



ELSEVIER

Contents lists available at ScienceDirect

## Comptes Rendus Physique

www.sciencedirect.com



Liquid and solid foams / Mousses liquides et solides

## Effect of particles and aggregated structures on the foam stability and aging

*Effets des particules et des structures agrégées sur la stabilité et le vieillissement des mousses*Anne-Laure Fameau<sup>a,\*</sup>, Anniina Salonen<sup>b</sup><sup>a</sup> Biopolymères Interactions Assemblages, INRA, rue de la Géraudière, 44316 Nantes, France<sup>b</sup> Laboratoire de physique des solides, UMR 8502, Université Paris-Sud, 91405 Orsay, France

## ARTICLE INFO

## Article history:

Available online 11 October 2014

## Keywords:

Foam  
Stability  
Aging  
Particles  
Protein aggregates  
Surfactant aggregates

## Mots-clés :

Mousse  
Stabilité  
Vieillessement  
Particule  
Agrégats de protéines  
Agrégats de tensioactifs

## ABSTRACT

Aqueous foams are formed of air bubbles dispersed in a water phase. Despite the simplicity of these ingredients, the resulting foams can have an impressive range of material properties. In this review, an overview will be given on recent results obtained on the foaming properties of particles, self-assembled and aggregated structures. We will highlight how the presence of objects inside the foam can drastically modify the foam stability from unstable to ultrastable.

© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## R É S U M É

Les mousses aqueuses sont formées de bulles d'air dispersées dans une phase aqueuse. En dépit de la simplicité de ces ingrédients, les mousses qui en résultent peuvent offrir une panoplie surprenante de propriétés physiques. Cet article passe en revue des résultats récents obtenus quant aux propriétés moussantes des particules, des structures auto-assemblées agrégées. On mettra en lumière comment la présence d'objets à l'intérieur de la mousse peut modifier de manière drastique la stabilité de celle-ci, d'instable à ultrastable.

© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## 1. Introduction

Aqueous foams are formed of air bubbles dispersed in a water phase. Despite the simplicity of these ingredients, the resulting foams can have an impressive range of material properties. The foam can have a fleeting existence, as champagne bubbles that disappear within minutes on top of the glass. They can also be solid, yet fluid under the shear of the razor blade in shaving foam. Bubbles also transform cream to a sensual delight, by making it airy and light. In addition to these few examples foams are found in a whole range of applications: detergents, oil recovery, food, and cosmetic products [1]. The reasons for the omnipresence of foams are due to the very different properties that they can have. These properties

\* Corresponding author.

E-mail addresses: [anne-laure.fameau@nantes.inra.fr](mailto:anne-laure.fameau@nantes.inra.fr) (A.-L. Fameau), [anniina.salonen@u-psud.fr](mailto:anniina.salonen@u-psud.fr) (A. Salonen).

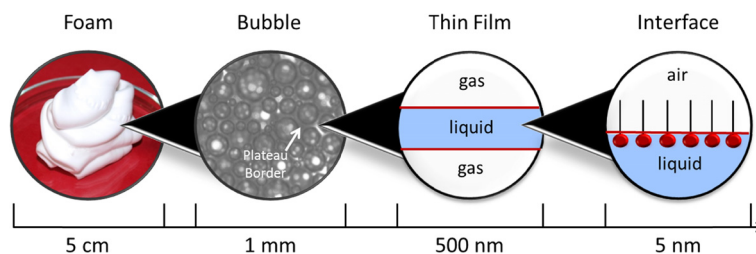


Fig. 1. (Colour online.) Foam structure at different length-scales, starting at the left at the macroscopic, and decreasing gradually down to the nanometric.

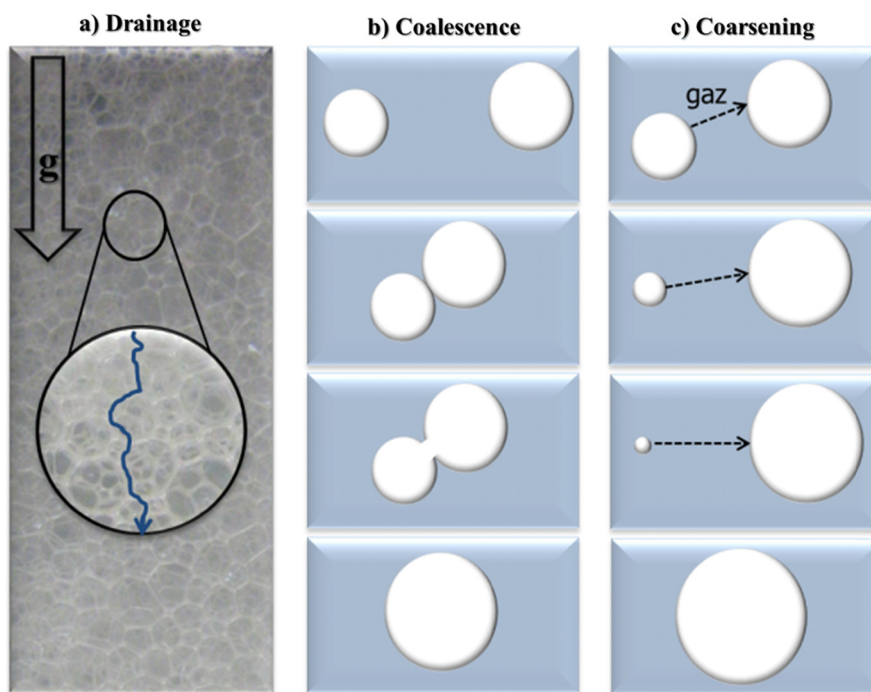


Fig. 2. (Colour online.) Scheme of the three main foam destabilization mechanisms. (a) Drainage of the liquid due to gravity, (b) coalescence of two bubbles and (c) coarsening of the bubbles due to the Laplace pressure.

are due in part to the physical properties of *bubble size* and *liquid fraction*, but even more importantly to the *physicochemical properties* of the foaming solutions. The types of objects such as molecules or particles that are used, either to adsorb onto the interfaces or to change the solution properties are endless. Indeed, the foams that can be made are only limited by our control over the physical chemistry of the foaming solutions and the understanding of the underlying physical and chemical processes that lead to foam stabilisation and destabilisation. The subject is vast. In this review we will first remind the reader of the basics of foam stability, before giving some examples of how to control their ageing using the tools of physical chemistry, especially through the use of solid particles, surfactant assemblies and protein aggregates.

