referred to in the following text as pseudototal wetting, consists of a macroscopic lens of the floating liquid covered by a thin film of the bath (Figure 3). This situation has already been observed by Sebilliau et al.¹⁸ in their study of the spreading of a viscous liquid on a moving bath, but their description and interpretation of this wetting state were only qualitative.

In the first part of this article, the key ingredients used in this analysis are reviewed. Then, the Neumann equilibrium, which is usually used in the case of partial wetting ($S < 0$), and its condition of validity are analyzed. It arises from this analysis that condition $S < 0$ is not sufficient to have partial wetting and can lead to pseudototal wetting. In the third part, the different equilibrium states are described by taking into account the effect of the disjoining pressure and are compared to the available experimental results of the literature. Dedicated experiments on the pseudototal wetting state are presented in

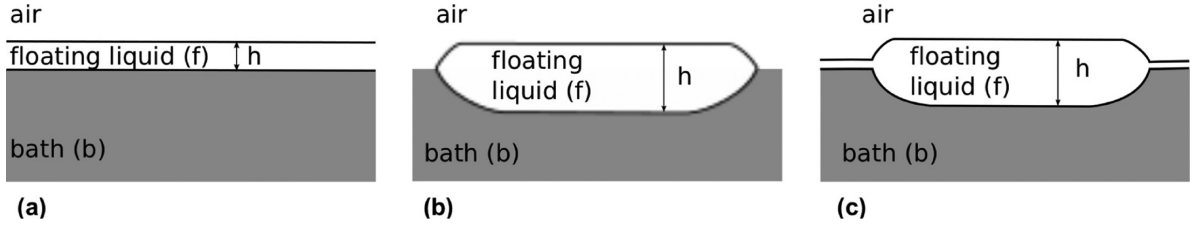


Figure 1. Sketch of the three expected equilibrium states. (a) Total wetting, (b) partial wetting, and (c) pseudopartial wetting.

the fourth section. Finally, conclusion and perspectives are given.

KEY PARAMETERS FOR THE PREDICTION OF EQUILIBRIUM STATES

To predict the equilibrium state of a volume of a floating liquid spread on the surface of a (denser) liquid bath, one has to take into account the effects of surface tension, intermolecular interaction acting through the floating liquid, and hydrostatic pressure. This is usually done by discussing the free energy per unit area F of the floating liquid film of thickness h

$$F(h) = \gamma_f + \gamma_{fb} + P(h) + \frac{1}{2}\rho_f g \Delta h^2 \quad (1)$$

where γ_f and γ_{fb} are respectively the surface tension between the floating liquid and the gas and between the floating liquid and the bath, $\Delta = (\rho_b - \rho_f)/\rho_b$ and $P(h)$ is the interaction energy per unit area through the thickness of the floating liquid. This interaction energy is related to the disjoining pressure Π_d via

$$\Pi_d(h) = -\frac{dP(h)}{dh} \quad (2)$$

For small thicknesses, one has to retrieve the interfacial energy of the bath γ_b , which leads to

$$\Pi_d(h \rightarrow 0) = S_{fb} = \gamma_b - \gamma_f - \gamma_{fb} \quad (3)$$

where S_{fb} is the spreading parameter of the floating liquid on the bath. Because the surface tension is related to the intermolecular forces,^{34–37} one can relate the surface tension between the two liquids γ_{fb} to the surface tension of each liquid. This can be done by introducing Good's interaction parameter Φ ,^{34,36} yielding

$$\gamma_{fb} = \gamma_f + \gamma_b - 2\Phi\sqrt{\gamma_b\gamma_f} \quad (4)$$

This interaction parameter is defined as

$$\Phi = \frac{W_{fb}}{\sqrt{W_{ff}W_{bb}}} \quad (5)$$

where W_{fb} is the work of adhesion in vacuum and W_{ff} and W_{bb} are the work of cohesion in vacuum. Because two neutral molecules always attract each other in vacuum, these three work functions are always positive and thus Φ must be positive. One can notice that the interfacial energy between the two liquids γ_{fb} is always inferior or equal to the sum of the surface tensions of the two liquids ($\gamma_f + \gamma_b$) and could be negative. A negative surface tension corresponds to miscible fluids for which an interface is unstable and finally disappears. Because this analysis is restricted to immiscible liquids, γ_{fb} must be positive. Despite the difficulty of computing Φ , especially for a polar fluid, this approach gives rise to an interesting qualitative classification of fluid. The situation $\Phi > 1$ corresponds to

liquids where specific interactions appear at the interface although they do not exist in both pure phases. The situation $\Phi < 1$ corresponds to liquids having unlike predominant forces (hydrogen bonds or metallic bonds against van der Waals forces). The special case $\Phi = 1$ corresponds to liquids interacting only through the London dispersion force.

For liquids in which intermolecular forces are only van der Waals forces, several relations among the surface tension, disjoining pressure, and Good intermolecular parameters can be found. The surface tension of a pure phase is given by

$$\gamma_f = \frac{A_{ff}}{12\pi r_{0f}^2} \quad (6)$$

where A_{ff} is the Hamaker constant and r_{0f} the intermolecular equilibrium distance. Assuming that the intermolecular equilibrium distances are not too different for the two liquids, one can easily find³⁶

$$\Phi = \frac{A_{fb}}{\sqrt{A_{ff}A_{bb}}} \quad (7)$$

For such liquids, the intermolecular energy through the thickness of the floating sheet has the form

$$P(h) = \frac{A_{fb} - A_{ff}}{12\pi h^2} \quad (8)$$

These simple relations for liquids interacting only through van der Waals forces will be used in the following text to derive the typical order of magnitude. Nevertheless, the form of the disjoining pressure depends strongly on the type of interactions and can be very complex (hydrogen bond or metallic bond).³⁷

Depending on the sign of the spreading parameter S_{fb} and on the evolution of $P(h)$, one can find three different equilibrium states—total wetting, partial wetting, and pseudopartial wetting—that are similar to the equilibrium states of a liquid spread on a solid substrate. Nevertheless, such an analysis will be incomplete because, contrary to the case of a solid substrate, the bath is highly deformable and can wet the floating liquid puddle under the given conditions. Such a wetting film has already been observed¹⁸ for negative spreading parameter S_{fb} , and as will arise from this analysis, this equilibrium state can be predicted by taking into account the sign of both the spreading parameter of the floating liquid on the bath S_{fb} and the spreading parameter of the bath on the floating liquid S_{bf} .

NEUMANN EQUILIBRIUM CONDITION AND ITS VALIDITY

This section is dedicated to the analysis of the Neumann equilibrium condition,³⁸ which is usually used when the spreading parameter $S_{fb} = \gamma_b - \gamma_f - \gamma_{fb}$ is negative (it must be modified for pseudopartial wetting). In this case, the equilibrium state expected is a lens of macroscopic thickness of

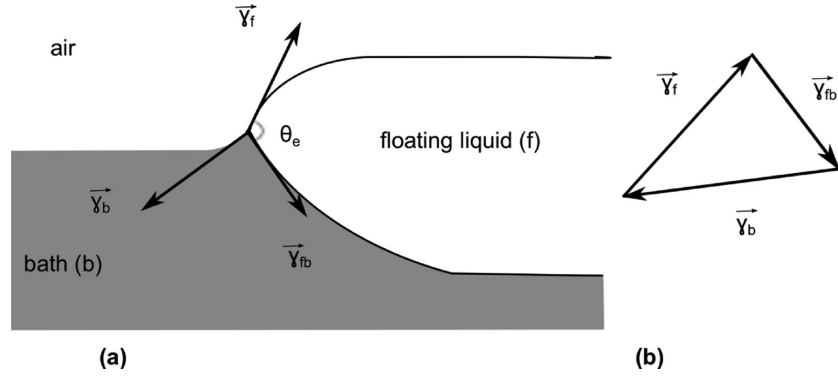


Figure 2. (a) Sketch of the Neumann equilibrium at the edge of the lens. (b) Neumann triangle.

