THEORY OF LIQUID FOAMS

Introduction

In many industries, using liquid foams provide advantages: foams are lightweight and easy to handle; foams allow to use less raw material for a fixed volume of the final product; foams have interesting expansion properties... Being able to generate a controlled liquid foam (geometrical structure, liquid fraction) and understanding the phenomena responsible of its destabilization is hence crucial to optimize products formulation and industrial processes.

1. Definition of a liquid foam

A foam is a dispersion of gas in a liquid. The tightly packed gas bubbles occupy most of the volume. The liquid phase, which consists of the soap films and their junctions, is continuous, unlike the gas phase.

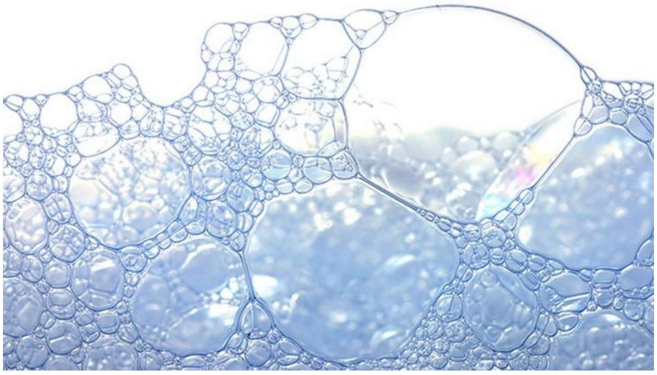

Fig1: Soap foam

Foams properties which make these materials unique and potentially useful in various industrial applications.

- **Physico-chemical constituents:** Foam contains surfactants, which stabilize the bubbles by arranging themselves at the liquid/gas interfaces. Different properties can be obtained by changing each constituent.
- **Geometrical and physical properties:** The large quantity of gas makes a foam a markedly less dense material than the liquid it contains and thus fills the same volume or covers the same surface for a lower cost. A Foam also contains many interfaces, therefore an enormous surface area per unit volume: with 50 or 100 grams of water, one can easily make a liter of foam with 10 m2 of interface!
- **Mechanical properties:** A foam behaves either as a solid or a liquid!

2. Liquid foam, key concepts

A liquid foam consists in a suspension of gas bubbles in a liquid continuous phase. Its appearance can vary considerably from one system to another. A liquid foam can be:

- Monodisperse: composed of bubbles of the same size
- Polydisperse: Composed of bubbles of different sizes
- Dry: containing a small amount of liquid (angular aspect)
- Wet: with rounded bubbles

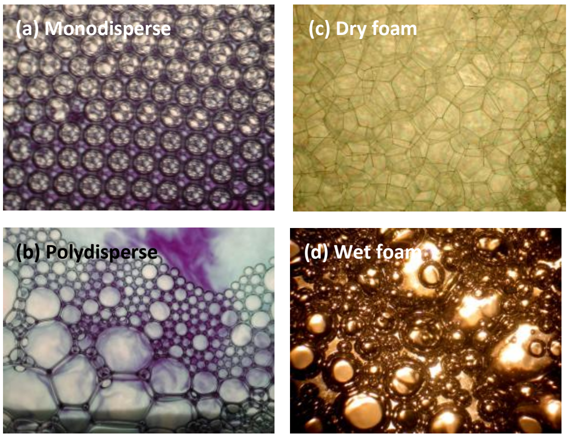

Fig2: Foams with different structures (pictures by A. van der Net)

The liquid volume fraction Φ_l is used to characterize the amount of liquid contained in a liquid foam (Fig3) and it corresponds to:

$$\Phi_l = \frac{V_{liquid}}{V_{foam}}$$

$\Phi_l > 0.36$→ Bubbly liquid
$\Phi_l < 0.36$ → Liquid foam

Depending on the value of Φ_l, different foam structures can be observed.