**Foam structure.** Depending on the bubble size and the liquid fraction, the foam will self-organize into different structures, principally to minimize the energetically costly surface area (as discussed more in Review of W. Drenckhan and S. Hutzler). This structure spans over several length-scales starting at the molecular scale ( $\sim$  nm) and going up to the macroscopic scale (Fig. 1). The properties of the foam result from a complex coupling between them. Starting at the smallest length-scales, at the nanometer scale, there are the gas–liquid interfaces at which the adsorbed stabilizers are found. Where two interfaces are in close proximity there are thin films separating the individual bubbles. Zooming further out, at the microscopic sizes, the thin films join to create Plateau borders (PBs), which form the main liquid skeleton of interconnected channels. Looking at individual bubbles, their diameter ( $D$ ) can vary from tens of micrometres to centimetres (although in practical applications bubbles above a few millimetres are rarely found). The macroscopic scale corresponds to the whole foam, whose properties are dictated by those in all the length-scales below.

**Foam ageing.** All foams are thermodynamically unstable and disappear with time [2]. The foam is destabilised by three known mechanisms: *drainage*, *coalescence*, and *coarsening* (Fig. 2). Drainage refers to the separation of the gas and the liquid by the flow of the liquid out of the foam downward through the liquid channels due to the difference in density (Fig. 2a) [3]. Drainage lowers the liquid fraction and leads to drier foams. If the film between two bubbles is unstable it can break

leading to the merging of the two bubbles. This mechanism is called coalescence (Fig. 2b), and it is also responsible for foam collapse, as the bubbles coalesce at the top of the foam leading to the disappearance of the foam [4]. The third mechanism of destabilisation is coarsening. Gas diffuses between bubbles of different radii due to differences in the Laplace pressure (the smaller the bubble the higher the pressure) [3]. The gas is transferred from smaller to bigger bubbles leading to the disappearance of the smaller bubbles (Fig. 2c) [5]. Coalescence and coarsening lead to an increase of the average bubble size with time. The three mechanisms are very interdependent and can accelerate one another. For example, the drainage of the fluid between bubbles leads to a closer approach of the bubble surfaces and can lead to the rupture of the thin liquid film when a critical thickness is reached [6]. In order to be able to *generate foam* the bubbles have to be sufficiently rapidly stabilised to avoid immediate coalescence and disappearance of the bubbles. Therefore foam generation can be described by the same ageing mechanisms, but at much shorter time-scales (typically less than seconds), and taking into account the adsorption kinetics of the stabiliser. For more information see the review from W. Drenckhan and A. Saint-Jalmes.

*Role of the liquid and gas in the foam stabilization.* Liquid foams always have at least three components, liquid, gas and foam stabilizer [7]. These are the three physicochemical levers on which we can pull to modify or control the foam (the bubble size and the liquid fraction being others), starting with the nature of the gas, which diffuses through the liquid to coarsen. Using a gas which is very poorly soluble in water will slow down the gas transport across the water phase compared with a more soluble gas. Therefore, foam stability is higher in presence of N<sub>2</sub> gas than CO<sub>2</sub> due to the poorer solubility of in water than N<sub>2</sub> compared with CO<sub>2</sub>. The coarsening can be slowed down even more by using gases of very low solubility (such as fluorinated gases) [8]. Another possibility to improve foam stability by slowing down coarsening is to use a small amount of a poorly soluble gas. The transfer of the more soluble gas will be faster, therefore the large and the small bubbles will have different mixture compositions of gas. This leads to a difference in osmotic pressures, which can help balance the Laplace pressure [9]. This will slow down the coarsening. Concerning the liquid phase, one important parameter is the viscosity of the liquid phase which modifies the drainage strongly, as well as influencing coarsening and coalescence (coarsening and coalescence are slowed down because they require rearrangements of the bubbles in the carrier fluid, and an increased viscosity slows down the rate of bubble rearrangements slowing down the bubble growth). Thus, to slow down the foam drainage, one of the simplest ways is to increase the fluid viscosity. For example, the addition of some glycerol in the liquid phase leads to an increase of the bulk viscosity which results in a decrease of the drainage rate [10]. The drainage of non-Newtonian fluids inside foams has also been studied, but for shear-thinning fluids no influence was observed as long as the correct bulk viscosity was used [11]. The nature of the gas and the viscosity of the liquid phase are simple parameters to tune which can lead to an increase of the foam stability and they are used in many industrial products such as shaving foam.