the floating liquid on the “dry” bath. Then at the edge of the lens (i.e., at the contact line), the equilibrium is given by the Neumann condition (Figure 2a).

$$\vec{\gamma}_b + \vec{\gamma}_f + \vec{\gamma}_{fb} = \vec{0} \quad (9)$$

The Neumann condition has a simple geometrical interpretation known as the Neumann triangle (Figure 2b). Then all of the surface tensions should obey the triangle inequality that leads to the following conditions:

$$\begin{cases} \gamma_b \leq \gamma_f + \gamma_{fb} \\ \gamma_f \leq \gamma_b + \gamma_{fb} \\ \gamma_{fb} \leq \gamma_f + \gamma_b \end{cases} \Leftrightarrow \begin{cases} S_{fb} = \gamma_b - \gamma_f - \gamma_{fb} \leq 0 \\ S_{bf} = \gamma_f - \gamma_b - \gamma_{fb} \leq 0 \\ \gamma_{fb} \leq \gamma_f + \gamma_b \end{cases} \quad (10)$$

It clearly arises that to ensure the Neumann condition both the spreading parameters of the floating liquid on the bath S_{fb} and the spreading parameter of the bath on the floating liquid S_{bf} must be negative. The third condition concerns the surface tension between the two liquids and, as shown in the previous section, is always verified. Introducing the Good intermolecular parameter Φ into the previous conditions leads to

$$\begin{cases} S_{fb} = 2\gamma_f \left(\Phi \sqrt{\frac{\gamma_b}{\gamma_f}} - 1 \right) \leq 0 \\ S_{bf} = 2\gamma_b \left(\Phi \sqrt{\frac{\gamma_f}{\gamma_b}} - 1 \right) \leq 0 \\ \Phi \geq 0 \end{cases} \Leftrightarrow 0 < \Phi \leq \min \left(\sqrt{\frac{\gamma_f}{\gamma_b}}, \sqrt{\frac{\gamma_b}{\gamma_f}} \right) \quad (11)$$

It is noticeable that for liquids having a Good intermolecular parameter $\Phi \geq 1$, partial wetting cannot be observed. Therefore, the partial wetting state might occur only for liquids having a Good intermolecular parameter $\Phi < 1$. In this case, the Neumann condition directly provides an expression for the contact angle of the lens θ_e (Figure 2a) depending on the surface tension

$$\cos \theta_e = \frac{\gamma_b^2 - \gamma_f^2 - \gamma_{fb}^2}{2\gamma_f \gamma_{fb}} \quad (12)$$

This expression can be rewritten using the Good intermolecular parameter as

$$\cos \theta_e = -1 + 2\Phi \frac{\sqrt{\frac{\gamma_b}{\gamma_f}} - \Phi}{1 + \frac{\gamma_f}{\gamma_b} - 2\Phi \sqrt{\frac{\gamma_f}{\gamma_b}}} \quad (13)$$

With this last form, one can clearly see that when $S_{fb} = 0$ corresponding to $\Phi = (\gamma_f/\gamma_b)^{1/2}$ the limiting contact angle θ_e is null and when $S_{bf} = 0$ corresponding to $\Phi = (\gamma_b/\gamma_f)^{1/2}$ the limiting contact angle is π . Then one can expect that when $S_{bf} > 0$ and $S_{fb} < 0$, the equilibrium state is a lens of floating liquid covered by a thin film of the bath as observed by Sebilleau et al.¹⁸ This situation, pictured in Figure 3, will be called

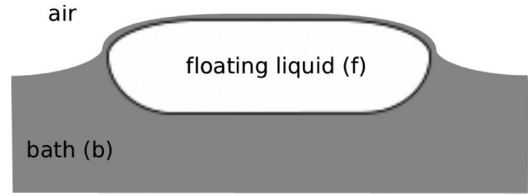


Figure 3. Sketch of the pseudototal wetting.

pseudototal wetting to make a clear distinction from pseudopartial wetting (where a lens of floating liquid will also form but will be in equilibrium with a thin film of the floating liquid covering the bath surface).

At this point, one can remark that the Neumann condition might have been enhanced by taking into account the line tension²³ linked to the curvature of the contact line. This line tension has been estimated to be on the order of 2×10^{-6} N by Harkins,²² and experimental measurements lead to values ranging between 10^{-11} N to 10^{-6} N in the case of liquid lenses^{24,26,39} with a negative or positive sign. If the higher order of magnitude of this line tension is taken to be 10^{-6} N, then the line tension is on the order of the interfacial tension for a lens of radius 0.1 mm. Thus, for centimetric lenses one can expect this effect to be negligible.

EQUILIBRIUM THICKNESS

In this part, the equilibrium thickness of a large volume of floating liquid spread on a liquid bath is predicted by taking into account the effect of the hydrostatic and intermolecular energy through the floating film thickness $P(h)$ and the sign of both spreading parameters S_{fb} and S_{bf} . For total partial and pseudopartial wetting, this prediction arises directly from the minimization of the free energy of the floating liquid puddle \mathcal{F} of given volume $V = \mathcal{A}h$. For pseudototal wetting, one has to take into account the wetting of the bath on the upper part of the lens and the fact that the thin film of the bath will be in equilibrium with a reservoir (the bath itself).

Total, Partial, and Pseudopartial Wetting. As already mentioned, it is convenient to discuss the free energy per unit

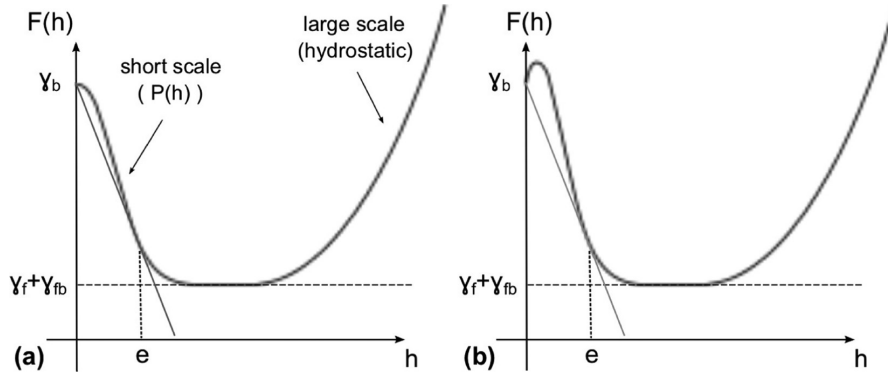


Figure 4. Sketch of $F(h)$ in the case of total wetting ($S_{fb} > 0$ and $S_{bf} < 0$). (a) $F(h)$ is a monotonically decreasing function. (b) $F(h)$ exhibits a maximum.

