Formation of Soap Films from Polymer Solutions

Robijn Bruinsma

Department of Physics, University of California, Los Angeles, California 90024

Jean-Marc di Meglio,∗ David Quéré, and Sylvie Cohen-Addad

Laboratoire de Physique de la Matière Condensée,† Collège de France, 75231 Paris Cedex 05, France

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The classical Frankel law describing the formation of soap films was recently found to break down for polymer solutions. We discuss in this paper how this could be due to the effects of normal stresses and slip of the polymer along the surfactant-covered surfaces. We also study the consequences of a detailed description of the surface layer including the Marangoni effect, in the case of soluble surfactants (using the classical Gibbs theory) as well as in the case of insoluble surfactants. These predictions are compared to experimental results.

I. Introduction

Pulling liquid films out of a reservoir (and the reverse process of film drainage) has been a problem of interest for many years. In a celebrated paper, Landau and Levich1 theoretically derived the law relating the thickness d of a film entrained on a flat plate to the pulling velocity. Frankel2 calculated a similar law for a soap film entrained on a frame (see section II):

\[ d/\kappa_0^{-1} = 1.89 (Ca)^{2/3} \]  

Here Ca is the capillary number:

\[ Ca = \eta V/\gamma_0 \]  

η is the viscosity of the solution, V the upward velocity of the frame, \(\gamma_0\) the liquid surface tension, and \(\kappa_0^{-1}\) the capillary length:

\[ \kappa_0^{-1} = (\gamma_0/\rho g)^{1/2} \]  

ρ is the density of the liquid and g the gravitational acceleration. This law is valid when van der Waals interactions can be neglected (i.e., when film thicknesses are larger than 0.1 \(\mu\)m) and when the gravitational pressure can be neglected with respect to the capillary pressure (i.e., for \(Ca \ll 1\)). \(\kappa_0^{-1}\) is typically a few tenths of a centimeter, and Ca lies between \(10^{-4}\) and \(10^{-2}\) in most experiments: the thickness d thus ranges between 0.01 and 100 \(\mu\)m. The Frankel prediction is in close agreement with experimental results obtained with solutions of sodium dodecyl sulfate (SDS).3

In a number of practical applications (e.g., foams), hydrophilic polymers are added to the soap solutions. This increases the viscosity η, which in turn decreases the drainage velocity and thus stabilizes the film. Recently, two of us4 studied the formation of films from soap (SDS) solutions containing a hydrophilic polymer (poly(ethylene oxide) (PEO)). It was observed, surprisingly, that the addition of PEO of high molecular weight modifies the dependence on Ca of the film thickness: thinner films are observed for the lowest Ca values, and we find a stronger dependence on Ca than predicted by Frankel's law; the polymer not just increases the bulk viscosity, and a simple shear thinning mechanism cannot describe the change of the Ca dependence.4

The aim of this paper is to reexamine the derivation of Frankel's law to understand how polymer additives can cause it to fail. In section II, we review the derivation of Frankel's law to expose the underlying assumptions. In section III, we investigate how polymers can affect the flow inside the film, emphasizing non-Newtonian flow and slip boundary conditions. In section IV we examine the effects of the Marangoni phenomenon in the surfactant layer for the case of water-soluble (Gibbs layer) or water-insoluble (Langmuir layer) surfactant molecules.

Throughout, we use dimensional arguments to derive scaling relations between \(\kappa d\) and Ca. More accurate calculations are discussed in the Appendix and compared with the scaling relations. In section V, we confront our predictions with the experimental data of ref 4.

II. Frankel Theory

Assume a reservoir from which a film is pulled. Choose the z axis to be normal to the reservoir surface with z = 0 the surface far from the film. The x axis is chosen to be normal to the film, and the film thickness at a distance z above the surface of the reservoir is chosen to be \(2h(z)\) (Figure 1). Far above the surface (\(z \gg \kappa_0^{-1}\)), \(h(z)\) approaches a constant value, \(d/2\), so

\[ \lim_{z \to \infty} h(z) = d/2 \]  

Since for \(z \to 0\), \(h(z)\) must describe the reservoir surface, we also demand that

\[ \lim_{z \to 0} h(z) = \infty \]  

The film is pulled up by a wire frame moving at velocity V. The surface of the film is covered by surfactants which are assumed to form an inextensible flexible sheet. The sheet is attached to the wire frame and thus moves also with a velocity V.