*Role of the foam stabilizer at the air/water interface.* Many types of stabilizers can be used: surfactant molecules, proteins, polymers and solid particles. To be efficient, the foam stabilizer has to get rapidly to the gas/liquid interface in order to produce foam. Adsorption onto the interface is not sufficient and a low surface tension does not in any way lead to stable foam. For example ethanol-water mixtures have a very low surface tension (40% Ethanol in water leads to surface tension of 30 mN/m), but make very unstable foams [12]. The stabilizer has also to create a surface which is stable against coalescence by making it sufficiently viscoelastic. The viscoelasticity can arise from steric, or electrostatic interactions between the stabilising objects or through the formation of a mechanically rigid layer [13]. In the case of surfactants, the mechanisms of stabilization of bubble interfaces are linked to their ability to resist surface tension gradients. The resistance to changes in the surface area or surface concentration is described by the interfacial viscoelasticity. In the case of the most common surfactants (SLES, SDS and TTAB) as foam stabilizer, they adsorb rather rapidly to the interface and populate the gas/liquid interfaces leading to the formation of surfactant monolayers. The presence of this surfactant monolayer influences the coarsening process depending on the mechanical properties of the surface. The requirement to decrease the coarsening process is that the surfactant monolayers exhibit a surface elastic modulus and a resistance to compression. The elastic modulus is defined as:

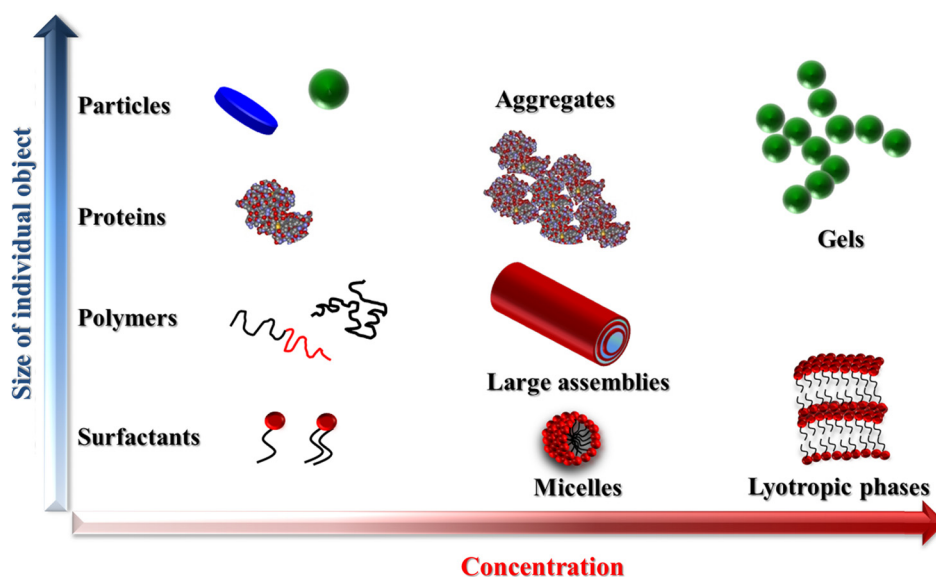
$$E = A \frac{d\gamma}{dA}$$

where  $A$  is the bubble area and  $\gamma$  is the surface tension. A high compressional surface elasticity means that small changes in surface area lead to large changes in  $\gamma$ .

In the case of surfactant monolayers, an exchange of surfactant monomers can occur between the bulk and the interface due to the freely desorption and adsorption of the monomers at the interface for soluble surfactants. This phenomenon leads to a low resistance of the monolayer to compression. The resulting foam resistance to coarsening is low. In the same way, the mobility of the surfactant at the interface can have an impact in the drainage rate. In the case of surfactant monomers which can desorb from the interface, the surface coverage can be in some cases too low to avoid the coalescence phenomenon. The presence of a surfactant monolayer influences the coarsening process depending on the mechanical properties of the surface [14,15].

Despite decades of research, the correlation of the foam stability and aging mechanisms to the chemical nature of the foam stabilizer remains a great challenge at the frontier between chemistry and physics [16]. Indeed, the foam properties cannot be only explained by the molecular structure of the foam stabilizer as the way in which they behave depends also on the bubble size and the liquid fraction.

*Role of the foam stabilizer in foam liquid channels.* The behaviour of different stabilising agents as a function of bulk concentration is schematised in Fig. 3. Starting at the bottom left hand corner, with low concentrations of surfactants, the



**Fig. 3.** (Colour online.) A drawing of the basic building blocks used for the stabilization of foams. Starting at the bottom left corner, surfactant monomers are the smallest objects, increasing their concentration leads to the formation of micelles, and liquid crystalline phases. Increasing the object size to polymers, proteins and eventually to particles in general increases the adsorption energy. These objects can also aggregate with an increased concentration (and added attraction) even to form self-supporting gels.

most widely used foam stabilisers. They are monomers at low concentration and with increasing concentration they start to self-assemble into a whole variety of structures. Many surfactants form spherical micelles, but wormlike micelles, vesicles, lamellar phases, or liquid crystalline phase are also found at higher concentrations (Fig. 3). The size and stability of the objects can change considerably depending on the surfactant type and on the medium (pH, salinity etc.), which is why this self-assembly can play a very important role on the foam stability and aging [17,18]. As we increase the size of the individual objects and pass onto polymers and proteins, the adsorption energies are typically larger. This means that the molecular exchange at the interface is slowed down and the surfaces are often more viscoelastic than those with surfactants. Proteins can also be made to aggregate into a range of structures, such as fibres or fractal aggregates [19]. The types of aggregate can be changed by increasing the concentration or by external treatment leading to different foam behaviour in comparison with proteins in their molecular state [19–22]. The wide variety of polymers and proteins, leads to almost infinite possibilities for the production of foams. The particles used for foam stabilisation are in general larger than polymers or proteins (Fig. 3), which increases the adsorption energy even further and can lead to even more elastic interfaces. Indeed it is possible to completely arrest the ageing of the foams with suitably chosen particles [23]. The choice of particles is enormous, and as with all the soft matter building blocks the interactions can be tuned to have more or less hydrophilic, more or less interacting particles. As particles with attractive interactions are used (often the case when the particles are partially hydrophobic) various aggregated structures can be obtained, which can also lead to the formation of an elastic network (Fig. 3). Foams that are stable indefinitely can be obtained due to such a network, if the elasticity is sufficiently high to arrest both drainage and coarsening [24].