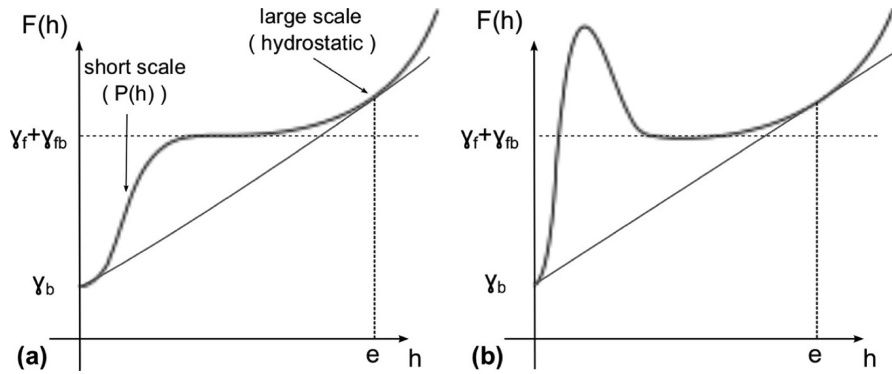


Figure 5. Sketch of $F(h)$ in the case of partial wetting ($S_{fb} > 0$ and $S_{bf} < 0$). $F(h)$ is either (a) a monotonically increasing function or (b) exhibits a maximum.

area F of a floating liquid film of thickness h (eq 1) to predict the equilibrium state. This free energy per unit area is related to the total free energy of the floating liquid puddle \mathcal{F} of given volume $V = \mathcal{A}h$:

$$\begin{aligned} \mathcal{F}(h) &= \mathcal{F}_0 + \mathcal{A} \left(P(h) - S_{fb} + \frac{1}{2} \rho_f g \Delta h^2 \right) \\ &= \mathcal{F}_0 + \mathcal{A} (F(h) - \gamma_b) \end{aligned} \quad (14)$$

Because this analysis is focused on the flat part of the large floating liquid puddle, curvature terms have been neglected. More generally, if one wants to compute the equilibrium shape of the lens, he has to solve to a Young–Laplace equation for each of the interfaces. A general study of these equations has been addressed by Pujado et al.,¹¹ and Burton et al.²¹ has developed a *Mathematica* tool to achieve the numerical computation. The minimization of $\mathcal{F}(h)$ with the constraint $V = \mathcal{A}h$ leads to

$$S_{fb} = e \Pi_d(e) + P(e) - \frac{1}{2} \rho_f g \Delta e^2 \quad (15)$$

where e is the equilibrium thickness of the liquid puddle. Equation 15 can also be put in the form

$$\gamma_b - e \frac{dF(e)}{de} = F(e) \quad (16)$$

which shows how the equilibrium solution can be found graphically by searching the tangent to the free energy per unit area that intersects the y axis at γ_b .

Total Wetting. This state arises if the spreading parameter S_{fb} is positive (and then S_{bf} is negative) and if the free energy per unit area $F(h)$ has one of the typical forms represented in Figure 4. In all cases, F is at its minimum when the liquid substrate is covered with a thick film of the floating liquid (in terms of the molecular scale). The equilibrium thickness can be found graphically using the tangent construction (Figure 4), and the equilibrium thickness e is on a short scale. Then one can use eq 15 and neglect the hydrostatic term to write

$$S_{fb} = e P_d'(e) + P(e) \quad (17)$$

This solution is similar to the one found in the case of spreading over a solid substrate,^{4,7,33} and the equilibrium thickness e is on the order of the molecular size. In the case of liquids interacting only through van der Waals forces, using eq 6, one can easily show that a positive spreading parameter S_{fb} induces $A_{fb} - A_{ff} > 0$ and thus a total wetting regime. Using the form of $P(h)$ (eq 8) in eq 15 leads to

$$e = \sqrt{\frac{A_{fb} - A_{ff}}{4\pi S_{fb}}} \quad (18)$$

which is similar to the equilibrium thickness for the spreading over a solid substrate. This state has been observed experimentally with PDMS oil on pure water.^{19,20} Using neutron reflectivity and ellipsometry, a thickness of the wetting film varying from 6.5 Å for low surface concentration (less than 0.75 mg·m⁻²) of PDMS to 14 Å for high surface concentration (more than 2.25 mg·m⁻²) is reported. It is interesting that for high surface concentration the authors report that after 9–12 h

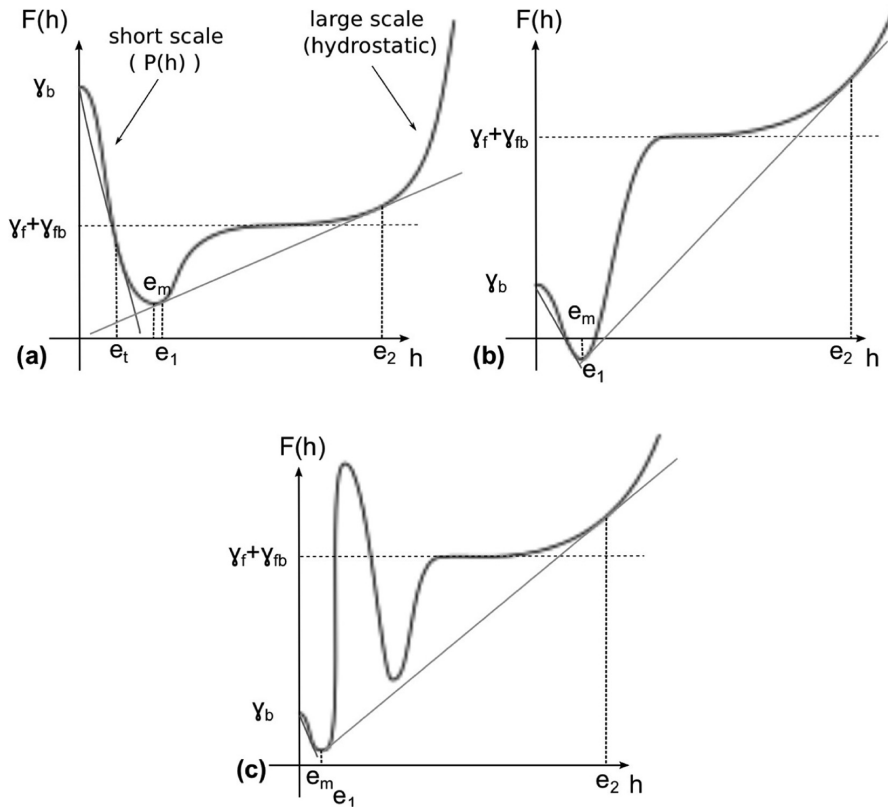


Figure 6. Sketch of $F(h)$ in the case of pseudopartial wetting ($S_{fb} > 0$ and $S_{bf} < 0$ or $S_{fb} < 0$ and $S_{bf} < 0$).

the wetting film becomes uniform with a thickness of 2.5 Å. Using eq 18 with the last value of the equilibrium thickness and their measured value of the spreading coefficient $S_{fb} = 13.1 \text{ mJ}\cdot\text{m}^{-2}$ leads to $A_{fb} - A_f = 3.1 \times 10^{-20} \text{ J}$, which is the typical order of magnitude expected.

Partial Wetting. This state arises if both spreading parameters S_{fb} and S_{bf} are negative and if the free energy has one of the typical forms pictured in Figure 5. In this situation, the free energy per unit area has an absolute minimum for zero thickness, allowing an equilibrium between the dry substrate and a liquid lens. The tangent construction shows that the equilibrium thickness e of the floating liquid is macroscopic. Then by using eq 15 and neglecting the effect of intermolecular force through the thickness of the film, one can find

$$e = \sqrt{\frac{-2S_{fb}}{\rho_f \Delta g}} \quad (19)$$

which corresponds to the Langmuir prediction¹⁰ for a large liquid lens thickness. In this situation, the Neumann condition on the edge of the liquid lens is valid and one can compute the value of the equilibrium contact angle using eq 12. The most famous example of partial wetting is certainly liquid glass on a tin bath. These liquids are used in the float glass process⁴⁰ where the spreading of the liquid glass on the tin bath provides great uniformity of the lens thickness and thus good optical quality. As reported by Pilkington,⁴⁰ the liquid glass forms a lens of thickness of ~7 mm. Because the bath is a liquid metal (with metallic bonds as predominant interactions) one can expect the Good parameter to be $\Phi < 1$, and the equilibrium state can be partial wetting. The case of 1-octanol and 1-decanol on pure water was studied by Aratono et al.⁴¹ In this

study, the authors did not check the equilibrium thickness of the large lens but compared their measurements of the equilibrium contact angle of the lens with the prediction obtained from the Neumann triangle (eq 12). They found excellent agreement for both the alcohols over a large range of temperature (285–315 K).

