Generation of soap films with instantaneously adsorbed surfactants: Concentration-dependent film thinning

J. Seiwert, I. Cantat*
Institut de Physique de Rennes, UMR 6251 CNRS/Université de Rennes 1, Rennes, France

HIGHLIGHTS

• Deviation from the Frankel's law predicting the soap film thickness is computed.
• The film thickness varies non-monotonically with the surfactant bulk concentration.
• The elastic interface behavior is recovered at small solubility.
• The predictions are compatible with available experimental data.

ARTICLE INFO

Article history:
Received 27 October 2014
Accepted 12 November 2014
Available online 18 December 2014

Keywords:
Soap film
Theory
Numerics
Surfactant
Lubrication

ABSTRACT

In this theoretical work, we predict the steady state thickness of soap films pulled from a bath of surfactants. Assuming simplified thermodynamical properties for the surfactants, we compute the interfacial stresses by taking explicitly into account surfactant convection along the film. We make no assumption on interfacial rheology: the rigidification of the interfaces results entirely from confinement and depletion effects. Two main approximations are used: the concentration of surfactants is supposed homogeneous within the thickness of the film, and at equilibrium with the adsorbed layer. With these hypotheses, we show that the thickness of the film follows Frankel's law at low capillary numbers, and that deviations occur at higher pulling velocities. We study the dependence of the film thickness with the characteristics of the surfactant used and especially with its initial concentration, and we show that our predictions are compatible with available data by Saulnier and coworkers.

1. Introduction

The generation of soap films when extracted from a bath at a constant velocity is one of the staple problems featuring hydrodynamics in the presence of surfactants. The great and constant interest in this seemingly simple set up has several origins: it appears in numerous industrial processes, and it features the same key ingredients as the central mechanisms for foam evolution and rheology, namely the coupling between hydrodynamics and surfactant dynamics. By extending the work of Landau, Levich [1] and Derjaguin [2], Frankel [3] has first predicted the steady state thickness of the film and its power law dependency with the capillary number $Ca = \eta U/\gamma$, with $U$ the pulling velocity, $\eta$ the solution viscosity and $\gamma$ its surface tension. Numerous experimental studies have confirmed the great accuracy of this theory, over a large range of capillary numbers and for a large sample of surfactant solutions [4–6].

However, at large enough capillary numbers, several surfactant solutions exhibit a clear deviation from Frankel's law [7–9]: the measured film thickness is lower than predicted by Frankel, and exhibits a maximum at a given capillary number. In [7,8,10,9], these observations are explained by a finite elasticity of the

* Corresponding author. Tel.: +33 2 23 23 56 28.
E-mail address: isabelle.cantat@univ-rennes1.fr (I. Cantat).

http://dx.doi.org/10.1016/j.colsurfa.2014.11.022
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interface. Scaling analysis shows that a deviation from the Frankel’s law, which assumes incompressible interfaces, is expected for capillary numbers larger than (E/γ)1/2, with E = ∂γ/∂(ln(A)) the elasticity of the interface. Depending on the type of surfactant used, this may or may not be in the range of capillary numbers accessible to experiments, which explains why only some solutions exhibit the aforementioned deviation. The main shortcoming of this approach is related to the fact the underlying physical mechanisms at the origin of the elasticity E are most often not explicit.

For insoluble surfactants with negligible surface diffusion, or when the exchange of surfactant between the interface and the bulk is slow enough that it can be excluded from the process, this elasticity arises directly from the variation of surface tension with the surface excess Γ. Indeed, in that case mass conservation of surfactants implies that ∂Γ be constant so d ln(Γ) = − d ln(A) and thus E = − ∂γ/∂ ln(Γ). This elasticity is known as the Marangoni elasticity 𝐸𝑀 [11].

However, for soluble surfactants, exchange with the bulk phase modifies the mass balance equation and the interface elasticity becomes an effective quantity which potentially depends on the complicated interplay between surfactant dynamics and hydrodynamics, through advection, diffusion and adsorption processes. As a general picture, fast adsorbing surfactants may repopulate instantly any interface that is stretched, and should not lead to any interfacial gradients and Marangoni stresses: the effective elasticity or viscosity associated with exchanges with the bulk should vanish for such surfactants. The film systems that we consider here, however, have a very peculiar aspect ratio, as their thickness is generally several orders of magnitude smaller than their extent.

In the confined films, the physical origin of interfacial stresses, and thus of the effective interfacial elasticity, is generally assumed to lie in surfactant depletion within the film [12,11,13]. As interfaces stretch, surfactant molecules within the volume of the film are adsorbed, thereby lowering locally their concentration, increasing locally surface tension and generating Marangoni stresses. This depletion effect becomes important if the thickness of the film becomes smaller than the typical length ℓ = Γ/c, where Γ and c are respectively the interface and volume concentration of surfactant [13]. For typical surfactants used in film withdrawal experiments, this length varies between 1 μm and 100 μm, which is comparable or larger than film thicknesses (1–10 μm).

When the thin film deformation is a pure stretching deformation, a film element constitutes a closed system. The surfactant mass balance, involving interface and bulk contributions, can thus still be used to relate area variations to surface excess variations. This leads to the definition of an effective surface elasticity of the film, namely the Gibbs elasticity 𝐸𝐺 [12,11], that consistently takes into account the depletion effect. In contrast, in more complex dynamical situations, such as film extraction, the velocity of the fluid is not homogeneous across the width of the film, and the local mass balance at the origin of the definition of the Gibbs modulus is not valid anymore. Surfactants are convected along the film and interface stretching at a given place of the film can therefore lead to a surface tension increase at another place of the film. An effective surface elasticity, coupling locally area variation and surface tension, cannot be rigorously defined.