Three regions can be distinguished during the formation of the film (Figure 1): a static meniscus at the bottom, then a "dynamic" region where the profile is controlled by large pressure gradients, and finally, for \(z \to \infty\), the film itself of constant thickness d.

a. Static Meniscus. The profile \(h(z)\) is here determined by the balance of the Laplace pressure (\(\gamma_0/R\) with R the radius of curvature of the interface) with the
thickness is of order the characteristic height of the dynamic region. Since, Appendix, section a. The solution of that equation must by a gradient of the viscous stress tensor:

\[ \frac{d^2h}{dz^2} = \kappa_0 \frac{\gamma_0}{\kappa_0^2} \]  \hspace{1cm} (II.3)

From eq II.3, it is simple to get the height \( z_0 \) of the meniscus, \( z_0 = 2^{1/2} \kappa_0^{-1} \), and the curvature at the top of the meniscus which is \( 2^{1/2} \kappa_0 \).

b. Flat Film. Well above the reservoir, for \( z > z_0 \) the film is flat and \( h(z) \approx d/2 \) as mentioned. Inside the film there are no flow gradients so there are no viscous stresses, and since the film is flat, there is no capillary pressure either. The pressure inside the film is thus equal to the atmospheric pressure.

c. Dynamic Regime. Separating the static meniscus and the asymptotic film, there is a crossover region with a rapid increase of pressure from \(-\rho g z_0^{-1}\) to zero. The large pressure gradient attempts to squeeze liquid out of the film. In the film interior, the pressure gradient must be balanced by compensating forces. In the Frankel theory, one assumes that the pressure gradient is balanced by a gradient of the viscous stress tensor:

\[ \delta \sigma_{ij} = \frac{\partial}{\partial z} \left( \frac{\partial u}{\partial x} \right) \]  \hspace{1cm} (II.4)

with \( \sigma_{ij} = \eta \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial z^2} \right) \) and \( u \) the flow velocity. To a good approximation, \( u \) is along the \( x \) direction and varies predominantly along the \( x \) direction. In that limit (the lubrication approximation), eq II.4 reduces to

\[ \eta \left( \frac{\partial^2 u}{\partial x^2} \right) = -P \frac{\partial}{\partial z} \]  \hspace{1cm} (II.5a)

\[ 0 = \eta \frac{\partial}{\partial z} \frac{\partial u}{\partial x} \]  \hspace{1cm} (II.5b)

Since \( P \) varies little with \( x \), we can equate it with the Laplace pressure \( P_c \) and eq II.5a becomes for small film curvature

\[ \eta \left( \frac{\partial^2 u}{\partial x^2} \right) = \gamma_0 \frac{\partial^2 (h(z))}{\partial x^2} \]  \hspace{1cm} (II.6)

If we combine eq II.6 with mass conservation, we obtain a differential equation for \( h(z) \) which is discussed in the Appendix, section a. The solution of that equation must be matched to the asymptotic regime for \( z \to \infty \), so \( h(\infty) = d/2 \) while \( h'(\infty) = h''(\infty) = 0 \), and to the static meniscus at \( z_0 \) where \( h''(z_0) = 2^{1/2} \kappa_0 \). This procedure is carried out in the Appendix.

A dimensional analysis provides more directly the film thickness dependence on the pulling velocity \( V \). Let \( \xi \) be the characteristic height of the dynamic region. Since, near \( z_0 \) the curvature \( h'' \) must be \( 2^{1/2} \kappa_0 \), and since the film thickness is of order \( d \) near \( z_0 \), we conclude that

\[ d/\xi^2 = \kappa_0 \]  \hspace{1cm} (II.7)

The dimensional analysis of eq II.6 gives

\[ \eta V/\xi^2 = (1/\xi) (\gamma_0 \kappa_0) \]  \hspace{1cm} (II.8)

Eliminating \( \xi \) gives

\[ \kappa_0 d = (\kappa_0)^{3/2} \]  \hspace{1cm} (II.9)

which is the Frankel law.