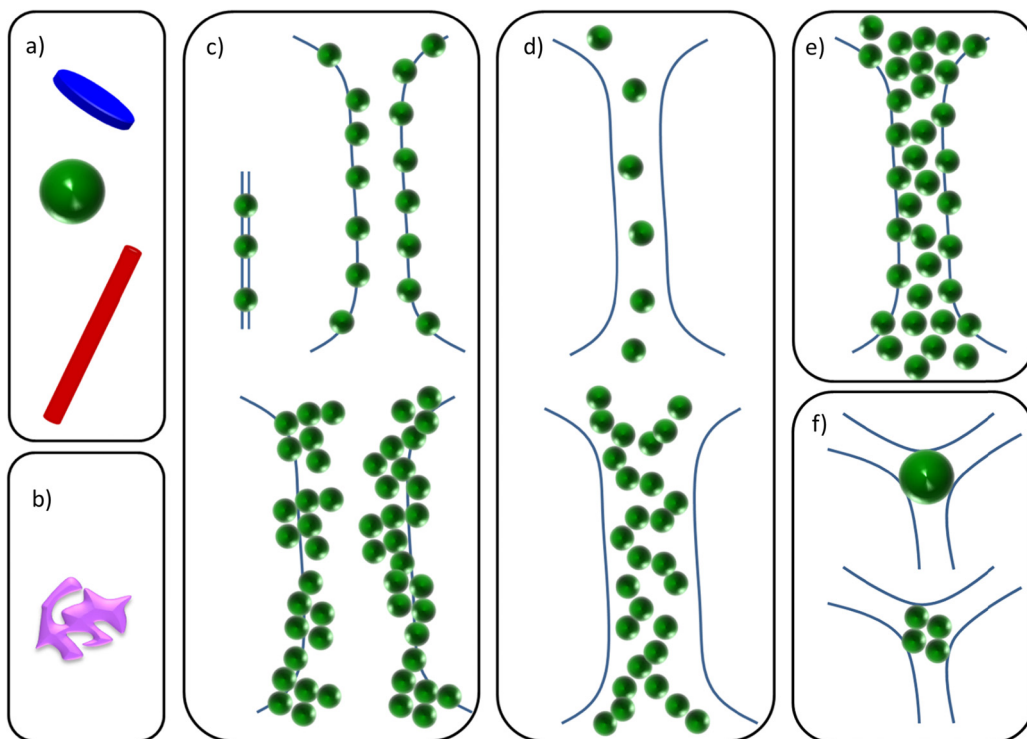
All these self-assembled and aggregated structures can be blocked inside the foam liquid channels and increase the viscosity of the liquid phase leading to slow down or arrest drainage. They can also adopt various configurations at the air/water interfaces with possibilities of rearrangement inside the films due to the confinement. The challenge remains to link the behaviour of all these objects in bulk (not in foams) to their behaviour when they are inside, or stabilising foams. The main question is to determine if the self-assembly or aggregate structure is modified because of the presence of the interfaces and the confinement within the soft walls. Similar challenge concerns the understanding of emulsions stabilized by particles, aggregated proteins and surfactant self-assemblies, as described in a recent review [25].

In this review, an overview will be given on recent results obtained on the foaming properties of particles, self-assembled and aggregated structures. We will highlight how the presence of objects inside the foam can drastically modify the foam stability from unstable to ultrastable.

## 2. Foams with solid particles

### 2.1. Particles at the air/water interface

Solid particles can be used in foams either to suppress foaming, or to increase foam stability. The way in which the particles interact with the bubbles can be coarsely predicted by the hydrophobicity or hydrophilicity of the particles, which is described by the contact angle the particles make with the interface. A hydrophobic particle would mainly be immersed



**Fig. 4.** (Colour online.) Scheme of the foam stabilization by particles. (a) Particles of different shapes or (b) surface roughness. (c) Particles adsorbed at the interface, either as a monolayer or as thick multilayers. (d) Individual hydrophilic particles, and aggregated or gelified particles in the foam liquid channels. (e) Aggregated particles both adsorbed at the interfaces and in the bulk. (f) Large aggregates or individual particles in Plateau borders, size comparable to the PB.

in the gas phase, and have a small contact angle, while hydrophilic particles will stay mostly in the aqueous phase and have large contact angles. Particles of intermediate wettability sit squarely at the interface, and have contact angles in the vicinity of  $90^\circ$ . In general *hydrophobic particles act as antifoams*, and are widely used for such purposes [26–28]. We will not discuss foam destabilization using particles any further, but will concentrate on the cases where particles can be used for the enhanced stability of foams.

The presence of particles that are *hydrophilic* or that have *intermediate wettability* often *help stabilize foams* [29–31]. A cartoon of some of the possibilities for the use of particles in foams is summarized in Fig. 4. In the literature, the shape of the included particles stabilizing foams has been varied from spherical [32,33] to rod like [34], disk-like [35], and sheet-like [36] (Fig. 4a). The way in which the particles behave within the foam depends very closely on how they interact with the interface (e.g. particle surface chemistry) and how the particles interact with each other (e.g. capillary interactions, repulsive or attractive interactions). The control over the particle–interface and particle–particle interactions can be done by a variety of methods. The surface of the particles can be chemically changed (e.g., silanisation) or made more or less rough (Fig. 4b) [37]. Many of the hydrophilic particles used are charged and the surfaces can be modified by the addition of an oppositely charged surfactant, polymer or protein, which (in a given concentration range) makes the particles partially hydrophobic. The particle interactions can also be tuned by the addition of salt to screen charges, or polymer to induce depletion, both of these can also trigger aggregation. Most particles can thus be made more or less hydrophobic, and the use of particles adsorbed at the interfaces (Fig. 4c) (analogous to Pickering Emulsions) is discussed in more detail in a forthcoming paper.