We present here a model that rationalizes the depletion effect involved in the film generation process. The model takes surfactants convection explicitly into account by tracking surfactant concentrations in the volume and at the interface. We consider the case where surfactant adsorption is instantaneous: our model thus predicts the thickness of soap films for a given surfactant solution from its equilibrium isotherm and equation of state. Both the incompressible interface behavior and the elastic interface behavior are recovered, as limiting cases in the parameter space. This model allows a better understanding of surfactant transport phenomena, and, despite

![Figure 1](image-url)  
**Fig. 1.** Sketch of the problem: only half of the film is represented, the dashed line represents an axe of symmetry of the problem. The film is extracted at a constant velocity U from a meniscus of constant radius of curvature ℓ. We neglect the effect of gravity, so that the meniscus features, at rest, a constant radius of curvature ℓ. We further assume the problem to be bidimensional (the film has an infinite width in the z direction, perpendicular to the plane of the sketch), and we focus on steady state: far from the meniscus, the film has a constant thickness ℎ. In typical experiments, ℎ is on the order of micrometers, while the meniscus has a millimetric size. This large difference in sizes allows for the classical division of the system in three distinct regions [1]: (1) the flat film at the top, which is translated at a constant velocity U; (2) the static meniscus, the region of negligible flow where the meniscus is unperturbed and; (3) the dynamical meniscus of length ℓ and of typical thickness ℎ bridging the two, where viscous and pressure forces balance.

### 2. Model

The problem that we consider is sketched on Fig. 1. A film is withdrawn at a constant velocity U from a meniscus acting as a reservoir of surfactant solution (viscosity η, surface tension γ). We neglect the effect of gravity, so that the meniscus features, at rest, a constant radius of curvature ℓ. We further assume the problem to be bidimensional (the film has an infinite width in the z direction, perpendicular to the plane of the sketch), and we focus on steady state: far from the meniscus, the film has a constant thickness ℎ. In typical experiments, ℎ is on the order of micrometers, while the meniscus has a millimetric size. This large difference in sizes allows for the classical division of the system in three distinct regions [1]: (1) the flat film at the top, which is translated at a constant velocity U; (2) the static meniscus, the region of negligible flow where the meniscus is unperturbed and; (3) the dynamical meniscus of length ℓ and of typical thickness ℎ bridging the two, where viscous and pressure forces balance.

#### 2.1. Scaling analysis of Frankel’s law

In Frankel’s theory, the interfaces are incompressible, and they move with the tangent velocity U imposed by the operator. In that case, the viscous force (per unit volume) in the dynamic meniscus scales like ηU/ℏ². Moreover, the dynamic meniscus connects the flat film, where the pressure is p₀ (the atmospheric pressure), to the static meniscus where the pressure is p₀ − γ/ℓ. The balance between pressure gradient and viscous forces thus writes:

\[
\frac{ηU}{ℏ²} \approx \frac{γ}{ℓ
 \]

The length ℓ of the dynamic meniscus is determined by imposing that its curvature (of order ℏ/ℓ²) matches that of the static meniscus (1/ℓ) to ensure the continuity of pressure, so that ℓ ∼ ℏ. The well known prediction for the thickness of the film follows [3]:

\[
ℏ = 1.34r_mCa^{2/3}
\]
with \(Ca = \eta U / \gamma\) the capillary number. A consequence of this scaling is the length of the dynamic meniscus: \(\ell = r_m Ca^{1/3}\).

### 2.2. Marangoni stresses and elastic interfaces

Another prediction deduced from Frankel’s model is the stress arising at the interface in order to pull the film out of the reservoir. It does not appear explicitly in the calculation, since the imposed constant velocity \(U\) is used as boundary condition instead. However, it can be computed from the velocity field, since the surface tension gradient must balance, at each position along the interface, the viscous stress in the bulk of the film. This gradient is confined to the dynamical meniscus, and scales like \(\eta U / \gamma\).

In other words, the surface tension \(\gamma_s\) in the flat film region must be slightly larger than the surface tension \(\gamma_m\) in the static meniscus, in order to balance viscous dissipation and extract the film. Their difference \(\Delta \gamma = \gamma_s - \gamma_m\) is [10]

\[
\frac{\Delta \gamma}{\gamma} = \frac{\gamma_s - \gamma_m}{\gamma_m} = 3.84Ca^{2/3}
\]

(1)

Frankel’s theory assumes perfectly incompressible interfaces, where any surface tension difference may be generated with negligible interface deformation. For elastic interfaces, on the other hand, this difference in surface tension \(\Delta \gamma\) originates from a relative increase of interface area \(\Delta A / A\) which depends on the interface elastic modulus: \(\Delta A / A = \Delta \gamma / \gamma \sim Ca^{2/3} / \gamma_m / \gamma\). As pointed out earlier [7,9,10], when \(Ca \gg (\gamma / \gamma_m)^{2/3}\), interfacial deformation becomes negligible, and deviations from Frankel’s law are observed.

The elastic model will appear as a limit, for poorly soluble surfactants, of the more complex model presented below.