III. Non-Newtonian Effects Induced by the Polymer

We now can examine the assumptions made in view of possible violations under polymer addition. Polymer solutions are well known to exhibit unusual hydrodynamic behavior. Flow gradients create additional stresses (normal stresses) which must be included in the Navier–Stokes equation. These non-Newtonian effects appear when the Deborah number \( D_e \) (the product of shear rate and relaxation time) is larger than \( 1 \). The shear rate in the experiments range from \( 1 \times 10^4 \) s\(^{-1}\) while the relaxation time of semidilute PEO solutions (with \( M \approx 10^6 \text{D}_e \)) is of order \( 10^{-1} \) to \( 10^{-2} \) s, so \( D_e \) is of order 1. Moreover, an entangled polymer network resists shear and would tend to slip over the surfactant-covered film, provided that there is no strong attraction between the polymer chains and the surface. In this section we will examine whether these effects will alter the profile and the dependence of \( d \) on \( \text{Ca} \).

a. Normal Stresses. We will include non-Newtonian flow into the framework of the Frankel theory by adding to the usual viscous stress tensor the "normal" stresses which we will denote by \( \sigma_{ij}^N \). Normal stresses are well known to lead to the swelling of streams emerging from an orifice, and we expect that for the present case normal stresses will lead to the swelling of the film and thus to an increased dependence of \( d \) on \( \text{Ca} \). In our problem, the flow is directed along the \( z \) axis and the flow gradient is normal to the film, i.e., along the \( x \) axis (see Figure 1). In the limit of low shear rate (\( \partial u/\partial x \to 0 \)), the normal stress differences can be expressed as

\[ \sigma_{xx}^N - \sigma_{yy}^N = N_1 (\partial u/\partial x)^2 \]  \hspace{1cm} (III.1)

with \( N_1 > 0 \) and \( N_2 \) the first and second normal stress coefficients. Recent experiments have shown that, at \( \gamma = \partial u/\partial x \approx 100 \text{ s}^{-1} \) and for the same system as considered in ref 4, the first normal stress difference in a Couette flow is \( \sigma_{xx}^N - \sigma_{yy}^N \approx 0.01 \gamma^2 \text{Pa} \), which is equal to the first normal stress difference in a Couette flow

\[ \left( \sigma_{xx}^N - \sigma_{yy}^N \right) = \frac{2N_1 \partial u}{3 \partial x} \]  \hspace{1cm} (III.2)

The trace of the stress tensor has been absorbed into

\[ \sigma_{ij} = \begin{pmatrix} -\frac{N_1}{3} \frac{\partial u}{\partial x}^2 & 0 & \frac{N_1}{3} \frac{\partial u}{\partial x}^2 \\ 0 & -\frac{N_1}{3} \frac{\partial u}{\partial x}^2 & 0 \\ \frac{N_1}{3} \frac{\partial u}{\partial x} & 0 & \frac{2N_1}{3} \frac{\partial u}{\partial x}^2 \end{pmatrix} \]  \hspace{1cm} (III.3)


substrate. If the polymers do not have any chemical affinity for the substrate, then of a corresponding equal to a few angstroms. In either case, it was proposed that it should be allowed to slip with a (relative) velocity dependence of \( d/K-l \) on \( \text{Ca} \) than that of Frankel's law. A more careful discussion of eqs 11.3 and 11.4 is given in section c.

When non-Newtonian effects become large, we can, to lowest order, neglect the viscous stress in eq III.3. Balancing the normal stress with the capillary pressure then gives

\[
N_1 (\partial u/\partial x)^2 = -\gamma_0 (d^2 h/dz^2) \quad (\text{III.5})
\]

Using dimensional analysis on eq III.5 demands that we replace eq II.8 by

\[
N_1 (V/d)^2 \approx \gamma_0 \gamma_0 \quad (\text{III.6})
\]

In dimensionless units this leads, together with eq II.7 to a new scaling relation:

\[
d/\kappa_0^{-1} = [(N_1 \gamma_0 \kappa_0^{1/2})/\eta] \text{Ca} \quad (\text{III.7})
\]

The factor in brackets is of order 1–10 at higher polymer concentrations. As expected, eq III.7 predicts a stronger dependence of \( d/\kappa^{-1} \) on \( \text{Ca} \) than that of Frankel's law. A more careful discussion of eqs III.3 and III.4 is given in the Appendix, section b, with the results shown in Figure 2. The linear dependence is recovered at higher \( \text{Ca} \).

b. Slip Boundary Conditions. A polymer liquid strongly resists shear because of entanglement effects at the microscopic level. For this reason, it was proposed that a polymer liquid near a solid surface does not obey the standard nonslip boundary conditions but, instead, that it should be allowed to slip with a (relative) velocity \( V_p \) proportional to the applied viscous stress. If the flow is along the \( z \) direction and the surface normal along \( x \), then

\[
\sigma_{zz} = k V_p \quad (\text{III.8})
\]

with \( k \) the friction constant of the liquid sliding over the substrate. If the polymers do not have any chemical affinity for the substrate, then \( k \approx \eta_0 a \) with \( \eta_0 \) the viscosity of a corresponding monomeric liquid (in the case of a melt) or the solvent viscosity (for a more dilute solution) and \( a \) equal to a few angstroms. In either case, \( \eta_0 \approx 1-10 \text{ mPa} \text{s} \). If the monomers have chemical affinity with the substrate, then \( k \) may be much larger.