## 2.2. Particles in the continuous phase of the foam

When hydrophilic particles are added to foams they tend to remain in the aqueous phase (Fig. 4d). Depending on the size of the particles with respect to the dimension of the liquid channels of the foam (films, Plateau borders and nodes) the effect of the particles can be rather different.

Particles much smaller than the bubble diameter ( $D$ ) are initially found throughout the liquid volume, and in the gradually thinning films (Fig. 4d). Micelles and solid nanoparticles can behave differently in thin films than in the bulk, and so could change the stability of the films [38–40]. In the films, particles with repulsive interactions have been found to organize into crystalline structures as the film thickness becomes sufficiently thin to accommodate only a few layers of particles. This leads to oscillations in the disjoining pressure, resisting compression at multiples of the particle diameter and attracting the interfaces as the distance between the films is not a multiple of  $D$ . The influence on foam stability remains to be shown.

As the particle concentration is increased studies of individual films show that the stratification of even larger films can be obtained [39] and as the particle concentration increases, the bulk viscosity starts to increase leading to a slowing down of drainage even through the PBs (Fig. 4d). Even at low concentrations of hydrophilic particles ( $< 2$  wt% SiO<sub>2</sub>) it has been shown that drainage is strongly slowed down by the presence of the particles, as they can start aggregating in the foam network [41]. However, in order to make very stable foams, Murray and co-workers showed the importance of weakly gelling the particles in the bulk of the foam by adding considerable amounts of NaCl to partially hydrophobised silica particles [42,43]. Guillermic et al. studied the effect of the gelation of colloidal Laponite® (hydrophilic) in the presence of SDS on foam ageing [35]. The drainage of a foam arrests if the yield stress of the gel becomes higher than the gravity induced stress. In this case the gel would effectively behave like an elastic solid and the drainage is completely blocked. The time-scales of the foam drainage and the Laponite gelation could be tuned such that the foam would start draining as the particle gel starts to set; the gel becomes more and more elastic until sufficiently elastic to stop drainage. However, the gel is too weak to stop coarsening and as the bubbles grow in size the PBs grow too, until the gravitational stress becomes such that the Laponite gel yields and the drainage starts again.

Using colloidal particles in conditions where they make even stronger gels, allows for the creation of foams that are stable indefinitely, if the gel elasticity is sufficiently high to arrest both drainage and coarsening. This is often done with particles that are both surface active adsorbing onto the bubble interfaces (for example through the addition of a co-surfactant) and that gel in the bulk (Fig. 4e) [44,45]. Such foams are particularly interesting also for the creation of solid porous materials through removal of the water phase (only the solid gel network remains) [46–48]. This allows better control over the resulting solid foam properties, with a more environmentally friendly production method—as less aggressive solvents are required to wash the porous materials.

*The influence of larger particles or particle aggregates (similar size as the PBs)* has also been investigated. Such large particles are expelled out of the films during foam generation, and reside in the PBs and the nodes of the foam (Fig. 4f). The particles will change the fluid flow in the foams, changing both drainage [49] and the mechanical properties of the foams [50].

Studies at the scale of a single PB have shown how the transport of particles of different buoyancies is modified due to the presence of interfaces [51]. Depending on the size ratio of the particles to the PBs, the particles are more or less restricted in the middle of the PBs. Smaller particles are restricted in their motion and flow more slowly than the liquid, while slightly larger particles sediment faster than the flow of the liquid (in the middle of the channel) [51]. Of course if the particles are too big, their motion can be hindered by the walls. In a full foam, the particles do not always flow through, but can become trapped [50,52]. This phenomenon is particularly important in the field of flotation in mineral processing [53]. For individual particles, or aggregates with a definite size, a criterion for the capture of particles in the foam network has been proposed by Louvet et al. [52]. The particles are arrested in the network as the capillary forces become larger than the driving viscous drag (of the particles in the flowing liquid).

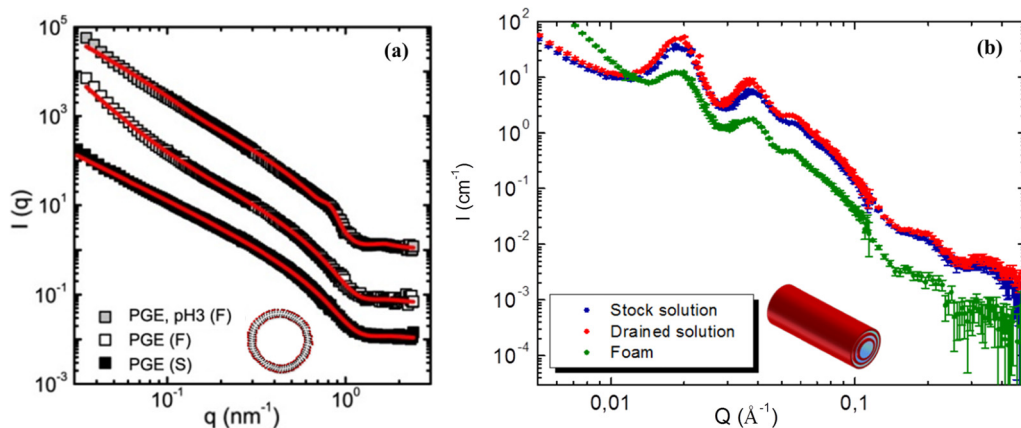
In more concentrated particle suspensions, where both the particle suspension and the foam have a yield stress, the suspended particles can even arrest drainage [49,53–55]. This happens when the yield stress of the particle suspension becomes higher than the gravitational stresses due to drainage [35]. However, in many cases coarsening continues which leads to an increase of the gravitational stress and an onset of drainage. For example through the use of emulsion droplets as the particles, making foamulsions [54,55], a way to make such a foam drain was shown by Goyon et al. [54]. A concentrated emulsion stabilized the foam against drainage until the foam was sheared and the emulsion behaved as a viscous fluid leading to separation of bubbles and emulsion.