### 2.3. Surfactant transport

Our model for surfactant transport is based on two main approximations:

1. surfactant concentration \(c(x)\) is homogeneous in the direction of the film thickness.
2. surfactant adsorption is instantaneous, so that bulk concentration \(c(x)\) is always at equilibrium with surface excess \(\Gamma(x)\).

Stresses and surface deformations only occur in the dynamical meniscus, so the validity of these approximations needs to be satisfied in this region. Concentration gradients across the thickness of the film decay by diffusion with a typical time \(t_d^0 = h_f^2 / D / r_m^{2/3} / D\), where \(D\) is the diffusion coefficient for the surfactant. On the other hand, changes in subsurface concentration occur on the time scale of the transit in the dynamical meniscus \(t_d^m = \ell / U / r_m^{1/3} / U = Ca^{-2/3} / \gamma_m / \gamma\).

Approximation 1 is valid as long as \(t_d^0 \ll t_d^m\), that is \(Ca \ll Ca_0 = \sqrt{\eta D / \gamma_m}\). With typical aqueous surfactant solutions \((D = 10^{-10} m^2 / s, \eta \approx 1 mPa - s, \gamma \approx 30 mN / m and r_m = 1 mm)\), \(Ca_0 \approx 10^{-4}\) is close to the upper limit of the range of capillary numbers tested in experiments \((Ca = 10^{-6} - 10^{-4})\), and approximation 1 is well satisfied at low velocities.

Evaluating approximation 2 requires the typical adsorption time \(t_{ads}\) of the surfactant. To estimate it, we assume a linear kinetic adsorption (Henry kinetics), where the flux of adsorbed surfactant molecules is proportional to the bulk concentration, and to the deviation from the equilibrium interfacial concentration: \(j = k_c (1 - \Gamma / \Gamma_{eq})\) [15]. Assuming small deviations of \(c^\vee\) and \(\Gamma\) around an equilibrium value, the equation for \(\Delta \Gamma = \Gamma - \Gamma_{eq}\) becomes, at first order in deviations from equilibrium, \(\frac{d \Delta \Gamma}{dt} = -k_{eq} \Delta \Gamma\). The interface thus repopulate on a timescale \(t_{ads} = k_{eq} / \Gamma_{eq}\).

The value of \(k\) depends on the surfactant used, and in the simplest cases it may be evaluated as a diffusion speed on a molecular length scale \(a [13]: k = D / a\). With \(a = 1 nm\) and \(D = 10^{-10} m^2 / s\), \(k \approx 0.1 m/s\). The ratio \(\ell_q = \frac{t_{ads}}{t_{dyn}}\) depends strongly on the concentration, and on the surfactant used. At the critical micellar concentration (cmc), \(\ell_q\) varies for example between \(1 \mu m\) for sodium dodecyl sulfate, and \(1 cm\) for Triton X-100 [15]. Above the cmc, since \(\Gamma\) remains approximately constant, the above estimations need to be multiplied by a factor \(c / c_{cmc}\), that may be of the order of 10. With these values, \(t_{ads}\) varies between \(10^{-2} - 10^{-1} s\). For the fastest surfactants, \(t_{ads}\) is always much shorter than \(t_{dyn}\) \((10^{-2} - 1 s)\), and approximation 2 is well satisfied. For other surfactants, however, this approximation is not correct anymore: the slowest surfactants behave like insoluble surfactants in this problem.

These set of approximations has been used previously to study the static thickness of soap films [16] and the (slow) drainage of Plateau borders [17] in the field of gravity. We showed here that their validity can be extended to our case.

In the following, we will also neglect any diffusion in the direction along the film (both in the volume and at the interface). Indeed, comparing a diffusion time based on \(\ell\) with \(t_{dyn}\) shows that longitudinal diffusion is negligible as long as \(Ca \gg \eta D / \gamma_m^{3/4} \approx 10^{-6}\). This is a very well satisfied approximation, since in most experiments other phenomena (such as disjoining pressure, evaporation, etc.) would become dominant at such low capillary numbers.

Lastly, we use the same set of hydrodynamics approximation as Frankel, namely: we assume a gravity-free lubrication flow in the dynamical meniscus and match it asymptotically to both the static meniscus and the film.

### 2.4. Shape of the dynamic meniscus

As we mentioned earlier, we model the dilution of surfactants that generates the necessary Marangoni stresses in the dynamic meniscus. The dilution is driven by interface stretching: correspondingly, interfacial velocity increases along the dynamical meniscus (from the static meniscus to the film). Five variables need to be tracked: the half with \(h(x)\) of the film, the bulk and interfacial surfactant concentrations \(c(x)\) and \(\Gamma(x)\), the surface tension \(\gamma(x)\) and the interfacial velocity \(\nu_s(x)\).

The adsorption isotherm and the equation of state relate \(\gamma\) and \(\Gamma\) to \(c\) (see Section 2.5), so three additional equations are needed to close the problem. These come from the conservation of the volume flux along the film, the balance of stresses at the interface and the conservation of surfactant molecules.