If we define the effective length \( b = \eta/k \), then for the experiments under discussion, \( b \approx a (\eta/\eta_0) \) must range between one and a few hundred angstroms assuming no chemical affinity and using the viscosities (1–100 mPa s) measured in ref 4. For strong chemical affinity, \( b \) would be correspondingly smaller.

For the present case the boundary conditions III.8, in the laboratory frame, become

\[
u(x=h(z)) - V = b (\partial u/\partial x)_{|x=h(z)} \quad (\text{III.9})
\]

Since \( \partial u/\partial x \approx V/d \), we can set \( u(x=h(z)) = V \) (the standard boundary condition) if \( b \ll d \). We then of course recover Frankel's law. In the opposite limit, \( b \gg d \), \( \partial u/\partial x \) must be of order \( V/b \) in order to obey eq III.9. Again using dimensional analysis, we now replace eq II.9 by

\[
\eta V/b \approx \gamma_0 \gamma_0 \quad (\text{III.10})
\]

With \( d/\xi^2 \approx \kappa_0 \), this gives in dimensionless units

\[
d/\kappa_0^{-1} \approx (\xi^2/b^2) \gamma_0^2 \quad (\text{III.11})
\]

The dependence of \( d \) on the capillary number thus again has been altered, now to an even stronger (\( \text{Ca} \)) behavior. The crossover from \( d/\kappa_0^{-1} \approx (\text{Ca})^{1/2} \) to \( d/\kappa_0^{-1} \approx (\text{Ca})^2 \) around \( d \approx b \) is shown in Figure 3, as computed in the Appendix, section c.

IV. Surface Layer

The Frankel theory treats the surfactant layer covering the film as a sheet moving with the pulling velocity \( V \). In this section we will examine whether a more realistic description could lead to violation of Frankel's law under polymer addition. We start by noting that we can consider two limiting cases: either (i) we can assume perfect chemical equilibrium between surfactant molecules on the surface and in the film interior—possibly in micellar form—or (ii) we can assume that there are no exchange processes of surfactant molecules. Which limiting case is relevant depends on the surfactant solubility and on the exchange times. The first case (i) is relevant if exchange times are small compared to the time scale of the transport of a surfactant molecule over a distance \( \xi \) (i.e., if \( \xi/V \gg d^2/D \), with \( D \) the surfactant diffusion coefficient, and if \( \xi/V \gg \tau_s \) with \( \tau_s \) the time scale of exchange between film and surface) and if the surfactant molecules are at least partially hydrosoluble. The elastic properties of such films

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were treated by Gibbs, and we will call it a Gibbs layer. We may assume the opposite limit (ii) if the surfactant molecules are entirely insoluble or if the subsurface polymer network has dramatically slowed exchange processes. This is the limit commonly assumed in a Langmuir-trough experiment, and we will call it a Langmuir layer. In particular, adding polymers could transform a Gibbs layer into a Langmuir layer. We will start with the case of the Gibbs layer.

a. Gibbs Layer. If chemical equilibrium is maintained in the film, then the elastic strains in the surfactant layer which are created by the viscous drag of the subsurface liquid are characterized by the elastic modulus $E$ defined by

$$E = 2A(T) \frac{\partial(\gamma(A))}{\partial A}$$

(IV.1)

with $A$ the surface area of the film considered (the numerical factor 2 arises from the presence of two surface layers for a soap film). The dependence of surface tension on area is only present for films of finite $d$. An increase in film area by $\Delta A$ leads to transport of surfactant materials from bulk to surface. The energy cost is essentially the chemical potential $\mu$ per molecule times $\Delta A$. For an infinite bulk ($d \rightarrow \infty$), the chemical potential is fixed and $\gamma$ could not depend on $\Delta A$, so $E(d=\infty) = 0$, but for finite $d$, loss of surfactant from the film interior would change the chemical potential, leading to an area-dependent surface tension. Gibbs showed$^{10}$ that

$$E = 4\Gamma \left( \frac{d\mu}{dG} \right)$$

(IV.2)

where $\Gamma$ is the surface concentration of surfactant and $G$ the total amount of surfactant per unit area, $G = 2\Gamma + cd$, $c$ being the bulk concentration of the surfactant. Using the Langmuir–Szyszkowski isotherm relating $\Gamma$ and $c$,