$\Phi_l < 0.05$→ Dry foam, straight and sharp edges
$\Phi_l > 0.15$→ Wet foam, rounded bubbles

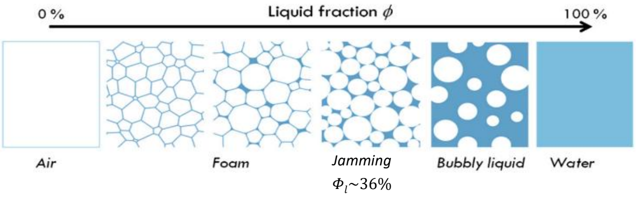

Fig3: schematic representation of the effect of Φ_l on the structure of the foam [2]

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The structure of liquid foam is governed by the:

- **liquid fraction,**
- **Polydispersity,**
- and **order/disorder.**

If these parameters are known, the structure of a liquid foam and the number of neighbors per bubble N can be predicted (Fig3).

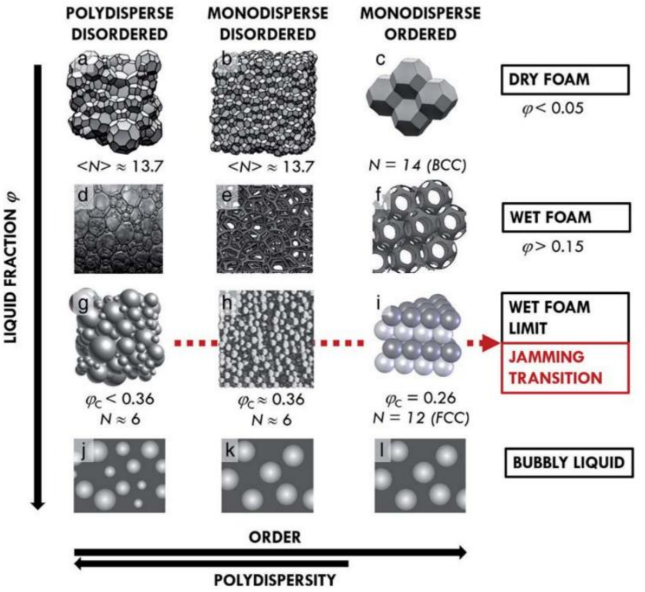


Fig3: Representation of different foam structures as a function of the following key parameters: liquid fraction ϕ, polydispersity and order/disorder [4]

3. Liquid foams at equilibrium

Foams are multiscale systems, to have a good understanding of their behavior, a study of their elementary components at different scales is necessary.

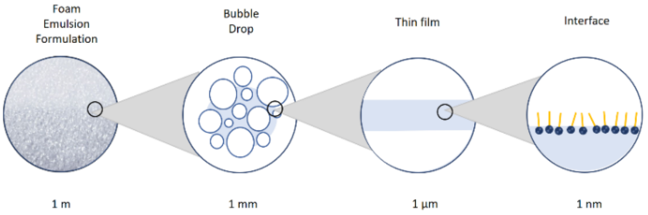


Fig4: The different scales of a liquid foam

3.1 Macro Scale

At the meter scale, liquid foams are **soft solids**. Specifically, they are Bingham plastic materials: when the applied stress is smaller than a threshold value τ_c, the foam behaves as an elastic body. Above this value, the foam flows. This complex behavior can be attributed to the microstructure of foams: when bubbles form a contact network, stresses result in elastic deformations. However, when the applied stress is important, the initial microstructure is lost, and the network fails inducing the flow of the foam (Fig5).

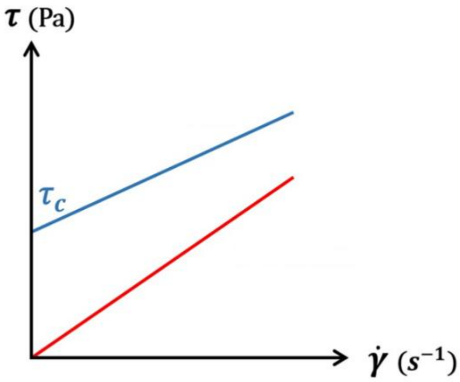
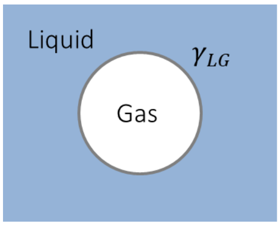


Fig 5: Stress as a function of strain rate for a Bingham plastic fluid and a Newtonian fluid

3.2 Millimeter-scale

At this scale, foam is composed of **bubbles.** These small reservoirs of gas are delimited by a liquid-gas interface. When unrestricted, a bubble will adopt a spherical shape to decrease its interfacial energy (Fig 6). However, in liquid foam, bubbles can be polyhedral because of the presence of other neighboring bubbles.