With the usual lubrication assumptions, symmetry around \(y = 0\) and an interfacial velocity \(\nu_s(x)\), the \(x\)-component of the fluid velocity within the film writes, at dominant order in \(h_f / \ell\) (subscripts are used to denote derivations):

\[
\nu(x, y) = -\frac{\gamma h_{xxx}}{2\eta} (y^2 - h^2) + \nu_s(x)
\]

(2)

At steady state, the volume flux \(q\) (in the half film) must be constant along the film, and may be evaluated in the flat film region where \(q = \mu h_f\) (with \(U\) the imposed velocity), giving the differential equation for \(h\) in the dynamic meniscus:

\[
q = \mu h_f = \frac{\gamma h_{xxx}}{3\eta} h^3 + v_s h
\]

(3)
The second equation relates the distribution of \( \gamma \) to the underlying flow by expressing the balance between the bulk viscous stress and Marangoni forces at the interface:

\[
\frac{\partial \gamma}{\partial x} = \frac{\partial v}{\partial \gamma} = -\gamma h_{\text{core}} h
\]  

(4)

The last relation that we use expresses the conservation of surfactant molecules. Since we neglect diffusion in the x direction, the flux of surfactants is only due to convection, and it has a bulk and a surface contribution: \( \dot{q}_{\text{surf}} = c q + \Gamma v \). It must be constant with respect to \( x \) at steady state:

\[
\frac{\partial}{\partial x} \left( c q + \Gamma v \right) = 0
\]  

(5)

Boundary conditions for \( h \) and \( v \), are specified in the flat film region: for \( x \to \pm \infty \), they must asymptote to constant values \( h_0 \) and \( U \), \( c \), \( \gamma \) and \( \Gamma \) must also reach constant values \( c_f \), \( \gamma_f \) and \( \Gamma_f \). However, in practice the concentration, and thus the value of \( \gamma \) and \( \Gamma \), is imposed in the static meniscus, which acts as a reservoir for surfactants due to its large size. Thus, the physical boundary condition for those variables is imposed for \( x \to -\infty \), where \( c = cmc \), \( \gamma = \gamma_m \) and \( \Gamma = \Gamma_m \).

2.4.1. System of equations

Surfactants are assumed to equilibrate instantaneously between the interface and the bulk (assumption 2), so that the equilibrium equation of state and adsorption isotherm may be used to relate respectively \( \gamma \) to \( \Gamma \) and \( \Gamma \) to \( c \). We discuss the shape of these functions in the next section, but we take them formally in account here by treating \( \gamma \) and \( \Gamma \) as functions of respectively \( \Gamma \) and \( c \) only.

Eq. (4) is rewritten, using Eq. (3), as:

\[
\frac{\partial \gamma}{\partial \Gamma} \frac{\partial \Gamma}{\partial c} = -3h_U - v_s h
\]  

(6)

Eq. (5) is integrated between \( x \) and the flat film region, where \( \Gamma(x) = \Gamma_f \), \( \nu_s(x) = U \), \( \nu_s(x) = c_f \), \( \gamma(x) = \gamma_f \), \( h(x) = h_f \)

\[
U h_U (c - c_f) + v_s \Gamma_U - U \Gamma_f = 0
\]  

(7)

2.5. Adsorption isotherm and equation of state

For the sake of simplicity we use simplified analytical expressions for the adsorption isotherm and the equation of state. Note that it is not necessary for our calculations, and arbitrary functions could be used instead. The adsorption isotherm \( \Gamma(c) \) has been chosen as a derivable function satisfying the two following important properties: a rapid increase of \( \Gamma \) from 0 to \( \Gamma_{\text{cmc}} \) when \( c \) increases from 0 to the ccmc, and a saturation of \( \Gamma \) above the ccmc. Indeed, we found that the non linearity in the isotherm is crucial for the generation of experiments (see Section 4.4), incidentally, it is the main difference, regarding surfactants dynamics, between our model, and the aforementioned studies on static films [16] and Plateau border drainage [17]. More precisely, we impose

\[
\frac{\Gamma}{\Gamma_{\text{cmc}}} = \frac{1 + K_f}{2} \frac{c}{\text{cmc}} + \frac{1 - K_f}{2} \left( 1 - \xi \log \left[ e^{\frac{c}{\text{cmc}}} - 1 \right] + e^{\frac{c}{\text{cmc}}} - 1 \right)
\]  

(8)

whose graph is plotted on Fig. 2. The parameter \( \xi \) is the size of the transition region at the ccmc. It does not affect the result of the model as long as it is small enough.

Below the ccmc, the above expression asymptotes to the linear relation \( \Gamma/\Gamma_{\text{cmc}} = c/\text{cmc} \). Due to the transition region, \( \Gamma \) is close, but slightly below, \( \Gamma_{\text{cmc}} \) for \( c = 1/\text{cmc} \). Above the transition, the adsorption isotherm reduces to \( \Gamma/\Gamma_{\text{cmc}} = 1 + K_f/c_{\text{cmc}} - 1 \). We chose an affine relation with a very small slope \( K_f \) above the ccmc instead of a strict saturation. A non-vanishing value for \( K_f \) is indeed required for numerical stability. We additionally believe that this parameter \( K_f \) is a physical parameter, even if difficult to measure. Stuber-Rauch and collaborators [18] measured for example a decrease of the surface tension of a solution of C\( \text{12}\)E\( \text{6} \) close to 2 nN/m as the concentration goes from \( c = \text{cmc} \) to \( c = 10 \text{cmc} \). Even such a small variation of \( \gamma \) above the ccmc may not be neglected a priori: as we already stressed, in these films, minute surface tension variations (on the order of 0.01 % to 1%, that is 0.01–1 nN/m) have a strong effect.

