"Young" soap films

P. G. DE GENNES

Collège de France, 11 place M. Berthelot
75231 Paris Cedex 05, France

March 21, 2022

Abstract

If we pull out rapidly a metallic frame out of a surfactant solution, we arrive at a "young" soap film with relatively simple features, as noticed first by Lucassen. The weight of the film is equilibrated by a vertical gradient of surface tension. At each level, the local solution concentration $c(z)$ equilibrates with the local monolayers, of surface concentration $\Gamma(z)$.

A detailed analysis of the young films was started by us in 1987. We present here an approach which is more illuminating a) the concentration profiles decay exponentially at large heights, with a characteristic length $\lambda \sim \text{meters}$ b) the surface is protected up to a thickness $h_{\text{in}}$ larger than $\lambda$. c) we also review the dynamic requirements. The surfactant must reach the surface in a time shorter than the free fall time of a pure water film.

This discussion explains (to some extent) the compromise which is achieved in practice by good foaming agents.

1 Introduction

Can a given surfactant produce a strong foam? there are some qualitative rules. We know, for instance, that a strongly insoluble surfactant cannot cover the surface of a rapidly growing bubble, while a soluble surfactant may succeed -by diffusion from the bulk solution. We would like to make this more precise- to characterise a surfactant solution by a few control parameters, which tell us what are its activities.

One of the methods for generating soap films is provided by a mechanical egg beater. Or, more scientifically, by pulling rapidly a metallic frame out of a surfactant solution (fig. ) as described in the book by Mysels et al.

We might first think of pulling the film at constant vertical speed. This is a version of a classical Landau Levich problem. But the quality of the surfactant plays only a minor role in this process: the surfactant is pulled up at (essentially) the same speed than the solution, and no fresh surface is generated.
A more relevant situation was invented by Lucassen [4]. Here, the film is pulled abruptly, and its height \( h \) is comparable to (or larger than) the horizontal span of the reservoir. Thus we must create fresh surface by pulling the frame, and migration of surfactant from the water phase to the surface is dominant.

This situation corresponds to what Lucassen [4] called a "young film". We discussed some aspects of the young films in a note [5]. But we missed some important points: a) we chose as our central variable the local surface tension. It turns out that it is more illuminating to study first the concentration \( c(z) \) at all levels in the film b) we did not discuss the dynamical features which tell us if the young film can indeed be made - or not c) some serious misprints occurred in [5].

Here, we return to the static structure of the young films: in section 2 we deal with concentrations \( c \) below the vertical micelle concentration \( (c^*) \). We find two characteristic heights: both are relevant for a discussion of film stability. In section 3 we extend this to \( c > c^* \). In section 4 we consider the major time constants involved: the young film must achieve its protective surface before falling.

## 2 Profile of a young film \((c < c^*)\)

### 2.1 Basic equations

The film is drawn vertically (along \( z \)) and has a certain width \( \delta(z) \) (fig. 1b). We assume that, in each interval \( dz \), there is a rapid equilibration between solution (concentration \( c(z) \)) and surface (with monolayer concentration \( \Gamma(z) \)). The total number of surfactants was originally \( c_B \delta \) (where \( c_B \) is the bulk concentration in the reservoir), and remains the same. Thus we must have:

![Diagram of a young film](image-url)
\[ c_B \delta = \delta c + 2\Gamma \]  

We assume that equilibrium has been achieved, and this may be written in the differential form:

\[ \Gamma^{-1}d\Pi = d\mu(c) \]  

where \( \Pi = \gamma_0 - \gamma \) is the Langmuir pressure, describing the shift of the surface tension from \( \gamma_0 \) (for pure water) to \( \gamma \) (at concentration \( c \)) and \( \mu(c) \) is the chemical potential of the surfactant in solution.

These equations must be supplemented by a requirement of mechanical equilibrium: the weight of the film must be balanced by Marangoni forces:

\[ -\frac{2d\Pi}{dz} = \rho g \delta \]  

(\( \rho = \) water density, \( g = \) gravitational acceleration).

### 2.2 Concentration profile

Combining eqs (1, 2, 3) we arrive at:

\[ -\frac{2d\Pi}{dz} \equiv -2\Pi \frac{d\mu}{dz} \frac{dc}{dz} = \frac{\rho g 2\Gamma}{c_B - c} \]  

In this section, we focus our attention on the dilute case \( c < c^* \). Then:

\[ \mu = kT \ell n c + \text{constant} \]  

and eq. (4) becomes:

\[ -\frac{dz}{\lambda} = \frac{dc}{c_B} \left( \frac{c_B - c}{c} \right) \]  

where we have introduced a characteristic length \( \lambda \) such that:

\[ \rho g \lambda = c_B kT \]  