$$\gamma = \gamma_N - RT \log \left( 1 + \frac{c}{\alpha} \right)$$

(IV.3)

where $\Gamma_N$ and $\alpha$ are, respectively, the saturation adsorption and the Szyszkowski constant and $\gamma_N$ is the surface tension without surfactant. Using eqs IV.2 and IV.3, surfactant conservation and the Gibbs relation $d\gamma = -\Gamma d\mu$, the Gibbs modulus becomes

$$E = 4RT \left[ \frac{5}{2} \frac{\gamma_N - \gamma}{d(c + \alpha)^2 + 2\alpha} \right]$$

(IV.4)

On increasing the surfactant concentration, this modulus first increases because of the adsorption of the surfactant and then decreases because of the enhanced exchange between bulk and surface. It is also simple to understand that $E$ is a decreasing function of the film thickness: the thinner the film, the higher the surface/volume ratio. The expression IV.4 for $E$ does not however take into account aggregation phenomena. We will, for simplicity, take $E$ at its maximum:

$$E \approx \frac{\gamma_N}{d}$$

(IV.5)

with $l$ a characteristic length which is a function of $c$, $\alpha$, and $\Gamma_N$; from data discussed in ref 11, it follows that $l$ is of order 1 $\mu$m.

Let us imagine a series of parallel equidistant lines along the $z$ axis on the reservoir surface far from the film. Let $D_0$ be the spacing and $A_0$ the area of a strip bounded by two lines. Now allow these lines to be advected by the surface flow toward the wire frame. Because the surface flow velocity $u_0 = u(x-h(z), z)$ depends on $z$, neighboring lines will adjust their spacing as they flow up the film. We now treat every strip as a Langmuir trough characterized by a surface tension $\gamma(A(z))$ with $A(z) \neq A_0$, the area of a strip at a distance $z$ above the reservoir surface. The strips feel a force per unit area due to the gradient of $\gamma$ which must be balanced by pressure gradients. Balancing the two terms, in analogy to eq II.5, gives

$$\eta \frac{du}{dz} \bigg|_{x=h(z)} = (d/dz)\gamma(A(z))$$

(IV.6)

If $A(z)$ is close to $A_0$, we can expand

$$\frac{\eta du}{dz} \bigg|_{x=h(z)} = \left. \frac{E \, d}{2A_0 \, dz} \right|_{x=h(z)}$$

(IV.7)

To evaluate $A(z)$, let $z_i$ be the location of the $i$th line at a time $t$. Then $A(z)/A_0 = (z_{i+1} - z_i)/D_0$. By assumption, $d_A(t)/dt = u(z_i)$. It is then easy to show that

$$A(z)/A_0 = u(z)/V$$

(IV.8)

Using eq IV.8 in eq IV.7 gives our desired boundary condition:

$$\eta \frac{du}{dz} \bigg|_{z=h} = \frac{E}{2V} \frac{\partial(u(z))}{\partial z}$$

(IV.9)

which must replace Frankel's boundary condition $u(z) = V$.

To gain insight in the meaning of the new boundary condition, assume that for some $\Delta u$

$$u(z) \approx V + (\Delta u)e^{z/l}$$

(IV.10)

Then we can write eq IV.9 as

$$\eta \frac{du}{dz} \bigg|_{z=h} = \left( \frac{E}{2V} \right) \frac{\partial(u(z))}{\partial z}$$

(IV.11)

If we compare this to eq III.9, we see that this corresponds to an effective slip length $b$ given by

$$b = 2\eta V/e$$

(IV.12)

or, using eq II.8 for $\xi$

$$b = 2d(Ca)(d/k_d)^{1/2}$$

(IV.13)

For $k_d = 10^{-3}$, $Ca \approx 10^{-5}$, $d \approx 1$ micrometers, and $b/d \approx 10^{-3}$. We saw earlier that, for $b \ll d$, Frankel's law remains valid. We thus conclude that including Gibbs elasticity does not violate Frankel's law.

b. Langmuir Layer. We now assume that the addition of polymers hinders the exchange of surfactant molecules between bulk and surface. We are now in the regime of the Langmuir layer. We will characterize the layer by a surface pressure $\Pi(A)$. The boundary condition IV.1 now becomes

$$\eta \frac{du}{dz} \bigg|_{z=h} = -A(d\Pi(A))/dA$$

(IV.14)