Pseudopartial Wetting. This state arises if S_{fb} is positive (and then S_{bf} is negative) or both S_{fb} and S_{bf} are negative and if the free energy per unit area $F(h)$ presents a minimum at finite thickness e_m . (Some examples of the free energy per unit area are pictured in Figure 6.) This minimum can be linked to oscillations of $F(h)$ due to short-range interactions (Figure 6c). In this case, the equilibrium state depends on the volume of the floating liquid puddle. For small volume $V < \mathcal{A}_s e_m$ where \mathcal{A} is the total surface of the bath, the equilibrium thickness can be found by the tangent construction. It corresponds to e_t in Figure 6a. For large volume (i.e., $V > \mathcal{A}_s e_m$), the equilibrium state consists of a thin film of thickness $e_1 \simeq e_m$ in equilibrium with a residual liquid lens of macroscopic thickness e_2 . Such a state is pictured in Figure 1c. These thicknesses can be found by a common tangent construction that ensures the equality of disjoining pressure (and thus of chemical potentials), which is an essential condition for coexistence. To predict the macroscopic thickness e_2 , one has to take into account the effective surface tension γ_e of the thin film of thickness e_1

$$\gamma_e = \gamma_f + \gamma_{fb} + P(e_1) + e_1 \Pi_d(e_1) \simeq \gamma_f + \gamma_{fb} + P(e_m) \quad (20)$$

This effective surface tension can be deduced from the variation $d\mathcal{F}$ of the free energy of the thin film associated with an increase $d\mathcal{A}$ of the surface at constant volume V . Then the macroscopic thickness e_2 can be computed using eq 19 where

the surface tension of the bath γ_b has been replaced by the effective surface tension γ_e , leading to

$$e_2 = \sqrt{\frac{2(\gamma_f + \gamma_{fb} - \gamma_e)}{\rho_f \Delta g}} = \sqrt{\frac{2P(e_m)}{\rho_f \Delta g}} \quad (21)$$

This last expression leads to the Langmuir equation when e_m is set to be zero. It is interesting that for liquids interacting only through van der Waals interactions such a state is possible only if both spreading parameters are negative. This state is achieved with PDMS oil on water saturated with AOT surfactant (the concentration being 3 times the critical micelle concentration).²⁰ In this system, adding a 5 mL drop on the surface of the brine covered with a monolayer produces a stable lens that remains for more than 7 days, and thus one can expect this coexistence between a lens and a thin molecular film on the surface of brine to be the equilibrium configuration. Other examples of pseudopartial wetting can be found in studies on the wetting transition of linear alkanes on water or brine. Because these studies deal with volatile liquids in a saturated atmosphere, the presence of an absorbed monolayer of the volatile fluid on the surface of the bath is expected even for the partial wetting state, but ellipsometric measurements of the film thickness surrounding the liquid lens show a clear difference between the absorbed monolayer (partial wetting) and the pseudopartial wetting.^{6,28} For pentane on water in a saturated atmosphere, Ragil et al.⁴² measured a thickness of the film surrounding the liquid lens of 50 Å that is too large to be an absorbed monolayer. Then pentane on water in a saturated atmosphere exhibits pseudopartial wetting, which explains the observation of Del Cerro et al.²⁷ who described a complex state where pentane does not spread or form a stable lens. In addition to this observation, Del Cerro et al. computed the van der Waals interaction energy and obtained a marked minimum for pentane on water, which is a necessary condition for pseudopartial wetting. Similarly for longer alkane chains, this state appears at higher temperature or surfactant concentration.^{6,28,29}

Pseudototal Wetting. This state arises if S_{fb} is negative and S_{bf} is positive. In this situation, the Neumann condition does not work and the final state is a floating liquid lens covered with a thin film of the bath (Figure 3). Because S_{bf} is positive, the bath is then either totally wetting or pseudopartially wetting. In both situations, the bath has to climb the edge of the liquid lens to wet its surface and is in equilibrium with a reservoir. To predict the equilibrium thickness of the liquid lens, one first has to describe the equilibrium thickness of the thin bath film.

Equilibrium Thickness of the Thin Bath Film. As mentioned, the thin film is in equilibrium with the bath and then the minimization of the free energy under the constraint of a constant volume V can no longer be used. Because the thin bath film has to climb the upper part of the lens (of thickness Δh), its equilibrium thickness e_b can be directly found by minimizing the gravitational and intermolecular energies:^{4,6}

$$\Pi_{d_b}(e_b) = \rho_b g \Delta (\Delta h + e_b) \quad (22)$$

For the macroscopic thickness of the lens, the film thickness e_b is large enough to consider only the long-range interactions.^{4,6} Then for nonpolar fluids, one can retain only the long-range interactions in the disjoining pressure Π_{db} leading to

$$e_b = \sqrt[3]{\frac{A_{fb} - A_{bb}}{6\pi\rho_b g \Delta^2 h}} \quad (23)$$

The typical order of magnitude of this thickness is $e_b \simeq 300$ Å. This value is small enough to neglect the retardation effect³⁷ and is 2 orders of magnitude larger than the molecular thickness observed for total wetting with a fixed volume.

For polar liquids, one can consider the long-range interactions to be electrostatic double layer interactions. Such interactions have been observed between water and oil⁴³ and are linked to the spontaneous adsorption of hydroxyl ions at the interface. In this case, the disjoining pressure has the form³⁷

$$\Pi_{d_b}(e_b) = \frac{\epsilon_0 \epsilon_r}{2e_b^2} \left(\frac{\pi k_b T}{ze} \right)^2 \quad (24)$$

and the equilibrium thickness of the thin bath film is given by

$$e_b = \frac{\pi k_b T}{ze} \sqrt{\frac{\epsilon_0 \epsilon_r}{\rho_b g \Delta^2 h}} \quad (25)$$

The typical order of magnitude of this thickness is 500 nm, which is 3 orders of magnitude larger than the molecular thickness observed for total wetting with a fixed volume. This order of magnitude is in fair agreement with the experiments of Marinova et al.,⁴³ who report a film thickness larger than 100 nm. One can notice that both of these equilibrium thicknesses e_b depend on the lens thickness h and so have to be considered while minimizing the free energy of the floating lens.

Equilibrium Thickness of the Liquid Lens. If we turn to the equilibrium thickness of the liquid lens, it can be predicted by minimizing eq 14 where the surface tension of the floating liquid γ_f has been replaced by an effective surface tension $\gamma_e = \gamma_b + \gamma_{fb} + P_b(e_b)$. This leads to

$$\frac{1}{2} \rho_f g \Delta h^2 = 2\gamma_{fb} + h \frac{dP_b(e_b)}{dh} + P_b(e_b) \quad (26)$$

where the intermolecular terms linked to the thickness of the lens have been neglected because this thickness is macroscopic. If the contribution of the thin bath film is neglected, then the equilibrium thickness of the floating lens is simply

$$e_{f_0} = \sqrt{\frac{4\gamma_{fb}}{\rho_f \Delta g}} \quad (27)$$

which is the expression proposed by Sebilliau et al.¹⁸ where they just replace the surface tension of the floating liquid γ_f by $\gamma_b + \gamma_{fb}$ in the Langmuir prediction (eq 19).