Finally, we assume an affine relationship between \( \gamma \) and \( \Gamma \). The equation of state is thus

\[
\frac{\gamma}{\text{ycmc}} = \frac{\gamma(0)}{\text{ycmc}} - \frac{\Gamma}{\Gamma_{\text{cmc}}} \left( \frac{\gamma(0)}{\text{ycmc}} - 1 \right)
\]  

(9)

with \( \gamma(0) \) the surface tension of pure water.

3. Numerics

3.1. Rescaling

We define the dimensionless variables as follows, and separate them by uppercasing, or tilding. \( h \) and \( v_s \) are rescaled by their value in the flat film: \( h = h_U h_f \), \( v_s = v_s / U \). The concentrations and the surface tension are rescaled by their value at the ccmc: \( C = c / \text{cmc}, \Gamma = \Gamma / \Gamma_{\text{cmc}}, \gamma = \gamma / \gamma_{\text{ycmc}} \). Consistently, the space variable becomes \( X = x \text{Ca}^{1/3} h_f / \text{Ca} \) with \( \text{Ca} = \eta U / \gamma_{\text{ycmc}} \). This capillary number \( \text{Ca} \) is based on the value of surface tension at the ccmc. It is slightly different than the capillary number used, for example, to describe experimental studies, based on the surface tension of the solution (at whatever surfactant concentration is used), which we denote by \( \gamma_s \).

Eqs. (3), (6) and (7) become, with \( \Gamma \) and \( \gamma \) explicit functions of \( C \) given by Eqs. (9) and (8):

\[
H_{\text{XX}} = 3 \frac{1 - V_s H}{\gamma} - \frac{1 - V_s H}{H^3}
\]  

(10)

\[
\frac{\partial \gamma}{\partial t} \frac{\partial \Gamma}{\partial C} = -3 \text{Ca}^{2/3} 1 - \frac{V_s H}{H^2}
\]  

(11)

\[
\alpha \beta \text{Ca}^{2/3} (C - C_f) + V_s \Gamma - \Gamma_f = 0
\]  

(12)

where we introduce the coefficient \( \beta \) defined by \( h_f = \beta \eta \text{Ca}^{2/3} \) (which is the quantity that we are trying to determine) and the coefficient \( \alpha = \eta \text{mcmc} / \Gamma_{\text{cmc}} \). The coefficient \( \alpha \) is a crucial non-dimensional parameter of our model, which compares the
concentration of surfactants in the bulk to that at the interface. It compares \( r_m \) to the length \( l_{mc} = \Gamma_{mc}/c_{mc} \), which is the thickness of a liquid layer containing as many surfactants as the corresponding interface, at the cmc. Depending on the surfactants used, it can range from 1 \( \mu m \) to 1 cm, and accordingly \( \alpha \) ranges from 1 to 1000 for millimetric menisci.

3.2. Boundary conditions and resolution

For numerical reasons, the boundary conditions must be imposed in the flat film region. As \( X \rightarrow +\infty \):

\[
H = 1, \ H_X = 0, \ H_{XX} = 0 \\
C = C_f \\
V_s = 1
\]

(13)

The integration is started for \( H = 1 + \varepsilon_0 \) and \( X = X_0 \) with \( \varepsilon_0 \) a small but finite quantity. The starting values for the other variables and the derivatives of \( H \) are found by linearizing the problem in the flat film region. The profile is then integrated to \( X = 0 \), toward the static meniscus.

Typical profiles are shown in Fig. 3. The important feature is that we choose \( X_0 \) to be large enough that both \( H_{XX}, V_s \) and \( C \) tend toward well converged constant values as \( X \) decreases. This ensures the validity of the asymptotic matching to the static meniscus.

3.3. Matching to the static meniscus

The matching to the meniscus imposes that the curvature tends to \( 1/r_m \) for negative \( x \). This condition can be written with non-dimensional variables as

\[
\frac{1}{r_m} = h_{XX}(-\infty) = H_{XX}^{\infty} \frac{\Gamma_{mc}}{\beta h_f}
\]

Given \( \beta = \beta r_m \Gamma_{mc}^{2/3} \) this imposes

\[
\beta = H_{XX}^{\infty}
\]

(15)

This numerical parameter \( \beta \) appears in Eq. (12), and it can thus not be freely chosen. Instead, the matching to the meniscus requires to solve the implicit equation \( \beta = H_{XX}^{\infty}(\beta) \). With \( \beta \) the solution of this equation, the film thickness is obtained as:

\[
h_f = \beta r_m \Gamma_{mc}^{2/3}
\]

(16)

In Frankel’s problem, the solution is \( h_f^{FR} = 1.34 r_m \Gamma_{mc}^{2/3} \) with a capillary number \( \Gamma = \eta V / \gamma m \). To compare our predictions to Frankel’s, we use the fact that \( h_f h_f^{FR} = (\gamma_{mc} \Gamma_{mc}^{2/3} \beta)/1.34 \). Note that, as the surface tension variation is very small above the cmc, \( C_a \) and \( C_{ac} \) differ significantly only below the cmc and the distinction between both is made only when necessary.

Lastly, since the concentration of surfactants is in practice imposed in the static meniscus, a shooting method is used to select the right value of \( C_f \) (concentration in the film), given the value of \( C_m \) (in the static meniscus) that is imposed.

This procedure allows us to solve the problem, given the following set of independent numerical parameters: \( C_m, C_{ac}, \alpha \) and the parameters of the equation of state and of the isotherm equation \( \gamma(0), K_f \) and \( \delta \).