Fig6: 6-Interfacial energy of a bubble in a liquid foam



$$E = \gamma_{LG} A$$

With E the interfacial energy of the bubble, γ_{LG} the surface tension of the liquid-gas interface and A the surface area of the bubble

3.3 Micro/ nanoscale

1. Liquid films: In liquid foam, bubbles are separated by liquid films. These films are usually curved due to the pressure difference between neighboring bubbles. Their thickness can range between a few nanometers to one millimeter depending on the liquid volume fraction of the foam.
2. Plateau borders: They correspond to the liquid channels formed at the intersection of films separating bubbles (3 films if the foam is at equilibrium). Their section is quasi-triangular, and their cross-sectional

area depends on the liquid volume fraction of the foam (dry foam→ thin Plateau borders)

3. Nodes: They correspond to the intersection of Plateau borders (4 Plateau borders if the foam is at equilibrium.

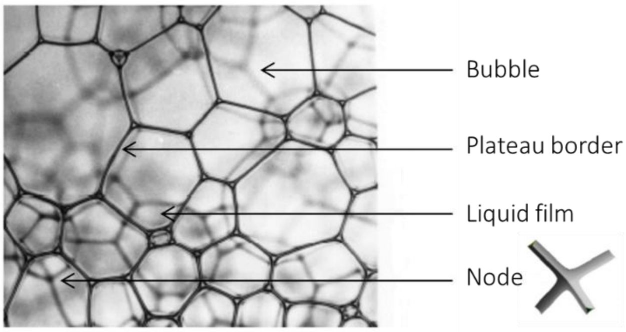


Fig7: Picture of dry foam and its elementary components [1]

3.4 structure and organization

At equilibrium, the structure of liquid foams is governed by the minimization of the total surface area of liquid-gas interfaces. In the case of an ideal foam, this minimization translates into simple rules at the scale of films and bubbles called Plateau's laws.

What is an ideal foam?

- A very dry foam ($\Phi_l < 0.05$)
- A foam at mechanical equilibrium
- A foam where the energy is proportional to the total surface area of bubbles (requires very thin films, liquid-gas interfaces at equilibrium and very dry foams to neglect the gravitational energy)
- An incompressible foam: this approximation is valid at short times where gas diffusion through the liquid-gas interfaces can be neglected

Plateau's laws for ideal foam:

1. Liquid films are smooth and have a constant curvature defined by Laplace law (Fig 8)

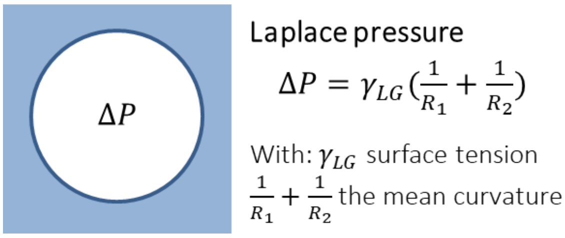


Fig8: Laplace pressure in a bubble

2. A Plateau border corresponds to the intersection of 3 liquid films forming angles of $arcos\left(-\frac{1}{2}\right) = 120°$
3. A node corresponds to the intersection of 4 Plateau borders forming angles equal to $arcos\,(-\frac{1}{3}) \approx$ 109.5°.

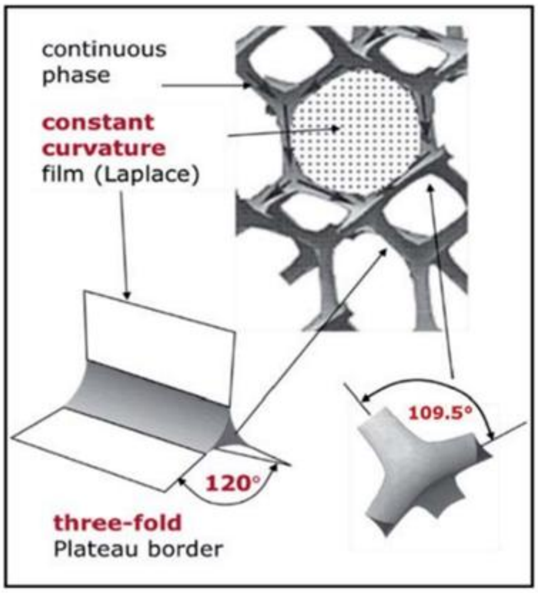


Fig9: Plateau's laws in a very dry foam [4]