For nonpolar fluids, using eqs 23 and 8 yields

$$\frac{1}{2} \rho_f g \Delta h^2 = 2\gamma_{fb} + \frac{5}{3} \left(\frac{A_{fb} - A_{ff}}{6\pi} \right)^{1/3} (\rho_b g \Delta^2 h)^{2/3} \quad (28)$$

Even if the previous equation has an analytical solution, where the thin film contribution is several orders of magnitude smaller than the hydrostatic one, it is more convenient to consider the first-order expansion:

$$e_f = \sqrt{\frac{4\gamma_{fb}}{\rho_f \Delta g}} \left(1 + \frac{5\rho_b}{6\rho_f} \sqrt[3]{\frac{\Delta(A_{fb} - A_{ff})}{3\pi\gamma_{fb}\rho_b g}} \right) \quad (29)$$

For water-type fluids, using eq 25 and the corresponding intermolecular potential yields

Table 1. Examples of Liquid Couples Exhibiting Pseudototal Wetting

floating liquid (F)/bath (B)	$\rho_f \text{ kg}\cdot\text{m}^{-3}$	$\rho_b \text{ kg}\cdot\text{m}^{-3}$	$\gamma_f \text{ mN}\cdot\text{m}^{-1}$	$\gamma_b \text{ mN}\cdot\text{m}^{-1}$	$\gamma_{fb} \text{ mN}\cdot\text{m}^{-1}$	Φ	$S_{fb} \text{ mN}\cdot\text{m}^{-1}$	$S_{bf} \text{ mN}\cdot\text{m}^{-1}$
water/carbon tetrachloride ³⁴	1000	1594	72.5	26.95	45	0.612	-90.55	0.55
water/chloroform ³⁴	1000	1420	72.5	27.15	31.6	0.764	-76.95	13.75
water/dichloromethane ³⁴	1000	1325	72.5	26.5	28.3	0.754	-74.3	17.7
water/ethylbromide ³⁴	1000	1460	72.5	24.2	31.2	0.779	-79.5	17.1
water/ <i>O</i> -nitrotoluene ³⁴	1000	1163	72.5	41.50	27.2	0.789	-58.2	3.8
water/ <i>M</i> -nitrotoluene ³⁴	1000	1157	72.5	41.40	27.7	0.785	-58.8	3.4
water/nitromethane ³⁴	1000	1127	72.5	36.8	9.5	0.964	-45.2	36.8
water/nitrobenzene ³⁴	1000	1205	72.5	43.9	25.7	0.802	-54.3	2.9
glycerin/Galden Ht-270 ¹⁸	1261	1850	59.5	25	26	0.758	-60.5	8.5
honey/Galden Ht-270 ¹⁸	1400	1850	64	25	14	0.9375	-53	25

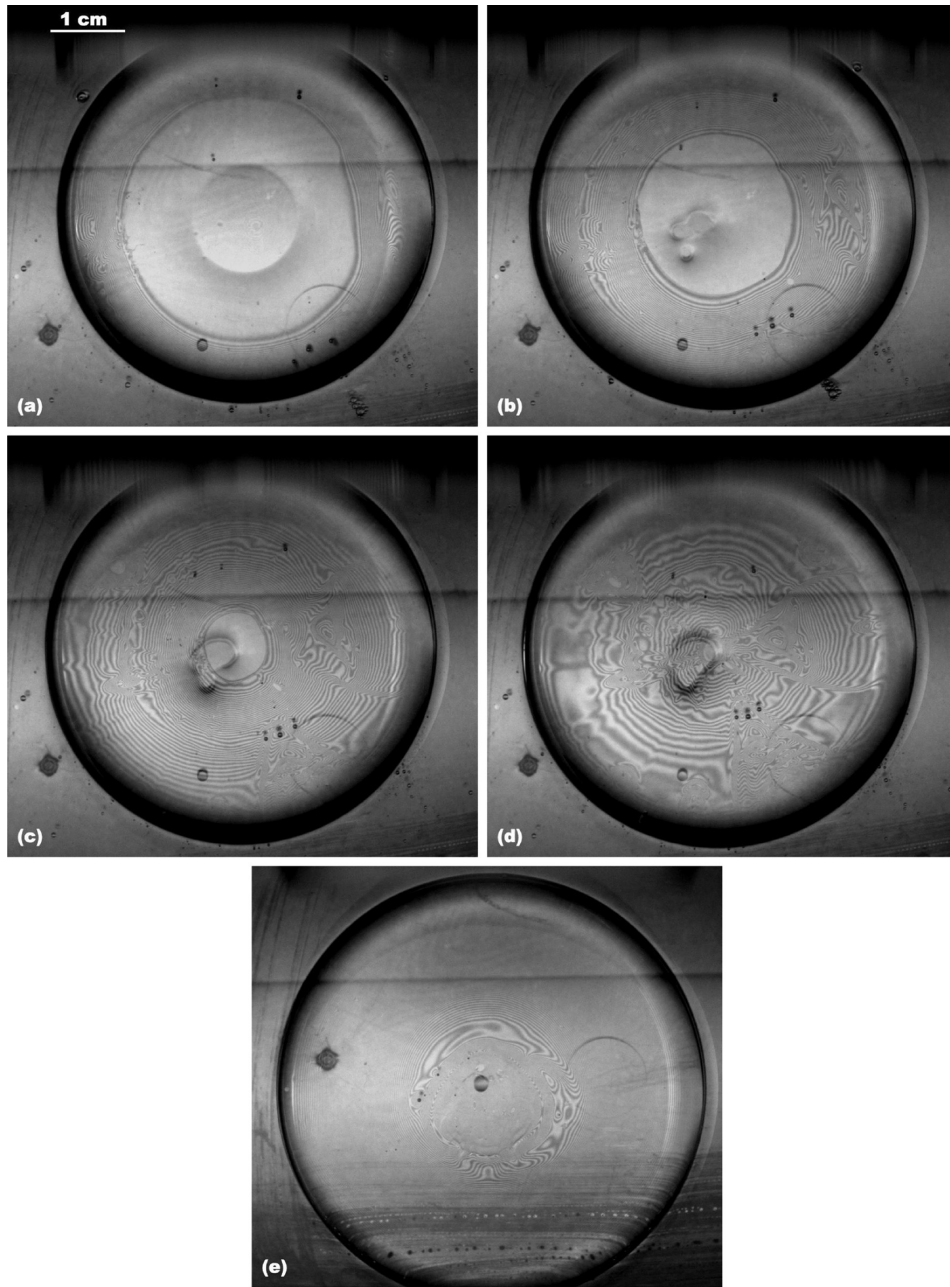


Figure 7. Time sequence of the upper surface of a 10 mL glycerin lens on a bath of LUBRILOG LY F 15. Time after the end of injection: (a) 1 s, (b) 11 s, (c) 21 s, (d) 31 s, and (e) 5 min. All pictures have the same scale.

$$\frac{1}{2}\rho_f g \Delta h^2 = 2\gamma_{fb} + \frac{3}{4} \frac{\pi k_b T}{ze} \sqrt{\epsilon_0 \epsilon_r \rho_b g \Delta^2 h} \quad (30)$$

Similar to the case of a nonpolar fluid, it is more convenient to consider the expansion of the analytical solution leading to

$$e_f = \sqrt{\frac{4\gamma_{fb}}{\rho_f \Delta g}} \left(1 + \frac{3}{8} \frac{\pi k_b T}{ze} \sqrt{\epsilon_0 \epsilon_r} \frac{\rho_b^{1/2}}{\rho_f^{1/4}} g^{1/4} \Delta^{3/4} \right) \quad (31)$$

In both cases, it is interesting that the thin film contribution implies some small corrections to the estimate (eq 27) proposed by Sebilliau et al.¹⁸

Examples of Liquid Couples in Pseudototal Wetting from the Literature. Using data found in the literature on the relationship of the surface tension between fluids and intermolecular forces^{18,34–36} and taking the denser liquid as the bath, one can find several liquid couples that exhibit pseudototal wetting as the equilibrium state. These liquid couples are given in Table 1.