### 3. Foams with self-assembled surfactant assemblies

Surfactants are amphiphilic molecules with a hydrophobic part and a hydrophilic part. They play an important role in both foam formation and their subsequent stability. When a surfactant is added to water, it spontaneously adsorbs at the surface and decreases the surface energy. When surfactants are adsorbed at the interface, a monolayer is formed, with the hydrophilic parts of the surfactant molecule in contact with water and the hydrophobic parts in contact with air. All the properties of the surfactant monolayers are directly linked to the nature (anionic, cationic and non-ionic) and the structure of the surfactant used to produce the foam [14]. For example, the quantity and stability of foam is closely linked to the length of the alkyl chain and in most cases the best foamers are those with chain lengths of 12–16 carbons [56]. This is probably because of the balance between solubility and surface activity. Of course it is possible to use more complex molecules such as dimers, trimers or tetramers which can slow down the exchange kinetics and increase the surface viscoelasticity, thus changing the foamability [18].

#### 3.1. Surfactant aggregation in bulk

In some surfactants systems, an increase in the surfactant concentration above a threshold concentration known as critical aggregation concentration (CAC) leads to the formation of aggregates in bulk such as lamellar phases, vesicles, tubes, etc. (Fig. 3). The structures formed by a specific surfactant depend on its molecular structure and the medium conditions (pH, ionic forces, temperature, etc.) [57]. If there are not sufficient numbers of monomers to cover the bubble surfaces, the micelles needs to be broken into the monomers to adsorb onto the newly created interfaces of the bubbles, which can take a certain time [58]. The aggregate structures can be present inside the foam and enhance the foam stability due to their



**Fig. 5.** (Colour online.) Two examples of foams stabilized by surfactant self-assemblies present in Plateau borders and characterized by SANS. (a) PGE vesicles in bulk (S) and inside the foam (F). (b) Fatty acid tubes in bulk (blue), in the drained liquid (red) and in the foam (green) (reprinted from [17,66] with permission).

surface activity, their presence in the interior of foam films and/or in the Plateau borders. Thus, very stable foams can be obtained for specific assemblies when they slow down or completely block the mechanisms of foam destabilization [17,59].

### 3.2. Surfactant aggregates in foams

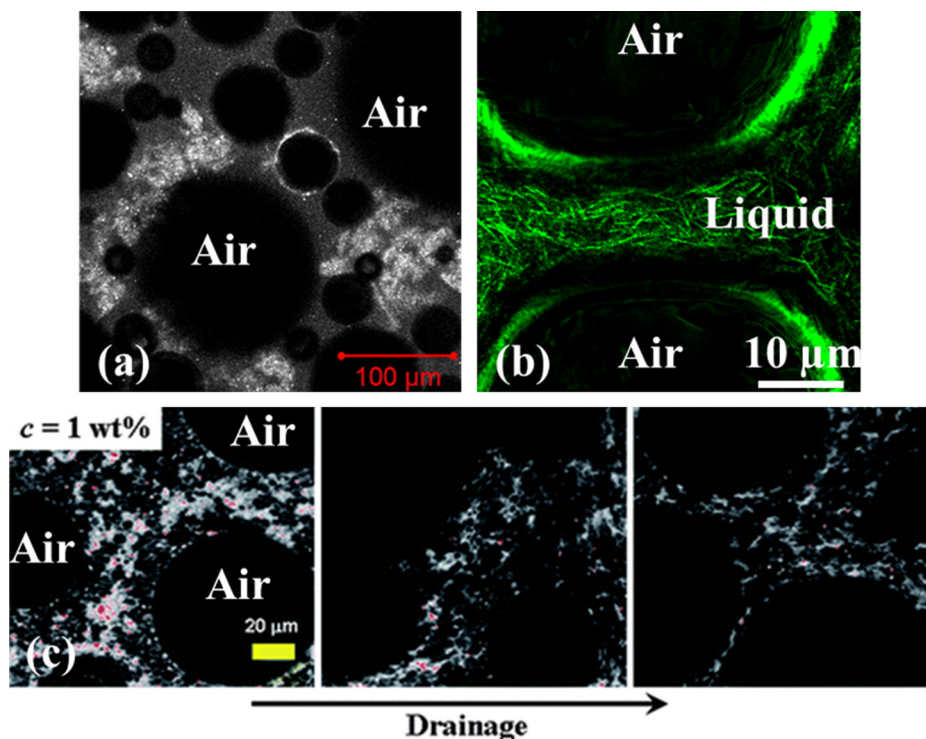
For the same surfactant molecule, various foaming stabilities can be obtained as a function of the surfactant aggregated structure. For example, some recent studies have focused on the effect of the fatty acid aggregate structure on the foaming properties [17,60,61]. In these systems, foamability of a given fatty acid seems to be independent of the fatty acid assembly. However, regarding the resulting foam stability, fatty acid systems forming spherical micelles in bulk lead to unstable foam in contrary to foams obtained with bilayers or micron-size tubes [17,61–63]. These examples point out the drastic effect of the aggregate structure on foam stability and aging. The interplay between the different length scales of the foam structure and the surfactant aggregate system controls the resulting foam stability.

In order to elucidate the link between the structure adopted by the aggregate inside the foam with the resulting foam stability and aging, multiscale approaches are necessary, starting with the characterization of surfactant aggregates in bulk before foaming, continuing with the structure under confinement in the Plateau borders and in the thin films and then at the air/water interface. Only recently, studies have clearly described the link between the surfactant aggregate and the resulting foam stability mechanisms using such an approach highlighting the importance of the aggregates at all length scales of the foam structure. Indeed, in the last decade new techniques have been developed and applied to characterize precisely the structures present inside a three dimensional aqueous foam leading to an accurate determination of the aggregate structures both in the Plateau borders or in the film and at the interface.