4. Life and death of liquid foams

Liquid foams are transient systems. After the generation step, their geometrical structure and liquid volume fraction evolve with time. Moreover, different aging mechanisms lead to the destabilization of the foam and ultimately to its destruction.

4.1 Generation of liquid foams

Different methods can be used to generate a liquid foam:

- Gas injection in a liquid through a porous media
- Mechanical stirring: mixer, shaker
- Liquid recirculation
- Chemical and biological reactions (Polyurethane, yeasts)
- Depressurization (fizzy drinks)

In all these processes, energy input is required but not sufficient to generate stable foams. **Surfactants play a key role on the foamability of a solution**:

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1. Surfactant adsorption:

During foaming, the interfacial area increases, and surfactant molecules adsorb at newly created interfaces. The adsorption kinetics of a surfactant depends on its nature, its concentration and the viscosity of the bulk fluid. To achieve good foamability, this adsorption should be fast enough to stabilize newly created bubbles.

2. Gibbs-Marangoni effect:

After their generation, bubbles migrate quickly to the free liquid-gas interface because of Buoyancy and deform when interacting with other neighboring bubbles. These deformations consist in a dilatation of the interfaces leading to a decrease of surfactant coverage and hence an increase of surface tension. To achieve equilibrium, surfactants molecules migrate to the stretched area and induce a flow of the subphase toward the thin part. As a result, the thinning is stopped. This process, usually referred to as “film elasticity” stabilizes the foam at its early stages [6].

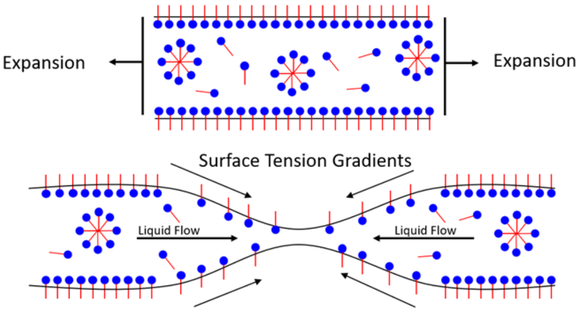

Fig10: Gibbs-Marangoni effect: surface tension gradients ”heal” the stretched film. Adapted from [13]

3. Maximum foamability at the CMC:

The efficiency of the Gibbs-Marangoni effect relies on a sufficient surface tension variation between the stretched part of the film and the neighboring parts. The surface tension barely varies as a function of concentration for low values of C (Fig11) and γ is even constant for values of C above the CMC. The maximum variation of γ leading to the most efficient Gibbs-Marangoni effect and hence to the best foamability is found slightly before the CMC in theory.
However, experimentally, the maximum foamability is observed at a concentration slightly above the CMC and the foamability does not vary up to a concentration ~ 10CMC [7]

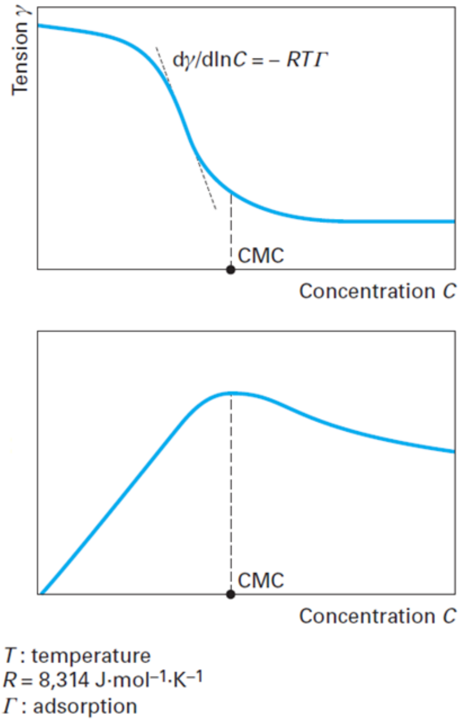

Fig11: Variation of surface tension and foamability as a function of surfactant concentration C [7]

Interfacial properties of surfactant laden liquid-gas interfaces play a major role in the generation process of liquid foams.
These properties (**adsorption speed of surfactants**, the **CMC** as well as the **interfacial elasticity**) can be characterized through surface tension measurements using a **drop tensiometer** (TRACKER™ by Teclis).