\( \lambda \) measures the osmotic pressure of the surfactant in terms of hydrostatic heights. Note that our definition of \( \lambda \) differs from ref. [5]. Eq. (6) integrates to:

\[ \frac{z}{\lambda} = \frac{c - c_B}{c_B} + \ell n \left( \frac{c_B}{c} \right) \]
This concentration profile is shown on fig. 2a. Two interesting limits are:

\[
\frac{c_B - c}{c_B} = \left(\frac{2z}{\lambda}\right)^{1/2} \quad (z < \lambda)
\]

\[(9)\]

\[
\frac{c}{c_B} = e^{-z/\lambda} \quad (z > \lambda)
\]

\[(10)\]

\[\text{Figure 2: Structure of a young film when the bulk concentration (}c_B\text{) is smaller than the } cmc(\text{c}^*)\text{. (a) concentration profile (b) variation of surface tension with height.}\]

2.3 Thickness profile

We can translate \(c(z)\) into a thickness profile \(\delta(z)\) using eq. (1). In most of the region \(c < c^*\), the monolayer concentration \(\Gamma\) is nearly constant (adsorption has taken place abruptly at very low \(c's\)). Then we have:

\[
\delta = \frac{2\Gamma_B}{c_B - c}
\]

\[(11)\]

where \(\Gamma_B\) is \(\Gamma(c = c_B)\). The thickness \(\delta(z)\) described by eq. (11) is a decreasing function of \(c\). When \(z > \lambda\), we have \(c << c_B\), and \(\delta\) reaches a simple limit \(\delta = 2\ell\), where:

\[
\ell = \frac{\Gamma_B}{c_B}
\]

\[(12)\]

The length \(\ell\) plays an important role in foaming problems: \(\ell\) is the minimal thickness of solution required to transfer surfactant from bulk to surface, achieving the required surface concentration \(\Gamma_B\).
2.4 Vertical variations of the surface tension $\gamma$

We know $c(z)$, and we know (from classical plots for usual surfactants) the surface tension $\gamma(c)$; thus we may construct $\gamma(z) = \gamma_0 - \Pi(z)$. The general aspect of this curve is shown on fig. 2b.

For $z > \lambda$ ($c << c_B$), we may write:

$$\frac{d\gamma}{dz} = -\frac{d\Pi}{dz} = \frac{\rho g \Gamma}{c_B - c} \approx \frac{\rho g \Gamma_B}{c_B} = \text{constant} \quad (13)$$

Thus $\gamma(z)$ increases linearly with $z$, up to a certain height ($h_m$), where we return to a bare surface ($\Gamma \sim 0, \gamma = \gamma_0$). This corresponds to:

$$h_m \frac{d\gamma}{dz} \sim \gamma_0 - \gamma_B \equiv \Pi_B$$

or:

$$h_m = \lambda \frac{\Pi_B}{kT \Gamma_B} \quad (14)$$

Note that $h_m$ is larger than $\lambda$, because $\Pi_B$ is much larger than an ideal gas pressure. The height $h_m$ is an absolute limit of stability for our young film. (But of course, other instabilities may occur in the regime of high $z$, low $\delta$).

3 Extension to higher concentrations $c_B > c^*$

3.1 Structure of the chemical potential at $c >> c^*$

At concentrations $c > c^*$, most of the surfactant is in a micellar form (concentration $c_M$). Only a small fraction ($c_1$) is present in a monomer form. Let us call $N$ the number of surfactants per micelle. Then a rough but convenient description (with $N$ fixed) of the micelle/monomer equilibrium, may be written in the form:

$$c_M = \frac{c_1^N}{c^{N-1}} \quad (15)$$

or for the total concentration:

$$c = c_1 + c_M = c_1 \left\{1 + \left(\frac{c_1}{c^*}\right)^{N-1}\right\} \quad (16)$$

The chemical potential is still:
\[ \mu = kT \ln c_1 + \text{constant} \]  

(17)

Let us consider only the limit \( c >> c^1 \). Then:

\[ \frac{c}{c^1} \sim \frac{c M}{c^*} = \left( \frac{c_1}{c^*} \right)^N \]  

(18)

and:

\[ \mu = kT \left\{ \ln c^* + \frac{1}{N} \ln \frac{c}{c^*} \right\} \]  

(19)

\[ \frac{d\mu}{dc} = \frac{kT}{Nc} \]  

(20)

### 3.2 Concentration profile

Returning to eq. (4), we see from eq. (20) that for \( c >> c^* \), we should replace \( \rho g \) by \( N \rho g \). Or, equivalently, the characteristic length in the high concentration regime is:

\[ \tilde{\lambda} = \frac{\lambda}{N} \]  

(21)

This is much smaller than \( \lambda \) since \( N \) is large (\( \sim 60 \)).

The resulting plot of \( c(z) \) is shown on fig. 3a. We start at \( z = 0 \) from a concentration \( c_B >> c^* \). Then upon increasing \( z \), the concentration decreases, and when \( c << c_B \), we have simply:

\[ c(z) = c_B \exp \left( -\frac{Nz}{\lambda} \right) \]  

\quad \text{for} \quad z < z^* \]  

(22)

This holds up to a height \( z^* \) where \( c = c^* \):

\[ z^* = \frac{\lambda}{N} \ln \frac{c_B}{c^*} \]  

(23)

At \( z > z^* \), we return to the low concentration regime (eq. 6), and ultimately, for \( z > \lambda \), we have:

\[ c(z) \sim c^* \exp \left( -\frac{z}{\lambda} \right) \]  

(24)
3.3 Surface tensions

In all the region \( c > c^* \), or \( z < z^* \), the surface tension keeps its minimum value \( \gamma^* \). Above \( z < z^* \), we return to the constant slope regime of eq. (13). The maximum height allowable \( h_m \) is still given by eq. (14) as shown on fig. (3b).