Noblin et al.¹⁶ studied the fast dynamic of the contact line of the water lens on carbon tetrachloride, and as pointed out in his thesis,⁴⁴ the spreading parameter of carbon tetrachloride on water is positive, which implies that a thin liquid film of carbon tetrachloride should invade the upper surface of the water lens. The experimental observation of the interference of the invasion of the upper surface of a lens has been reported by Sebilliau et al.¹⁸ with honey and glycerin floating on a perfluorinated oil (Galden HT 270).

EXPERIMENTS ON PSEUDOTOTAL WETTING

To observe the invasion of the upper surface of the liquid lens by a thin film of the bath, experiments similar to the one by Sebilliau et al.¹⁸ have been performed. The experimental setup consists of a transparent polystyrene box (12 cm × 18 cm × 7.5 cm) lit (from above) with a sodium lamp (Philips SOX 55 W) that is almost monochromatic (it presents two close emission rays at $\lambda_1 = 589$ nm and $\lambda_2 = 589.6$ nm). A linear beamsplitter is placed between the sodium lamp and the top of the container to allow image capture from the top with a PCO SENSICAM mounted with a 105 mm Nikon lens. The container, with an approximate thickness of 5 cm, is filled with LUBRILLOG LY F 15 perfluorinated oil ($\rho_b = 1870$ kg·m⁻³, $\gamma_b = 17.1$ mN·m⁻¹). On the top of this oil bath, a constant volume ($V = 5$ or 10 mL) of the floating liquid is injected with a syringe. As a floating liquid, glycerin ($\rho_f = 1261$ kg·m⁻³, $\gamma_f = 55$ mN·m⁻¹, $\gamma_{fb} = 18.3$ mN·m⁻¹, 98% purity, Merck), honey ($\rho_f = 1398$ kg·m⁻³, $\gamma_f = 65.4$ mN·m⁻¹, $\gamma_{fb} = 20.2$ mN·m⁻¹), and tap water ($\rho_f = 1000$ kg·m⁻³, $\gamma_f = 68$ mN·m⁻¹, $\gamma_{fb} = 26.2$ mN·m⁻¹) have been used without any modification. All given surface tensions have been measured with a pendant drop tensiometer (Krüss DSA 100), and the measured surface tension are similar to the ones measured by Sebilliau et al.¹⁸ with similar fluids. The density of honey has been measured by weighting 100 mL on an analytical balance. One interest in the use of a sodium lamp is that it provides monochromatic light with a coherence length on the order of centimeters. Then the typical thickness of the lenses of floating liquid ($h \simeq 5$ mm) is large enough not to produce interference so that the observed interference pattern is linked to the thin film invasion of the upper surface of the lens.

Glycerin on Perfluorinated Oil. Figure 7 presents a typical time sequence of the upper surface of a 10 mL glycerin lens on LUBRILLOG LY F 15 oil. During the injection, the presence of the thin bath film is observed only near the edge of

the glycerin lens. One second after injection (Figure 7a), the thin bath film has invaded approximately one-third of the upper surface of the lens as revealed by the interference pattern. It is interesting that the typical thickness of the bath film is on the order of 1 μ m whereas the bath invades the upper surface of the lens (Figure 7a–c). When the upper part of the length is totally wet by the bath, the interference fringes become more spaced (Figure 7d) and finally are hardly visible (Figure 7e). This evolution is certainly linked to the flattening of the thin film while it reaches its equilibrium thickness (because a flat film does not produce interference). Because glycerin is a liquid similar to water, this thickness must be compared to eq 25, which gave a similar order of magnitude. The dynamical mechanism of the film invasion will be discussed in the following text. The progressive covering of the upper surface is linked to an increase in the radius of the lens: 1 s after injection, the lens has a radius of $R = 2.67$ cm, and 5 min after injection, this radius is $R = 2.87$ cm and remains stable for more than 30 min. A longer time evolution could not be observed because these liquid lenses are very sensitive to perturbations and move on the bath surface until they touch the edge of the container where they pin. Another phenomenon can be seen in Figure 7: just after injection (Figure 7a), a circular front near the center of the lens can be observed; it rapidly reaches the center of the lens and gives rise to a deformation of the upper surface near the center (a little under and to the left of the center of the lens in Figure 7b). This deformation is linked to the formation of a small lens of the perfluorinated oil on the upper surface of the glycerin lens. Because the perfluorinated oil is heavier than the glycerin, this small lens sinks through the glycerin lens. This process takes time and can be observed in Figure 7 c,d (the edges of the formed hole are visible under the interference pattern a little under and to the left of center), but the oil lens eventually coalesces with the bath and is no longer visible (Figure 7e). This behavior could be linked to the pseudopartial wetting of the oil on the glycerin because it implies a coexistence between a thin bath film and a small lens. This evolution is quite reproducible, and the mean equilibrium radius has been found to be $R = 2.85 \pm 0.02$ cm (average over five experiments). From this mean equilibrium radius, one can compute the average thickness to be $e_f = 3.9$ mm. Nevertheless, this measurement is very sensitive to the volume, and a 5% error in the volume can lead to a 0.2 mm error in the average thickness. This value is smaller than the equilibrium thickness expected in partial wetting (eq 19), $e_f = 5.28$ mm but closer to $e_f = 4.26$ mm, which corresponds to eq 27 because the intermolecular part is unknown and thus has been neglected.

Honey on Perfluorinated Oil. Some pictures obtained in the case of honey on LUBRILLOG LY F 15 are given Figure 8. In this case, the injection becomes more difficult and the honey spreads as a finger that begins to fold (Figure 8a). This is certainly linked to the high viscosity of the honey and its ability to coil or fold. After the end of the injection, the floating liquid rapidly takes the form of a circular lens, but the thin bath film no longer invades the upper surface regularly (Figure 8b). To obtain a more regular spreading of the honey (and thus of the thin bath film), one can move the syringe while injecting to force a circular lens form. A result of this kind of injection is presented Figure 8c. The front of the thin film is clearly more regular, but during the injection, three honey drops were deposited on the thin film and did not coalesce with the honey lens. In any case, the interference pattern is less resolved than for glycerin but can still be seen with the change in contrast of

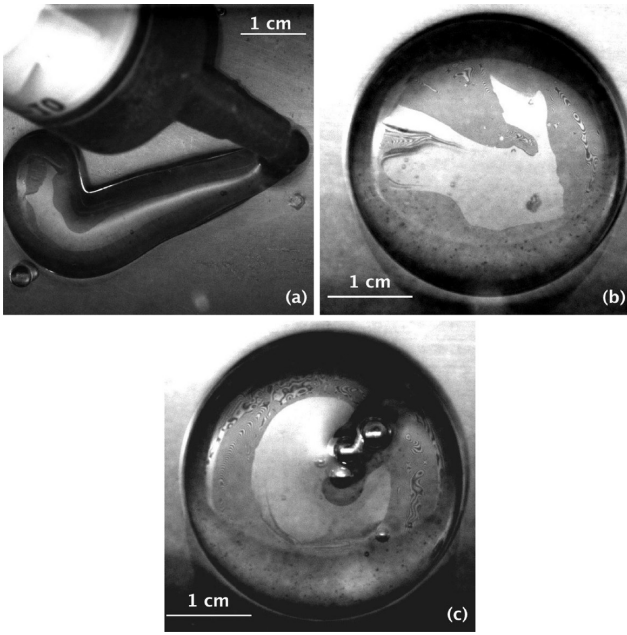


Figure 8. Pictures of honey on LUBRILLOG LY F 15. (a) During injection, the honey spreads as a finger that folds. (b) 9.7 s after injection, the nonregular wetting of the thin bath film is linked to the folding during injection. (c) 24 s after injection, where in this case the circular lens form has been forced during injection and some honey droplets have been deposited on the thin bath film and do not coalesce.

the upper surface of the lens. With honey, the average radius of equilibrium is $R = 1.65 \text{ cm} \pm 0.02 \text{ cm}$ for a volume of 5 mL. This leads to an equilibrium thickness of 5.9 mm, which is smaller than the Langmuir prediction $e_f = 6.3 \text{ mm}$ (eq 19). This equilibrium thickness is larger than the estimate $e_f = 4.8 \text{ mm}$ obtained with eq 27. This can be linked to the fact that the equilibrium was not reached in this case because the high viscosity of honey induces a long spreading time.