4.2 Evolution and aging of a liquid foam

Different aging mechanisms lead to foam destabilization

1. Drainage:

After the generation of a liquid foam, the macroscopic motion of bubbles stops, and the liquid starts draining in the Plateau borders toward the bottom of the foam due to gravity which induces variations in the liquid volume fraction. Prior to that, the Plateau borders collect the liquid initially trapped in the liquid films. This is due to the capillary suction that results from the curvature being higher in the Plateau borders.

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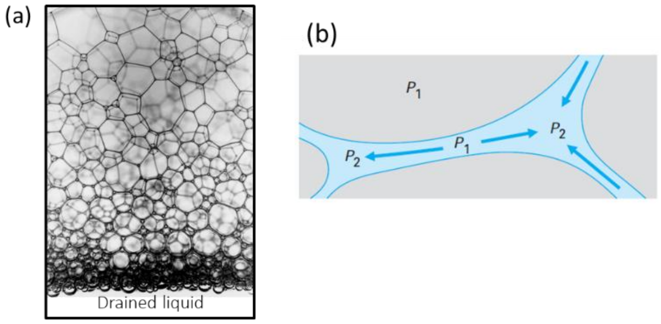

Fig12: (a) A foam after drainage [3]. (b) Liquid drainage due to capillary suction [7]

2. Ostwald ripening:

Ostwald ripening Definition

In liquid foam, bubbles don't have usually the same size. Since Laplace pressure is proportional to ${}^{1}/_{R}$ with R being the radius of the bubble, the gas contained in the smaller bubbles will migrate to the larger ones where the pressure is smaller. This is made possible by the permeability to gas of the liquid films between the bubbles.

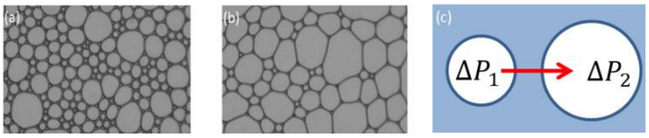

Fig 13: (a) and (b) show pictures of the same foam between two horizontal plates at t=0 and t=10 min. The bubbles are larger and fewer (pictures taken by Benjamin Haffner). (c) The gas inside the small bubbles where the pressure is higher migrates to larger bubbles.

Drainage and Ostwald ripening can be coupled [8]: the thickness of liquid films separating bubbles, that is directly impacted by drainage, is a key parameter during Ostwald ripening.
the liquid permeability to gas can be probed by performing a diffusion experiment using the drop tensiometer TRACKER™

Ostwald ripening - Gibbs criterion [9]

If surface tension varies with the surface area of the interface (**requires insoluble surfactants**), the condition to stability toward coarsening for a spherical bubble of radius R can be written as:

$$\frac{\partial \Delta P}{\partial R} = -\frac{4\gamma}{R^2} + \frac{4}{R}\frac{\partial \gamma}{\partial R} > 0$$

$$\frac{\partial \Delta P}{\partial R} = \frac{4}{R^2}(-\gamma + 2E) > 0$$

With: E the compression elastic modulus, ΔP Laplace overpressure and γ surface tension.

Hence, the Ostwald ripening can be slowed down and stopped if $E > \frac{\gamma}{2}$

The elastic properties of a surfactant laden liquid-gas interface can be characterized through oscillatory compression experiments using the drop tensiometer TRACKER™

3. Coalescence:

The coalescence corresponds to the rupture of a liquid film separating two bubbles. Coalescence can be due to local rearrangements of bubbles; it can also be coupled to drainage (thin films are more fragile) [10]. However, the thinning of liquid films can be slowed down in the presence of surfactants: when the thickness of a liquid film decreases, its liquid-gas interfaces come closer, and a repulsive interaction is observed thanks to the molecules populating these interfaces. If the surfactants are ionic, the interaction consists in an electrostatic repulsion. Non-ionic surfactants, amphiphilic polymers and proteins also induce a steric repulsion that inhibits the thinning of liquid films.