### 3.3. Surfactants aggregates in the continuous phase

In recent years, Small Angle Neutron Scattering (SANS) has been applied to investigate *in situ* three dimensional aqueous foam structure for various surfactant systems [17,64–66]. This technique is perfect for obtaining information about foam film thickness, surfactant aggregate structure present in PBs and bubble size in real three dimensional foams. Another approach to investigate the presence of surfactant aggregates in the interior of three dimensional aqueous foams is confocal microscopy. This technique has been applied successfully to visualize the surfactant structure surrounding the bubbles by using specific dyes to stain the surfactant molecules used. An important inconvenient is the difference in refractive indices of gas and water, which means that only structures closed to the interface can be visualized. Thus, by using SANS and/or confocal microscopy, it has been highlighted that self-assembled structures such as micron-size vesicles or tubes can be entrapped in the Plateau borders (Figs. 5 and 6) [17,66,67]. However, only SANS can determine if the self-assembled structures inside the Plateau borders keep their bulk structure or rearrange near the interfaces [17,66]. Some reorganization of aggregate structure could occur during foam formation and aging. Until now, for the few systems studied using this technique, no structural changes have been determined [17,65,66]. This observation can be explained by the fact that the bilayers of the micron-size vesicles or tubes are in a gel-like state, therefore leading to nearly indestructible objects. These objects can act like elastic micro-rods or elastic micro-spheres in the case of vesicles. The presence of these micron-size structures inside the PBs plays an important role in foam stability by increasing locally the viscosity of the liquid and reducing foam drainage.

The self-assembled structures can also remain entrapped in the foam films separating bubbles depending on their size and composition. For example, Curschellas et al. have shown by coupling SANS and confocal microscopy that polyglycerol ester surfactant vesicles are entrapped both in the Plateau borders and in the thin films (Fig. 6a) [66]. In the same way,



**Fig. 6.** (Colour online.) Three examples of foams stabilized by surfactant self-assemblies present in Plateau borders and thin film characterized by confocal microscopy. (a) PGE vesicles. (b) Fatty acid tubes and (c) catanionic vesicles (reprinted from [17,66,67] with permission).

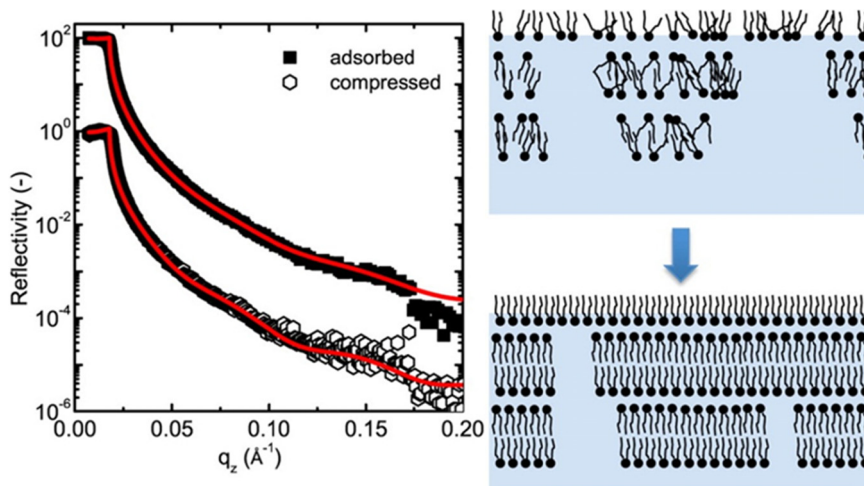
for foams made of catanionic vesicles it has been shown that vesicles are present both in the Plateau borders and in the films (Fig. 6c) [59]. The presence of self-assembled structures in the foam films increases the stability of the film by providing steric stabilization and also reduces the drainage out of the films stabilizing the foams against coalescence and coarsening [68].

### 3.4. Surfactants aggregates at interfaces

At the air/water interface, various techniques can be used to characterize the properties of interfacial layers made from self-assembled surfactant structures such as tensiometry, interfacial rheology, Brewster angle microscopy and scanning force microscopy. In the last decades, neutron reflectivity has been successfully applied to characterize the surfactant adsorption for various interfacial architectures such as monolayers, lamellar phases or multilamellar vesicles in the vicinity of the air/water interface [66,69,70]. By coupling the various techniques cited above, it is possible to obtain useful information leading to a relatively accurate comprehension on the structure and properties of the interfacial layer obtained from self-assembled structures.

If the surfactant has self-assembled, there is first the adsorption of free molecules and then a release of molecules from the aggregates to the air/water interface. In some cases the surfactants adsorb until the formation of a dense monolayer with low interfacial tension and high compression rigidity and elasticity [59,71–74]. The presence of such a dense monolayer can prevent the entry of the aggregates at the interface or induce a reorganization of the objects. The assembled structures can be adsorbed below the monolayer leading to a thick layer of a few hundred nanometres at the air/water interface. Neutron reflectivity is a powerful technique to characterize both the thickness and the structure adopted by the assembled structures at the air/water interface. For example, neutron reflectivity technique was used to determine the structure adopted by micron-size fatty acid tubes at the air/water interface [69]. These tubes have been shown to adsorb and to remain intact at the air/water interface below a dense monolayer. In the same way, in the case of polyglycerol ester surfactant vesicles, the structure of the interfacial film determined by neutron reflectivity experiments consists of a monolayer at the air/water interface supported by two underlying bilayers (Fig. 7). The presence of a thick multilayer often confers high compression rigidity, which is one of the prerequisites to obtain stable foams. Such a layer at the interface widens the film separating the bubbles and slows down coarsening. The presence of supramolecular structures at the interface significantly increases the stability of foam bubbles against coalescence and coarsening [17,59]. The reader must keep in mind that the problem remaining with all these techniques is that they provide information in static conditions and not in dynamic condition inside real aqueous foams.