4. Results and discussion

4.1. Influence of the capillary number

Fig. 4a shows the predicted value of \( h_f / h_f^{FR} \) as a function of \( \Gamma \) (in the range \( 10^{-6} \) to \( 10^{-2} \)), and for \( \alpha = 60, \gamma(0) = 2.06, K_f = 0.001 \) and \( C_m = 5 \). Fig. 4b shows the value of the velocity in the static meniscus \( V_m \) for the same parameters.

Frankel’s prediction, which corresponds to a vanishing interface extension, is recovered within 5%, for \( \Gamma < 10^{-5} \). Consistently, as seen on Fig. 4b, the velocity difference \( 1 - V_m \) between the static meniscus and the film, hence interface stretching, is negligible at these low capillary numbers. For some critical capillary numbers, interface deformation becomes relevant, as illustrated by the larger velocity difference. Accordingly, \( h_f \) departs from Frankel’s law.

A higher capillary numbers, there is no direct relation between interface stretching and film thickness, as evidenced by the fact that the non-monotonic behavior of \( h_f / h_f^{FR} \) for intermediate \( \Gamma \) is not observed for \( V_m \). Note that the physical thickness of the film \( (h_f = \beta r_m \Gamma_{mc}^{2/3}) \) does increase monotonically with \( \Gamma \).

4.2. Scaling law analysis for the velocity

Although there is no direct relation between the velocity difference \( \delta \nu \), between the film and the static meniscus and the thickness of the film \( h_f \), deviation from Frankel’s law only occur for significant interface stretching, that is values of \( \delta \nu \), of order one. A simple law can be derived for this parameter, based on the mass conservation. In this scaling law analysis, we separate formally the dynamic meniscus from the static part and the flat film region, as sketched on Fig. 5. We limit our analysis to small deviations from Frankel’s law. \( \Gamma, c, \gamma \) and \( \nu_s \), are assumed constant within the film (with respective values \( \Gamma_f, c_f, \gamma_f, \nu_s \)) and in the static meniscus \( (\Gamma_m = \Gamma + \delta \Gamma, c_m = c + \delta c, \gamma_m = \gamma - \delta \gamma, \nu_m = U - \delta \nu_s) \). We focus on the regime of small interfacial stresses, and we treat the problem at first order in \( \delta \Gamma \) and \( \delta \Gamma_f \).
At steady state, the net flux of surfactants going through the dynamic meniscus must be zero:

\[(c + \delta c)q + (\Gamma + \delta \Gamma)(U - \delta v_s) = c \Gamma + \Gamma_f U\]

At first order, using \( q \sim r_m Ca^{2/3} U \), we get:

\[\delta v_s = \frac{U}{\Gamma} \frac{\delta \Gamma}{\Gamma} \left(1 + r_m Ca^{2/3} \frac{\partial c}{\partial \Gamma}\right)\]

(17)

Lastly, the surface tension difference scales like \( \delta \gamma \sim \gamma Ca^{2/3} \) (see Eq. (1)), so that our final prediction for interface stretching is:

\[\frac{\delta v_s}{U} = Ca^{2/3} \frac{\gamma}{\Gamma} \frac{\delta \Gamma}{\delta \gamma} \left(1 + \frac{r_m}{\Gamma} Ca^{2/3}\right)\]

(18)

The surface dominated case corresponds to \( r_m Ca^{2/3} \partial c/\partial \Gamma \gg 1 \). In this limit, the predictions of the elastic interface model are expected and recovered, as verified in Section 4.3.

On the other hand, for a large meniscus radius, or above the cmc where \( \partial \Gamma/\partial c \) is very small, surfactants in the bulk are dominant \((r_m Ca^{2/3} \partial c/\partial \Gamma \gg 1)\). A new behavior is observed, which depends on the bulk concentration, as shown in Section 4.4.

In non-dimensional variables, Eq. (18) becomes

\[\delta V_s = 1 - V_m = Ca^{-2/3} \gamma(0) - 1 \frac{\gamma^{1/3}}{\Gamma_f} \left(1 + \frac{\alpha}{\gamma^{1/3}} \frac{1}{\partial \Gamma/\partial c} Ca^{-2/3}\right)\]

(19)

The variation of \( 1 - V_m \) with the capillary number is plotted in Fig. 6. The two power laws are not well separated, but can still be observed.

4.3. The limit of elastic interface

If the amount of surfactant in the bulk is much smaller than the amount of surfactant at the interface, then the exchange between interface and bulk becomes negligible and surfactant transport is governed by interfacial convection. In that limit, our model coincides with a model of insoluble surfactant, leading to a purely elastic interface, as studied in [10] and [8]. This limit is recovered when \( \Gamma_f \gg \gamma(0) \). For \( \Gamma_f \gg \gamma(0) \), more precisely (using Eq. (18)) when \( \Gamma_f/\partial c \gg r_m Ca^{2/3} \). The Ca dependence of the validity criterion simply stresses the fact that the relative contributions of surface and bulk transport vary with \( Ca \), as seen in Eq. (12).

For simplicity we restrict the case to \( c_m = c_{cmc} \). In that case, the previous condition becomes \( \alpha = r_m c_{cmc}/\Gamma_{cmc} \ll Ca^{-2/3} \) and the Marangoni elasticity is \( E = -\Gamma_f \gamma/\partial \Gamma = \gamma(0) - 1 \), as obtained from our equation of state (9).

