



Historical perspective

Foams: From nature to industry[☆]Christopher Hill, Julian Eastoe^{*}

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ABSTRACT

This article discusses different natural and man-made foams, with particular emphasis on the different modes of formation and stability. Natural foams, such as those produced on the sea or by numerous creatures for nests, are generally stabilised by dissolved organic carbon (DOC) molecules or proteins. In addition to this, foam nests are stabilised by multifunctional mixtures of surfactants and proteins called ransapumins, which act together to give the required physical and biochemical stability. With regards to industrial foams, the article focuses on how various features of foams are exploited for different industrial applications. Stability of foams will be discussed, with the main focus on how the chemical nature and structure of surfactants, proteins and particles act together to produce long-lived stable foams. Additionally, foam destabilisation is considered, from the perspective of elucidation of the mechanisms of instability determined spectroscopically or by scattering methods.

1. Introduction

This article provides an overview of recent advances in aqueous foam science, with the major emphasis of the first half being on understanding both the stabilisation and destabilisation of aqueous foams. This important area is always expanding, and as a result on average over four thousand scientific articles have been published over the past five years in the area of foams. The sections of this review do not delve into the detailed physics associated with these processes, and it should be noted that many reviews exist providing in depth accounts of the fundamental science in this area: for example, and not limited to [1–6].

As a way to distinguish this article from other reviews, the second half focuses solely on the science of both natural and man-made foams. In the natural foam section, highlights will be made on how nature forms foams, often under harsh conditions and with high stability. For example, foam nests produced by different species of fish, frogs and insects have been found to be stable for up to ten days under tropical conditions [7,8]. These nests are essential for providing their young with the necessary protection and moisture during incubation [9–13]. In an industrial context, foams are often considered to be a nuisance and much work has been done in the area of defoaming to combat undesired foams [14–18]. However, although this article does discuss defoaming, the main focus is on the positive and practical uses of foams in industries such as fire-fighting, mineral flotation and other recent advances.

From an historic perspective, the earliest recorded works associated

with foam science were carried out during the nineteenth century by Belgian physicist Joseph Plateau [19]. Although Plateau has been recognised as the pioneer in the field, and did lay down enduring foundations, surprisingly his publication [19] “Experimental properties of liquids resulting from their molecular forces” makes only fleeting references to foams. Plateau did establish the essentials, describing in his work how foams form within three-dimensional frameworks, in addition to describing practical aspects of establishing foams and outlining some of the underlying mathematics. The fundamentals, known as Plateau's laws, are:

- 1) The thin films are smooth, with a constant mean curvature
- 2) At a liquid edge (Plateau Border), no more than three films can come together and they form an angle of 120°
- 3) The Plateau borders that come together in one point are always in the number of four and foam angles of 109.5°

Since the nineteenth century, much work has been published on the subject of foams, including many books publications which are recommended to the reader [14,20,21].

A foam is generally defined as a dispersion in which a large proportion of gas by volume in the form of bubbles is dispersed in a liquid, solid or gel, hence forming closed cell structures. Foams have useful properties owing to their low density, very large surface area and because they exhibit both solid and liquid like behaviour. They are ubiquitous systems which have proved to be an essential part of our daily lives, playing key roles in aqueous applications such as a fire-

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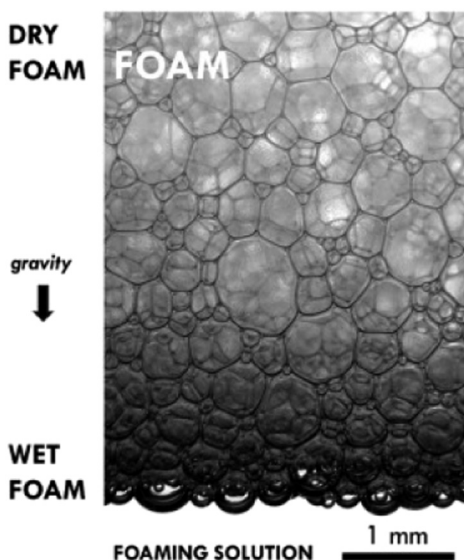


Fig. 1. Showing liquid drainage. Reprinted with permission from ref. [2]. Copyright 2015 Elsevier.

fighting, mineral flotation, detergents as well as applications such as upholstery, insulation, metal foams etc. [20] In addition, they can also be found in numerous instances in the natural world. Perhaps the most familiar natural examples are sea foams. When many aqueous systems are sufficiently agitated and begin to incorporate air foams may form, which are very weak and short lived. However, when stabilising agents, for example dissolved organic carbon (DOC) from decomposed organisms (e.g. plankton), are present long lasting foams are produced that can be seen being blown along the coast. So, in general, the presence of a foam is a good indicator of the occurrence of industrial or natural surfactants [21].