The surface tension $\gamma = (\gamma_0 - \Pi)$ can be expanded as

$$\gamma = \gamma_0 + \frac{\partial\gamma}{\partial \Pi} \bigg|_{\Pi=0} (\Pi - \gamma_0) = \gamma_0 \left( 1 - M \frac{\Gamma - \Gamma_0}{\Gamma_0} \right)$$

(IV.15)

where $\Gamma$ is the conserved surfactant concentration, $\Gamma_0$ is the surface concentration of the surfactant in the reservoir, and $M = (\Gamma_0/\gamma_0)(\partial\gamma/\partial \Pi)_{\Pi=0}$ is the Marangoni number. Since the surfactant concentration is conserved, we can write, neglecting surface diffusion

$$\frac{d}{dz}u(z) \bigg|_{z=h} = 0$$

(IV.16)

with solution $u(z) = V\Gamma_{-m}$. Surface diffusion of the surfactant molecules has been shown to be negligible when

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the Marangoni effect is present. We then deduce that (using $\Gamma\rightarrow \infty \approx \Gamma_0$)
\[
\begin{align*}
\frac{\mathrm{d} \rho}{\mathrm{d} z} &= \frac{\mathrm{d} \rho}{\mathrm{d} \Gamma} \\
&= \frac{- \rho_0}{\gamma_0} \left( \frac{\partial (\rho u)}{\partial \rho} \right) \\
&= \frac{- \rho_0}{\gamma_0} \left( \frac{\partial (\rho u)}{\partial \rho} \right) \\
&= \gamma_0 \frac{M \partial (\rho u)}{V} \\
&= \gamma_0 \frac{M \partial (\rho u)}{V} \\
&= \gamma_0 \frac{M \partial (\rho u)}{V}. \\
\end{align*}
\]
By using eq IV.17 in eq IV.8 and comparing to eq IV.9, we see that the Langmuir case and the Gibbs case are identical if we set $E = 2 \gamma_0 M$. As a consequence, the inclusion of a Marangoni effect for an insoluble layer would yield a slip length $b$ given by
\[
b = \frac{d(Ca/M)}{1/\xi} \frac{1}{d} \frac{1}{d}
\]
This expression for $b$ is similar to the one given by eq IV.13 if we set $l = d$ apart from the additional $M$ factor. But $M$ is of order 1 for a typical insoluble surfactant (except at a very small surface concentration in the gaseous state), so the Frankel law should still apply. We conclude that suppression of exchange of surfactant molecules by polymer addition does not lead to violation of Frankel's law. A special case would concern phase coexistence in the Langmuir film when $\partial P/\partial a \approx 0$ in eq IV.14. This would produce a low value for $M$ and thus higher values of $b$.

V. Comparison with Experiments and Discussion

We have studied the formation of soap films from polymer solutions for different polymer/surfactant pairs, namely, SDS/PEO, nonionic surfactant (C12EO7)/PEO, and zwitterionic surfactant/poly saccharide (Xanthan).13 among these systems, only SDS solutions containing high MW PEO have thicknesses that do not follow the Frankel equation, as mentioned earlier in the Introduction. It is well known that this system—in the concentration ranges that we have studied ($c_{SDS} = \theta_{cmc}$, $c_{PEO} > c^*$, the overlap concentration)—exhibits strong interactions between surfactants and polymers,14 which lead to the formation of a network of micelles bound by the macromolecules (in equilibrium with unbound micelles). The other systems should not allow any interaction between surfactant and polymer; the hydrophilic part of the nonionic surfactant has the same chemical structure as the polymer skeleton (C12EO7/PEO), and the zwitterionic surfactant should not interact by Coulomb interaction with the polysaccharide. The deviations from the Frankel law also vanish for the SDS/PEO system when using a low MW (106) PEO.

The results obtained with high MW PEO are shown in Figure 4 and reveal increasing deviations from the Frankel law on polymer addition. First it must be emphasized that the viscoelastic properties of PEO solutions are greatly enhanced by addition of SDS.7 Furthermore, in the shear rate range of the experiments, the viscosity decreases only slightly with the shear rate,15 and the first normal stress difference increases nearly as the square of the shear rate.7 So our experiments could in principal follow the theoretical description of section III; i.e., the film thickness should increase as $Ca$, and for large capillary numbers and for a

\[
given Ca, the smaller the viscosity (or the polymer concentration), the larger the discrepancy with Frankel's law. Neither of these effects are observed in the experiments. Hence, normal stresses probably present for our shear rates do not explain the results.