We compare in Fig. 7 the results obtained with the elastic model discussed in [10] and the results obtained with our calculations in different regimes. We plot the film thickness, renormalized by Frankel's thickness, as a function of the capillary number. The solid black curve is obtained with the elastic model, with \( E/\gamma = 0.1 \). For each other curve, obtained with the full model, we set \( \tilde{\gamma}(0) = 1 \), \( \tilde{\gamma}_f = 1 \) and \( \alpha = k Ca^{-2/3} \), with \( k \) a constant. For \( \alpha = 0.01 Ca^{-2/3} \) or \( \alpha = 0.1 Ca^{-2/3} \), both predictions for the thickness of the film agree,
as expected. Frankel’s law is observed at small capillary numbers and a thinner film is obtained if \( \partial \gamma > Ca^{2/3} \).

For higher values of \( \alpha ( \alpha = Ca^{-2/3}, \alpha = 10Ca^{-2/3} \text{ or } \alpha = 100Ca^{-2/3}) \), the solubility of the surfactant is increased and the bulk concentration becomes non-negligible with respect to surface concentration. Surface extension can be cured by a reabsorption of surfactants. The surface tension variation for a given interfacial extension is thus reduced at high solubility, which corresponds qualitatively to a smaller effective elasticity. Consistently, the departure from Frankel’s law occurs at lower capillary number for larger values of the solubility. Note that, in Fig. 7, the bulk concentration is fixed: the variation of the ratio \( c \gamma \) thus corresponds to a variation of \( \gamma \), at constant \( c \), that can be achieved by changing the surfactant used. The influence of the bulk concentration, for a given surfactant, is discussed below.

4.4. Effect of initial surfactant concentration \( c_m \)

An important aspect of our model is the ability to predict film thickness variations as a function of the concentration in the meniscus. The most important feature is a strong film thinning observed when the concentration goes from onecmc to several cmc.

The variation of \( h_f/h^f \) with \( C_m = c_m/c_{mc} \) is shown in Fig. 8, where we plot the result of our calculations for a constant pulling velocity, constant surfactant physicochemical constants, constant meniscus radius and increasing values of bulk concentration. For \( 1 < C_m < 6 \), an important thickness decrease is obtained. Note that Frankel’s film thickness \( h^f = 1.34(\eta l \gamma \gamma')^{1/3} \) used as a thickness reference, varies slightly with \( C_m \), as the surface tension varies (see the surface tension in the film and in the meniscus in Fig. 9b). However, this effect is only sensible much below the cmc and does not play any relevant role here.

The observed transition between a film close to the Frankel’s film and a much thinner film can be understood on the basis of the velocity scaling given by Eq. (19). The concentration decreases from the static meniscus to the film, and for \( 1 < C_m < 6 \), the film is almost at the cmc, as seen in Fig. 9a. For lower concentrations, the film is entirely below the cmc, whereas for higher concentrations, it is always above the cmc. It means that the non-linearity of the isotherm (i.e., the fact that the concentration crosses the cmc, where \( \partial \gamma / \partial C \) changes abruptly) has to be taken into account in the intermediate concentration regime only.

With the parameters of Fig. 8, we have \( K_T = 10^{-3} \ll \alpha Ca^{-2/3} = 0.13 \ll 1 \). The second term in Eq. (19), associated to bulk concentration effects, is thus negligible below the cmc, but non-negligible above, as the coefficient \( \partial \gamma / \partial C \) suddenly decreases from 1 to \( K_T \). The velocity difference thus jumps from a small value below the cmc to a much higher value above the cmc, thus explaining the sudden thickness decrease for meniscus concentrations slightly above the cmc.

Let us simplify the problem one final time by considering the limit where the surface tension variation above the cmc is negligible and the tension variation below the cmc very large (which corresponds to incompressible interfaces, as in Frankel’s work). Starting from a concentration in the static meniscus \( C_m > 1 \), the concentration must first decrease to the cmc, which generates no interfacial stresses, but does stretches the interface. Below the cmc, the necessary stresses may now be created with negligible concentration difference, hence negligible interface deformation. In other words, the entire interfacial elongation happens above the cmc, and corresponds to a decrease in concentrations from \( C_m > 1 \) to 1. Interface stretching thus increases with \( C_m \), which results in the thickness decreasing. The real curve is smoothed out by the small surface tension variation above the cmc, and by the finite size of the transition region between the affine regimes of the isotherm. The physical origin of the thickness decrease still holds: it is a signature of the non-linear isotherm.