Foams are referred to as being metastable, confusingly foams are also sometimes referred to being at equilibrium, however this is only used as a useful approximation due to the apparent rate of coarsening and destabilisation [20]. The structure of a metastable foam is determined by the minimisation of interfacial area for a given liquid volume fraction, and is determined by simple geometric rules at the scale of a film and a few bubbles [2]. Fig. 1 shows a photograph of a typical metastable aqueous foam, showing the effect of gravity on drainage and coarsening with height. The reason for this can be explained by considering the liquid volume fraction (ϕ , Eq. (1)), the key parameter used to describe the amount of liquid contained within a foam and therefore the shape of the bubbles. The other parameters Eq. (1) are the volume ratio of the liquid content (V_{liquid}) and the foam volume (V_{foam}). Physical and mechanical properties influenced by ϕ include, thermodynamic, acoustic, and rheological properties. Foams with ϕ higher than about 0.1 are referred to as wet foams. Wet foams are found towards the bottom of the foam column around the air/water interface and the bubbles are well approximated by contacting deformed spheres. Further away from the air/water interface, for decreasing values of ϕ , the bubbles become increasingly more distorted in shape. Foams with a volume fraction of < 0.05 are generally referred to as dry foams and can be described by Plateau's laws. These dry foams consist of thin films that are normally idealised as single surfaces and are polyhedral in shape [20]. The reader is referred to a recent review on the structure and energy of aqueous foams for more information [2].

$$\phi = V_{\text{liquid}}/V_{\text{foam}} \quad (1)$$

In general, the curvature is determined from the existence of surface tension. In general the shape is determined from the Young Laplace law, Eq. (2), where Δp is the pressure difference across the fluid interfaces, γ is the surface tension and R_1 and R_2 are the principal radii of curvature.

The Young Laplace law states that the pressure difference between the two sides of an interface is equal to the mean curvature of the interface multiplied by surface tension. Surface tension acts to flatten the surface whilst the pressure difference tends to curve it [21].

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

2. Foam stability

Single component pure liquids are not generally suitable for producing foams due to the rupturing of fluid films almost immediately as a result of thermal or mechanical perturbations. As well as this, foams do not form spontaneously and energy is required to disperse the gas in the liquid to create bubble surfaces. The energy cost (W) is broadly the product of the surface tension (γ , J m^{-2} or N m^{-1}) and of the area created (A , m^2) as shown in Eq. (3). Foams are thermodynamically unstable systems that tend to separate with time under the influence of van der Waals forces and gravity [22]. The lifetime can be used to distinguish transient and metastable foams. Transient foams may last for a few seconds, but metastable foam lives can vary from minutes to years [15]. The key to producing metastable foams is to modify the surface properties by use of stabilising agents, such as surfactants, polymers, proteins or particles. The role of stabilising agents is to stabilise the foams with respect to the different destabilisation mechanisms, which will be discussed in more detail in Section 3.

$$W = \gamma \Delta A \quad (3)$$

In the next section, a brief overview will be provided on the main components used to produce stable foams. As well as this, comparisons on the stability of foams will be made between the four stabilising agents and mixed stabilised systems will be discussed. These next sections present the necessary information to set the scene for the rest of the article and are not intended to offer in depth accounts. For a more detailed review of foam stabilisation, the reader is referred elsewhere [23].

2.1. Surfactant-stabilised foams

Most foams owe their existence to the presence of surface active agents or surfactants that accumulate at interfaces. Surfactants are used to reduce the surface tension and importantly when considering foams, stabilise the thin films against rupture [20]. The phenomenon of surface tension arises due to an imbalance of attractive intermolecular interactions at the surface of a liquid, and consequently creating an interface between a liquid and a gas requires additional energy which is attributed to the surface tension (γ) [21]. Without this reduction in surface tension, the liquid could not be transformed from its bulk state, with a minimal surface area, into a high surface area foam. Since surfactant molecules are amphiphilic, when used to produce foams, the molecules adsorb at the air/water interface until it is covered completely, with head groups in the water and tail groups in the air as seen in Fig. 2. In the case of ionic surfactants, this results in the formation of two double layer distributions of charges consisting of a plane of negative heads and an adjacent diffuse cloud of positive counterions. The two adjacent air/water surfaces in a foam are therefore covered by charged monolayers that repel each other, stabilising the foam at the thickness at which electrostatic attractions and van der Waals interactions are balanced [21]. The opposing electrostatic and van der Waals forces are typically balanced for film thicknesses in the range of 10–1000 nm. The wavelengths of visible light lie squarely in this range, resulting in the familiar result shimmering interference colours [24].

To achieve high foam stability and quality using surfactants, it is believed that the surfactants must be above their respective critical micelle concentrations (CMCs) [25]. For many industrial processes,

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