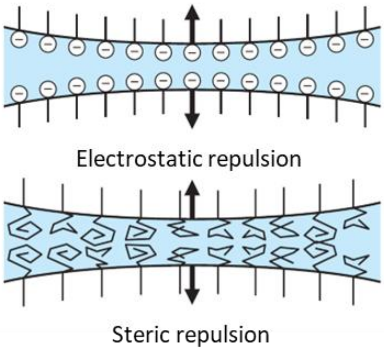

Fig14: Repulsion between two laden interfaces (adapted from [7])

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4. Evaporation:

Evaporation of the liquid may also play an important role in the aging of liquid foam. Liquid evaporation induces the thinning of liquid films separating bubbles which can result in the destruction of the foam.

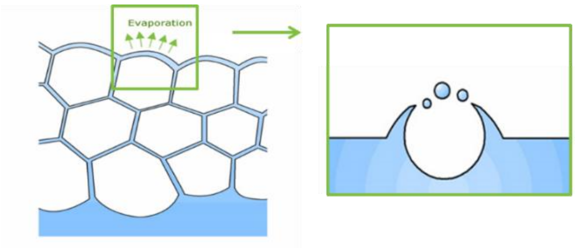

Fig 15: Evaporation in a liquid foam

4.3 How to stabilize liquid foams

1. By using surfactant molecules

Surfactant molecules play an important role in the generation of foams and their stability. By lowering surface tension, they act as **foaming agents**.
The **Gibbs-Marangoni effect they induce can be viewed as a "healing" process in thinning films** and, finally, the **repulsion interaction of surfactant laden interfaces slows down the drainage of liquid foams**.
The behavior of surfactants in liquid foam is mainly governed by two parameters:

- The concentration → 5 to 10 times the CMC is usually recommended. This is enough to cover the interfacial area created during foaming and to constitute a safety reservoir without affecting the foamability of the solution
- The surfactant characteristics → ionic, non-ionic, polymer, protein, the length of the hydrophobic chain… All these parameters control the efficiency of a surfactant.

2. By using solid particles

Hydrophilic particles increase the effective viscosity of the continuous phase → Drainage is slowed down.

3. By using Anti-foaming agents and defoamers

In many situations, foams are unwanted. A liquid foam can have a temporary utility which requires getting rid of it at the end of the process. In this context, a few methods have been developed to avoid the generation of foam (anti-foaming agent) or to destroy an already existing foam (defoamer).
Anti-foaming agents and defoamers can be divided into three categories:

- Liquid antifoams and defoamers: they are insoluble in the continuous phase (oil in water for example) and are hence dispersed in fine droplets in the liquid. By spreading liquid films between bubbles, they rupture them and hence destabilize the unwanted foam.
- Solid antifoams and defoamers: Micrometer sized hydrophobic solid particles are naturally good antifoams and defoamers. Examples: coal particles and fumed silica particles.
- Mixed antifoams and defoamers: They contain both oil and hydrophobic particles and they are the most efficient.

Conclusion

Liquid foams have a limited lifetime due to the following aging mechanisms: drainage, Ostwald ripening and coalescence. These mechanisms can be coupled resulting in a complex behavior in the foam.

Surface active molecules (surfactants) or solid particles play a key role in liquid foams aging.

- Drainage can be slowed down when the surfactant layers are rigid or when particles accumulate in the Plateau borders; it can be arrested only if the liquid of the foam either gels or solidifies, with a yield stress sufficiently high.
- Coarsening is slowed down when the films between bubbles are thick (or small) or when low water-solubility gases are used, and it can be arrested when the surface compression modulus E is large enough.
- The parameters governing coalescence are not yet fully elucidated. Coalescence seems however slowed down when the surface layers have larger elastic moduli E or when the films are very thick and/or rigid.

Unwanted foam can be destructed with anti-foaming agents and defoamers that can be liquid, solid (powders) or mixed systems (the most efficient).

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