Water on Perfluorinated Oil. Figure 9 presents pictures obtained with water on LUBRILLOG LF Y 15. In this case, the interference pattern can be observed during the injection (Figure 9a), and after injection, the upper surface of the lens presents both some interference and small lenses in coexistence with the thin film (Figure 9b,c). Thus, one can assume that LUBRILLOG LF Y 15 is pseudopartially wetting on water. The average equilibrium radius of a 10 mL lens is $R = 2.55 \pm 0.02 \text{ cm}$, which corresponds to an equilibrium thickness of 4.9 mm that is smaller than the Langmuir prediction of $e = 5.8 \text{ mm}$ but in good agreement with $e = 4.8 \text{ mm}$ obtained with eq 27.

Thin Film Dynamics and Implication. As already mentioned, the interference pattern reveals the invasion of the upper surface of the floating length by a thin bath film. Then the thickness of the bath film is large enough to produce interference (larger than 200 nm) that is the typical order of magnitude for electrostatic double layer interactions expected for waterlike liquids with oil (eq 25). However, it is also interesting that the viscosity of the floating liquid appears to have a clear effect on the dynamics of the thin bath film. For glycerin ($\eta \approx 1 \text{ Pa}\cdot\text{s}$), the measured velocity of the thin bath film is $V = 1.4 \pm 0.2 \text{ mm}\cdot\text{s}^{-1}$, and for honey ($\eta \approx 10 \text{ Pa}\cdot\text{s}$), $V = 0.15 \pm 0.02 \text{ mm}\cdot\text{s}^{-1}$, which is very fast for water. These observations suggest that the thin film is entrained on the upper surface while the lens is spreading. According to Hoult,² the first spreading regime for a viscous liquid results from a balance

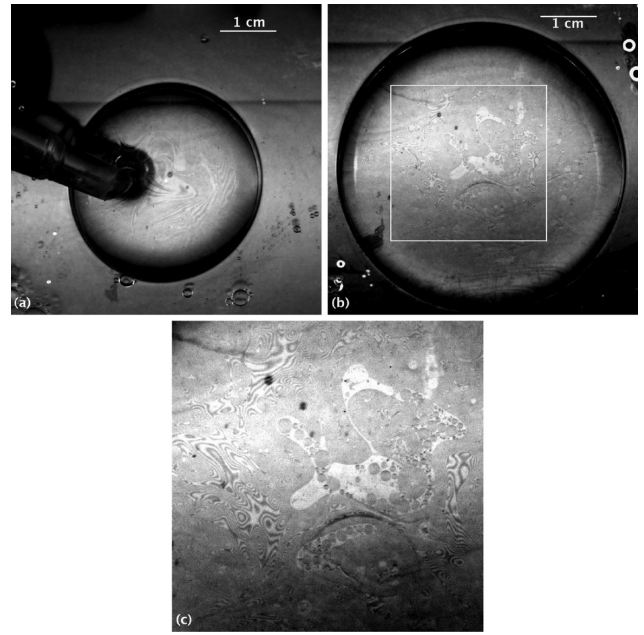


Figure 9. Pictures of water on LUBRILLOG LF Y 15. (a) During injection. (b) 32.3 s after injection, where the white square corresponds to the ($\times 2$) enlarged image in panel c.

between gravity and inertia. In this regime, the leading edge travels as a gravity wave, and thus one can expect recirculations at the leading edge because vorticity is always linked to the curvature in free surface flow. Within this scenario, the thin bath will induce a shear stress on the edge of the lens and then a delay to spreading, which has been observed by Sebilleau et al.¹⁸

In addition to its impact on the dynamics of spreading, the presence of a thin bath film can induce misleading results if one uses the Langmuir method to measure the line tension and equilibrium thickness of the lens. This method consists of measuring the radius of the lens for different volumes to deduce both the line tension and the spreading parameter (using eq 19 for very large lenses). As in pseudototal wetting, the equilibrium thickness is different from the Langmuir prediction, and the measurement of the spreading parameter with the Langmuir method will give wrong results. It is interesting to recall that the presence of the thin bath film induces noncoalescence when one gently places a drop of the floating liquid on the upper surface of the floating lens, and this method can be used to prove the existence of the thin film. Finally, the presence of the thin film can have an important influence on evaporation if the floating liquid is volatile.

CONCLUSIONS

In this work, the equilibrium states of a liquid spreading on the surface of another denser liquid have been characterized using free-energy minimization. It results from this analysis that four equilibrium states are possible: total wetting, partial wetting, pseudopartial wetting, and pseudototal wetting. The first three regimes are similar to those observed in the case of the spreading of a liquid on a solid substrate and have already been observed experimentally. The last regime appears to be specific to highly deformable substrates and consists of a macroscopic liquid lens covered by a thin film of the bath. It arises from this analysis that this state is always achieved for liquids presenting

specific interactions at the interface between them and for liquids interacting only through dispersion (London) forces. Nevertheless, other liquid couples can also achieve this state. The predictions for the lens equilibrium thickness have been compared with data in the literature for the first three regimes, and good agreement has been found. For pseudototal wetting, specific experiments have been carried out with glycerin, honey, and tap water on a perfluorinated oil and the results fairly agree with the model. The mechanism and the dynamics of invasion of the thin bath film have been discussed, and some implications of the thin film's presence have been presented. One of these implications is that the use of the Langmuir method to measure the spreading parameter and the line tension can give misleading results for both pseudopartial and pseudototal wetting.

The dynamics of spreading of the floating liquid in pseudototal wetting should be studied more intensively to draw conclusions for the presented mechanism of thin film invasion of the upper surface, and the effect of the thin film on the evaporation of the floating liquid can be interesting to study.

AUTHOR INFORMATION

Corresponding Author

*E-mail: julien.sebilleau@imft.fr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

I acknowledge N. Baker, M. Ciry, T. Hassi, M. Jalby, C. Journeau, E. Meyers, C. Vatiner, and A. Salvans, who have carried out some of the presented experiments during an experimental project. I also thank L. Limat and H. Bodiguel for fruitful discussions and P. Ern for her helpful comments on this work.