Turning to slip boundary conditions, we saw in section III.b that this can be described by introducing a slip length $b$: according to the ratio of the film thickness to $b$, two regimes are expected with $d > (Ca)^{1/3}$ and $d \approx (Ca)^{1/2}$. Indeed the results qualitatively follow this behavior. If we fit the data with the $(Ca)^{1/2}$—and the $(Ca)^{1/3}$—regimes, we can extract from the crossover length the values for $b$. These values are displayed in Figure 5 as a function of the PEO concentration. Unfortunately the measured $b$ values are far too large (about of order micrometers) compared to the predicted value $b(Ca)^{1/3}$, estimated in using the measured viscosity $\eta$, which in turn assumes that the PEO concentration inside the soap film is equal to its bulk value.

Clearly, we have not yet succeeded to explain the observed deviations from the Frankel law. The SDS/PEO system exhibits a very strong polymer/surfactant interaction, and a recent X-ray reflectivity measurement16 shows that the PEO chains penetrate the surfactant layers of a soap film; this should give birth to effects (such as unexpected surface elasticity, or surface viscosity enhancements) which are not accounted for here and appeal for more experimental investigations.

A possible source of the failure of the existing models could be due to the existence of a gradient of polymer concentration inside the film which would give in turn a gradient of osmotic pressure and thereby would alter the velocity profile.

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Appendix

a. Frankel Theory. For the classical theory, the velocity profile is symmetric and obeys the boundary condition
\[
\begin{align*}
\frac{d u}{d x} &= \pm h(x) = V \\
\end{align*}
\]
Solution of eq II.7 yields the following velocity profile:
\[
\begin{align*}
u = - \frac{x}{2h} \frac{d h}{d x} (x^2 - h^2) + V \\
\end{align*}
\]
Conservation of mass along the film imposes
\[
\begin{align*}
\int_{-h}^{+h} u(x) \, dx = V d \\
\end{align*}
\]
or
\[
\begin{align*}
V d = 2V h + \frac{2}{3} \frac{d^2 h}{d x^2} \\
\end{align*}
\]
This differential equation is transformed to
\[
\frac{d^3 \mu}{d \lambda^3} = \frac{1 - \mu}{\mu^3} \\
\]
by introducing the dimensionless variables $\mu = 2h/d$ and $\lambda = x/\xi$ with $d = (24(Ca)^{1/3})$ (the characteristic length
\[
\begin{align*}
\end{align*}
\]
Figure 4. Experimental results of the dimensionless film thickness $d/\kappa_0^{-1}$ as a function of the capillary number $Ca$, for SDS solutions with PEO at different concentrations $c$: (a) $c = 0$ (no polymer); (b) $c = 0.05\%$; (c) $c = 0.1\%$; (d) $c = 0.3\%$; (e) $c = 0.5\%$ (the concentration being the ratio of polymer mass to the total mass of the solution). The surface tension (independent of $c$) is equal to $33.0 \pm 0.2$ mN/m, and the viscosities are, respectively, $1, 3.4, 6.7, 62$, and $154$ mPa s. The full line represents the Frankel prediction. The discussion is restricted to "intermediate" capillary numbers: at small $d/\kappa_0^{-1}$ values ($d/\kappa_0^{-1} < 5 \times 10^{-3}$), van der Waals forces make the film thinner; at highest $d/\kappa_0^{-1}$ values, one observes a plateau due to an effect of the finite size of the frame.

of the dynamic meniscus). It is solved with the following limits:

$$
\lim_{\lambda \to 0} \begin{cases}
\mu(\lambda) = 0 \\
\frac{d\mu}{d\lambda} = 0 \\
\frac{d^2\mu}{d\lambda^2} = 0
\end{cases}
$$

(A.6)

We now match the curvature $\alpha$ of the solution of eq A.5 for $\lambda \to 0$ with the curvature at the top of the static meniscus which is $2^{1/2}\kappa_0^{-1}$. The entrained thickness is then

$$
d = 2^{1/3}3^{2/3}\alpha\kappa_0^{-1}(Ca)^{2/3}
$$

(A.7)

A standard numerical integration yields $\alpha = 0.643$, and thus $d/\kappa_0^{-1} = 1.89(Ca)^{2/3}$. This is the well-known Frankel law.$^2$

Figure 5. Variation of the slip length $b$ with the PEO concentration $c$.