Note the inequalities:

\[
h_m > \lambda > z^*
\]

(25)

4 Discussion

4.1 Summary of static predictions:

a) in a young film, we expect a concentration \( c(z) \) which decays exponentially at large \( z \), with a characteristic length \( \lambda \) (eq. 7). \( \lambda \) is typically a few meters. This statement holds for bulk concentrations \( c_B \) which may be lower or higher than \( c^* \).

b) the film thickness at high \( z \) is simply \( \delta = 2\ell \), where \( \ell = \Gamma_B/c_B \) \(- (c < c^*) \) or \( \ell = \Gamma_B/c^* \) for \( c > c^* \).

c) the film is bare and completely unstable at heights \( z > h_m \), where \( h_m \) is given by eq. (14), and is larger than \( \lambda \).

d) on the whole, going to bulk concentrations, \( c_B > c^* \) does not produce great alterations: most static film properties should be close to what they are for \( c_B = c^* \).
4.2 Characteristic times

1) A water film with no surfactant will collapse under its own weight in a time \( t_c \) governed by gravitational flow with the acceleration \( g \):

\[
t_c \sim \sqrt{\frac{h}{g}}
\]

where \( h \) is the height of the film. For \( h = 10 \text{ cm} \), \( t_c \sim 0.1 \text{ sec} \).

2) What is the time required for the surfactant to reach the surface? We consider here first the (relatively simple) case where \( c_B < c^* \): all the transport is via monomers. We also assume that there is no barrier at the surface opposing the surfactant adsorption. Then, we must transfer the surfactant by diffusion (coefficient \( D \)) over a distance \( \ell \) defined in eq. (12). The diffusion time is roughly:

\[
t_d = \frac{\ell^2}{D} = \frac{\Gamma^2_B}{c_B^*D}
\]

The condition of formation of a young film at \( c < c^* \) is essentially that \( t_d \) be shorter than \( t_c \). To get small \( t'_d \), we must use concentrations \( c_B \) which are as high as possible (but remain below \( c^* \)).

3) The extension of these ideas to \( c_B > c^* \) is quite delicate. Micelles provide a big reservoir of surfactant, but the delivery is slow.

a) Micelles can emit monomers which are then absorbed by the fresh surface: this process is fast (\( 10^{-6} \text{ seconds} \)) but inefficient, because each micelle cannot give more than 2 or 3 monomers (beyond that, the micellar free energy rises fast).

b) Micelles can split in two, and the corresponding characteristic time \( \tau_{\text{split}} \) is relatively long (\( 10^{-3} \text{ sec} \)). After splitting, the parts end up as monomers, and can feed the surface. This process has been documented by Shah [3].

c) The micelles may unfold by direct contact with the surface. The energy barriers for processes (b) and (c) are comparable – maybe the barrier for (c) is slightly lower.

If, for simplicity, we focus on process (b), the conclusion is that if we have \( t_{\text{split}} < t_c \), the young film should be realisable. The opposite limit \( t_{\text{split}} > t_c \) would occur only for very long surfactant chains.

4.3 Conclusions

a) To achieve young films of height \( h \), we need \( h_m > h \), where \( h_m \) is given by eq. (14). As shown by this equation, high \( h_m \) corresponds to high surface pressures (or \( \gamma < \gamma_0 \)) in the present solution. To achieve this, our surfactants must have an aliphatic tail which is not too short.

b) The surfactant must migrate fast to the water/air interface. For \( c \sim c^* \), this implies that \( \ell^* = \Gamma^*/c^* \) must be relatively small. The critical
micelle concentration $c^*$ should not be too small. The surfactant tails should not be too long.

Thus a good foaming agent results from a compromise: this does correspond to the empirical rule stating that the HLB should be in the range 7 to 9.

Acknowledgments: we have benefited from useful advice by D. Langevin and M. Schott.

References

[1] K. Mysels, K. Shinoda, S. Frankel, *Soap films*, Pergamon Press, London, 1959.

[2] V. Levich, Physico-chemical Hydrodynamics, Prentice Hall, 1962.

[3] D. Quéré, A. de Ryck, O. Ou Ramdane, Europhys. Lett., 37, p. 305 (1997).

[4] J. Lucassen, in *Anionic Surfactants* (Surfactant series, Marcel Dekker, NY 1981), chap. 6.

[5] P. G. de Gennes, C. R. Acad. Sci. (Paris), 305, p. 9 (1987).

[6] S. G. Oh, D. O. Shah, Langmuir, 7, p. 1316 (1991).