REFERENCES

- (1) Fay, J. A. *The Spread of Oil Slicks on a Calm Sea*; Pub-69-6; Massachusetts Inst of Tech Cambridge Fluid Mechanics Lab: Cambridge, MA, 1969.
- (2) Hoult, D. P. Oil Spreading on the Sea. *Ann. Rev. Fluid Mech.* **1972**, *4*, 341–368.
- (3) Dussan, E. B. On the Spreading of Liquids on Solid Surfaces: Static and Dynamic Contact Lines. *Ann. Rev. Fluid Mech.* **1979**, *11*, p371–400.
- (4) de Gennes, P. G. Wetting: Statics and Dynamics. *Rev. Mod. Phys.* **1985**, *57*, 827–863.
- (5) Leger, L.; Joanny, J. F. Liquid Spreading. *Rep. Prog. Phys.* **1992**, *55*, 431–486.
- (6) Bonn, D.; Ross, D. Wetting Transitions. *Rep. Prog. Phys.* **2001**, *64*, 1085.
- (7) de Gennes, P.; Brochard-Wyart, F.; Quéré, D. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*; Springer: New York, 2004.
- (8) Bonn, D.; Eggers, J.; Indekeu, J.; Meunier, J.; Rolley, E. Wetting and Spreading. *Rev. Mod. Phys.* **2009**, *81*, 739.
- (9) Harkins, W. D.; Feldman, A. Films. the Spreading of Liquids and the Spreading Coefficient. *J. Am. Chem. Soc.* **1922**, *44*, 2665–2685.
- (10) Langmuir, I. Oil Lenses on Water and the Nature of Monomolecular Expanded Films. *J. Chem. Phys.* **1933**, *1*, 756–776.
- (11) Pujado, P.; Scriven, L. Sessile Lenticular Configurations: Translationally and Rotationally Symmetric Lenses. *J. Colloid Interface Sci.* **1972**, *40*, 82–98.
- (12) Buckmaster, J. Viscous Gravity Spreading of an Oil Slick. *J. Fluid Mech.* **1973**, *59*, 481–491.
- (13) di Pietro, N. D.; Huh, C.; Cox, R. G. The Hydrodynamics of the Spreading of One Liquid on the Surface of Another. *J. Fluid Mech.* **1978**, *84*, 529–549.
- (14) di Pietro, N. D.; Cox, R. G. The Containment of an Oil Slick by a Boom Placed Across a Uniform Stream. *J. Fluid Mech.* **1980**, *96*, 613–640.
- (15) Camp, D. W.; Berg, J. C. The Spreading of Oil on Water in the Surface-Tension Regime. *J. Fluid Mech.* **1987**, *184*, 445–462.
- (16) Noblin, X.; Buguin, A.; Brochard-Wyart, F. Fast Dynamics of Floating Triple Lines. *Langmuir* **2002**, *18*, 9350–9356.
- (17) Noblin, X.; Buguin, A.; Brochard-Wyart, F. Cascade of Shocks in Inertial Liquid-Liquid Dewetting. *Phys. Rev. Lett.* **2006**, *96*, 156101.
- (18) Sebilleau, J.; Lebon, L.; Limat, L.; Quartier, L.; Receveur, M. The Dynamics and Shapes of a Viscous Sheet Spreading on a Moving Liquid Bath. *Eur. Phys. Lett.* **2010**, *92*, 14003.
- (19) Lee, L. T.; Mann, E. K.; Langevin, D.; Farnoux, B. Neutron Reflectivity and Ellipsometry Studies of a Polymer Molecular Layer Spread on the Water Surface. *Langmuir* **1991**, *7*, 3076–3080.
- (20) Bergeron, V.; Langevin, D. Monolayer Spreading of Polydimethylsiloxane Oil on Surfactant Solutions. *Phys. Rev. Lett.* **1996**, *76*, 3152–3155.
- (21) Burton, J. C.; Huisman, F. M.; Alison, P.; Rogerson, D.; Taborek, P. Experimental and Numerical Investigation of the Equilibrium Geometry of Liquid Lenses. *Langmuir* **2010**, *26*, 15316–15324.
- (22) Harkins, W. D. Linear or Edge Energy and Tension as Related to the Energy of Surface Formation and of Vaporization. *J. Chem. Phys.* **1937**, *5*, 135–140.
- (23) Chen, P.; Gaydos, J.; Neumann, A. W. Contact Line Quadrilateral Relation. Generalization of the Neumann Triangle Relation To Include Line Tension. *Langmuir* **1996**, *12*, 5956–5962.
- (24) Chen, P.; Susnar, S.; Mak, C.; Amirfazli, A.; Neumann, A. Lens Size Dependence of Contact Angle and the Line Tension of the Dodecane-Water-Air System. *Colloids Surf, A* **1997**, *129–130*, 45–60.
- (25) Aveyard, R.; Clint, J. H.; Nees, D.; Paunov, V. Size-Dependent Lens Angles for Small Oil Lenses on Water. *Colloids Surf, A* **1999**, *146*, 95–111.
- (26) Amirfazli, A.; Neumann, A. Status of the Three-Phase Line Tension: A Review. *Adv. Colloid Interface Sci.* **2004**, *110*, 121–141.
- (27) Cerro, C. D.; Jameson, G. J. The Behavior of Pentane, Hexane, and Heptane on Water. *J. Colloid Interface Sci.* **1980**, *78*, 362–375.
- (28) Bertrand, E.; Bonn, D.; Meunier, J.; Segal, D. Wetting of Alkanes on Water. *Phys. Rev. Lett.* **2001**, *86*, 3208–3208.
- (29) Wilkinson, K. M.; Bain, C. D.; Matsubara, H.; Aratono, M. Wetting of Surfactant Solutions by Alkanes. *ChemPhysChem* **2005**, *6*, 547–555.
- (30) Chen, L.-J.; Jeng, J.-F.; Robert, M.; Shukla, K. P. Experimental Study of Interfacial Phase Transitions in Three-Component Surfactant Systems. *Phys. Rev. A* **1990**, *42*, 4716–4723.
- (31) Aratono, M.; Kahlweit, M. Wetting in Water–Oil–Nonionic Amphiphile Mixtures. *J. Chem. Phys.* **1991**, *95*, 8578–8583.
- (32) Chen, L.-J.; Yan, W.-J. Novel Interfacial Phenomena at Liquid–liquid Interfaces of the Three-Component Surfactant System Water +n-Tetradecane+C₆E₂. *J. Chem. Phys.* **1993**, *98*, 4830–4837.
- (33) Brochard-Wyart, F.; di Meglio, J. M.; Quéré, D.; de Gennes, P. G. Spreading of Nonvolatile Liquids in a Continuum Picture. *Langmuir* **1991**, *7*, 335–338.
- (34) Girifalco, L. A.; Good, R. J. A Theory for the Estimation of Surface and Interfacial Energies. I. Derivation and Application to Interfacial Tension. *J. Phys. Chem.* **1957**, *61*, 904–909.
- (35) Fowkes, F. M. Attractive Forces at Interfaces. *Ind. Eng. Chem.* **1964**, *56*, 40–52.
- (36) Good, R. J.; Elbing, E. Generalization of Theory for Estimation of Interfacial Energies. *Ind. Eng. Chem.* **1970**, *62*, 54–78.
- (37) Israelachvili, J. N. *Intermolecular and Surface Forces*, 3rd ed.; Academic Press: Burlington, MA, 2011.
- (38) Neumann, F. E. In *Vorlesungen über die Theorie der Capillarität, Gehalten an der Universität Königsberg von Franz Neumann.*; Wangerin, A., Ed.; B. G. Teubner: Leipzig, Germany, 1894; p 234.

- (39) David, R.; Dobson, S. M.; Tavassoli, Z.; Cabezas, M. G.; Neumann, A. W. Investigation of the Neumann Triangle for Dodecane Liquid Lenses on Water. *Colloids Surf., A* **2009**, *333*, 12–18.
- (40) Pilkington, L. The Float Glass Process. *Proc. R. Soc. London* **1969**, *314*, 1–25.
- (41) Aratono, M.; Toyomasu, T.; Shinoda, T.; Ikeda, N.; Takiue, T. Dihedral Angle of Lens and Interfacial Tension of Air/Long Chain Alcohol/Water Systems. *Langmuir* **1997**, *13*, 2158–2163.
- (42) Ragil, K.; Meunier, J.; Broseta, D.; Indekeu, J. O.; Bonn, D. Experimental Observation of Critical Wetting. *Phys. Rev. Lett.* **1996**, *77*, 1532–1535.
- (43) Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Velev, O. D.; Petsev, D. N.; Ivanov, I. B.; Borwankar, R. P. Charging of Oil–Water Interfaces Due to Spontaneous Adsorption of Hydroxyl Ions. *Langmuir* **1996**, *12*, 2045–2051.
- (44) Noblin, X. Mouillage et Démouillage Inertiels: Triplons, Flaques Vibrées, Ondes de Chocs. Ph.D. thesis, Université Paris 6, 2004.