b. Normal Stresses. The boundary conditions remain eq A.1. Solution of eq III.4 with boundary condition $P = P_c$ (the capillary pressure) at $x = h(x)$ and
using eq III.2 give

\[ P = -\gamma \frac{d^2(h(z))}{dx^2} - \frac{N_1}{3} (\frac{\partial u^2}{\partial x})_{z=h(z)} \]  

(A.8)

Using eq A.8 in eq III.3 gives

\[ u = \sqrt{2\eta} \left( \gamma \frac{d^2h}{dx^2} + \frac{N_1}{3} (\frac{\partial u^2}{\partial x})_{z=h(z)} - \frac{1}{3} \frac{d(Kh)^2}{dx} \right) \]  

(A.9)

If the normal stress is zero, the velocity profile is parabolic. We treat the normal stress as a small perturbation around this state. Hence, we write \( u \) as \( V - \frac{(x^2 - h^2)}{2\eta} \), where the coefficient \( K \) is a function of \( z \) only. Identification with eq A.9 yields

\[ K = \frac{1}{\eta} \left( \gamma \frac{d^2h}{dx^2} + \frac{N_1}{3} (K^2 - \frac{1}{3} \frac{d(Kh)^2}{dx}) \right) \]  

(A.10)

To insure self-consistently that \( K \) does not depend on \( x \), we replace \( x^2 \) by its spatial average across the film: \( \langle x^2 \rangle = h^2/3 \). This gives a quadratic equation for \( K \):

\[ K = \frac{1}{\eta} \left( \gamma \frac{d^2h}{dx^2} + \frac{N_1}{3} K^2 \right) \]  

(A.11)

The total flux in terms of \( K \) is

\[ Vd = 2Vh + 2K^2h^3/3 \]  

(A.12)

We again introduce the reduced variables \( \mu \) and \( \lambda \) defined below eq A.5 and the dimensionless parameter \( \Gamma = 2N_1V/\eta h \). By eliminating \( K \) from eqs A.11 and A.12, we obtain the differential equation

\[ \frac{1 - \mu}{\mu^3} = \mu_{\lambda\lambda} - \Gamma \left( \frac{1 - \mu}{\mu^2} \right) \mu_\lambda \]  

(A.13)

which can be solved numerically as before. At low capillary numbers \( \Gamma \) is small; hence, the contribution of the second term in eq A.13 is negligible, and we recover the Frankel regime. Conversely at high \( \Gamma \), the normal stress contribution is comparable to the capillary pressure. As we saw in section III, a dimensional argument shows that \( d/\kappa_0^{-1} \) is proportional to \( \Gamma \). Between this linear regime and the Frankel regime, the thickness \( d \) depends on \( \Gamma \) through the function \( \alpha(\Gamma) \) according to

\[ d/\kappa_0^{-1} = 2^{1/3} Z^{2/3} \alpha(\Gamma) \kappa^{-2/3} \]  

(A.14)

This is represented in Figure 2 for \( N_1 = 0.01 \) (SI) and for different viscosities ranging from 1 to 60 mPa s.

c. Effect of Slip Boundary Conditions. The polymer solution slips on both walls, and the boundary conditions are (see eq III.9)

\[ u(x = \pm h(z)) = V - V_s \]  

(A.15)

with \( V_s = \pm b(\partial u/\partial x)_{z=\pm h} \). The velocity profile is given by

\[ u = V - \frac{\gamma}{2\eta} \frac{d^2h}{dx^2} (x^2 - 2hb - h^2) \]  

(A.16)

The total flux is

\[ Vd = 2Vh + 2 \frac{b\gamma h^2}{\eta} \left( 1 - \frac{h/3}{h} \right) \]  

(A.17)

From eq A.17, we can again find two limiting cases: (i) the film thickness is very large compared to \( b \), and we are back in the Frankel regime and (ii) the film thickness is much smaller than \( b \), and then our dimensional argument of section III shows that \( d \) goes as \( \kappa_0^{-1} \).

From the reduction of eq A.17, we obtain

\[ \frac{1 - \mu}{\mu^3} = (1 + 6e/\mu)\mu_{\lambda\lambda\lambda} \]  

(A.18)

where \( e = b/d \) and \( \mu \) and \( \lambda \) are the dimensionless width and height. The thickness of the film is given by

\[ d/\kappa_0^{-1} = 2^{1/3} Z^{2/3} \alpha(e) \kappa^{-2/3} \]  

(A.19)

In Figure 3 we have plotted \( d/\kappa_0^{-1} \) versus \( \Gamma \) (on a log–log scale) for a slip length \( b \) ranging from 5 \( \times \) 10\(^{-3}\) to 10 \( \mu m \).