As visible on the two enlargements of Fig. 8, the rescaled thickness increases slightly with \( C_m \) for \( C_m < 1 \) and for \( C_m > 6 \): surprisingly, for a given pulling velocity, the film thickness thus varies in a non-monotonic way with the concentration. For \( C_m < 1 \) or \( C_m > 6 \), the film is either always below the cmc or always above, as shown in Fig. 8. The variation of the surface concentration with the bulk concentration is thus affine: \( \partial \gamma / \partial C \) is either 1 (below the cmc) or \( K_T \) (above the cmc). Eq. (19) can then be simplified into

\[
\delta V_s = 1 - V_m = Ca^{-2/3}(\gamma(0) - 1) \frac{\gamma'^{1/3}}{\gamma} \left( 1 + \frac{\alpha}{\gamma'^{2/3}} \right) \frac{1}{K_T C_m^{2/3}}
\]

for the case \( C_m > 1 \) (the case \( C_m < 1 \) is obtained by setting \( K_T = 1 \)). In Fig. 8, \( C_m \) (i.e. the pulling velocity) is maintained constant, as well as the physicochemical properties \( \gamma(0) \) and \( \alpha \). In the previous equation, only \( \gamma \) and \( \gamma' \) vary with the concentration in the meniscus, and the main effect is the affine increase of \( \gamma \) with \( C_m \). Consequently, the velocity variation along the film decreases with \( C_m \), and the film thickness increases.
4.5. Comparison with experiments

As a final summary of our results, we compare our model to experimental data published by Saulnier and collaborators [8]. One of the central results of their work is the fact that deviation from Frankel law is observed above a certain capillary number, for a solution of C_{12}E_6 surfactant. Most importantly, they measured film thicknesses for different surfactant concentrations (C_m = 1, 3, 5 and 10 in our notations), and showed that this transition capillary number decreases with C_m.

As we mentioned in the previous section, our model does reproduce qualitatively this behavior. More precisely, we show in Fig. 10 a the best fit of their data by our model, with \( K_R = 0.0012 \) as the only adjustable parameter (\( \alpha = 63 \) has been estimated from \( \Gamma_{c_m} = 3 \times 10^{-6} \text{mol/m}^2 \) and \( C_{c_m} = 7.3 \times 10^{-5} \text{mol/L} \), as measured in [18]). In our model, C_m is imposed, instead of C_a, however, the difference between the two parameters is negligible above the cmc, as \( \gamma \) remains very close to \( \gamma_{c_m} \).

Our model captures the C_a and C_m dependence of the thickness quite well, except for the smaller C_m where it underestimates deviations from Frankel’s law.

The relevance of the fitted value of \( K_R \) is difficult to evaluate, since most studies on surface tension focus on concentrations below the cmc, and measuring \( \gamma \) with the appropriate precision is not straightforward. In one study [18], Stubbenauch and collaborators measured the surface tension well above the cmc. By fitting their data, we found a value of \( K_R \) on the order of 0.01.

Our model also predicts the surfactant concentration \( C_f \) in the extracted film (Fig. 10b). As C_a increases, the stresses needed to extract the film increase, hence \( C_f \) decreases to generate a larger surface tension difference across the system. For \( C_m = 3 \) and \( C_m = 1 \), the concentration C_m in the dynamical meniscus becomes low enough that it reaches the transition region of our isotherm (with \( \xi = 0.15 \), the transition region starts at \( C \approx 1.3 \)) for \( C_a > 10^{-4} \). The prediction is thus sensitive, for these \( C_m \), to the exact function used to describe this region. This may explain the discrepancy between our model and the data.

Lastly, our computations predict values of \( C_f \) significantly different from \( C_m \) (by up to 50 %). We believe that measuring this quantity would provide the most direct way to confirm or infirm the relevance of our work to experimental situations.

5. Conclusion

In the present study, we predict the steady-state thickness of soap films pulled from a bath of surfactants at constant speed. The originality of our work lies in the fact that we do not assume a particular effective interfacial rheology (i.e., incompressible or elastic or viscous interface). Instead, we take explicitly into account the transport of surfactant molecules, and we deduce the Marangoni stresses at the interface, which serve as boundary condition for the hydrodynamics within the film, from their repartition.

In our model, the apparent rigidification of the interfaces comes explicitly from depletion/confinement effects: interface stretching lowers locally the concentration of surfactants, because molecules in the bulk adsorb on the newly created interface. The peculiar thinness of the films makes this mechanism particularly efficient to
create interfacial stresses. We use two key approximations to track surfactants: their concentration is supposed homogeneous within the thickness of the film, and bulk and surface adsorbed surfactants are supposed at equilibrium.

We show that this mechanism suffices to create the necessary stresses to pull a film out of a reservoir. For low enough capillary numbers, Frankel’s law is recovered. Much like what is observed in experiments, deviations from this law occur at higher pulling velocities. We identify a regime of “insoluble” surfactants, where the elastic interface model is recovered. Outside of this regime, bulk molecules have to be taken into account and lead to a less “rigid” interfaces.

Most importantly, with our approximations, the entire problem is computed from equilibrium properties of the surfactant molecules. In particular, the resulting Marangoni stresses, hence the thickness of the film, depend strongly on the form of the adsorption isotherm and the equation of state. We use here a simplified form for these two functions, but more realistic ones could be as easily incorporated. In fact, we found that the non-linearity of the adsorption isotherm (namely the fact that its slope change abruptly around the cmc) is crucial to the generation of films.

Lastly, the most obvious prediction of our model is the thickness of the film, because it can be easily measured. We show that its results are compatible with available data by Saulnier and coworkers [8]. Our calculations additionally compute the repartition of surfactants, and the interfacial velocity. Although these quantities are much harder to measure in experiments, they are much more closely related to the mechanisms at work: the lower concentration in the film is a direct effect of depletion, while the lower interfacial velocity in the static meniscus comes from interface stretching.

Acknowledgements

We would like to thank E. Rio and B. Dollet for fruitful discussions. J.S. acknowledges financial support from Région Bretagne (CREATE MOUSPORE) and Agence Nationale de la Recherche (ANR-13-PDOC-0014-01-HYDROSURFDYN).

References