**Fig. 7.** (Colour online.) Neutron reflectivity curves and corresponding fits obtained for a film formed from a PGE vesicles solution before and after an area compression of 20%. The symbols represent the measured data, and the solid lines correspond to the fitted three-layer model which is illustrated by the sketch (reprinted from [66] with permission).

#### 4. Foams with protein aggregates

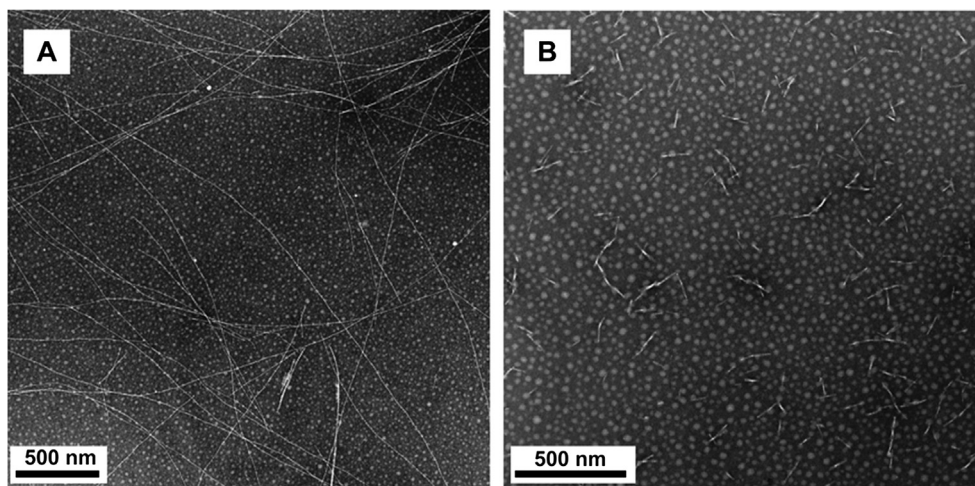
Proteins are the foam stabilizer of choice in the food industry. They are amphiphilic components that can adsorb at the air/water interface because they possess both hydrophobic regions (amino acid residues) and hydrophilic ones. In most proteins, the hydrophobic regions tend to be shielded away from the aqueous phase by the more hydrophilic regions which make the proteins water soluble. Thus, factors which tend to increase the exposure of hydrophobic regions to the aqueous phase will increase the protein surface activity. Protein adsorption at the interface and the subsequent changes in interfacial properties depend on the protein structure, the net charge, the exposed hydrophobicity and the size of the proteins. Nevertheless, while there is plenty of literature about foaming and interfacial properties of proteins, there are only few generalized concepts on protein stabilized foams [19].

##### 4.1. Protein aggregation in bulk

More complex systems of aggregated protein structures attract more and more interest. Recently several studies have been published focusing on the effect of protein aggregates on the properties of interfaces and foams. In most cases, the protein aggregates are obtained from heat or pressure treatment. As a function of the nature of the protein and of the treatment, various aggregates can be obtained. For example, the heating of globular proteins can lead to four types of aggregates: long semi-flexible fibrils, flexible strands, dense spherical particles and fractal aggregates [75]. The type and size of the aggregates can be controlled by the medium conditions such as the pH, the ionic force, the protein concentration and the heating temperature (Fig. 8). The aggregation of the globular proteins modifies the bulk rheology. An important parameter to keep in mind for these systems is the presence in almost all cases of a fraction of non-aggregated proteins. These non-aggregated proteins have a strong effect on foam properties, because they adsorb more quickly at the interface and can saturate the interface even if their weight fraction is small.

##### 4.2. Protein aggregates in foams

Solutions of protein aggregates can have different foaming properties in comparison with solutions of non-aggregated proteins depending on the protein nature, the structure and size of the aggregate and on the solution conditions. In the case of foams obtained from whey protein fibres, the foam stability and foamability have been shown to be significantly improved in comparison with non-fibrous whey proteins [76]. Moreover, several research groups have shown a drastic effect on the foam stability in the presence of protein aggregates although no effect on the interfacial properties was observed [77–79]. Another important parameter seems to be the size of the aggregated structures, as already discussed for solid particles. For fractal betalactoglobulin structures, it has been shown that for small aggregates (< 70 nm), foaming properties are better compared to non-aggregated proteins, whereas for large aggregates (> 120 nm), foaming is worse [80]. In this case, to obtain the most stable foams, both non-aggregated and aggregated proteins are needed. Similar results have been obtained for napin (vegetal protein)/pectin complexes compared with pure napin solutions. Smaller aggregates (200–500 nm) form more stable foam than larger aggregates (1500 nm) [81]. A mixture of both free napin proteins and napin/pectin complexes is required to obtain stable foams. Each species has a specific role in the foaming properties. Free proteins contribute to



**Fig. 8.** Transmission electron microscopy images of heat-induced  $\beta$ -lactoglobulin fibres in water. (A) long fibres and (B) short fibres (reprinted from [90] with permission).

the foam formation and the soluble napin/pectin complexes can slow down the drainage by their presence in the Plateau borders.

The mechanism by which aggregates contribute to foam stabilization is not completely elucidated. It is not clear why one type of aggregate is more useful than another to improve formation and stabilization of foams. Depending on the size and the structure, the proteins aggregates can increase or decrease the foam stability in comparison with their analogous non-aggregated protein. The presence of protein aggregates plays a role at all foam length scales. To perfectly understand how these structures can stabilize the foam, multiscale approaches have been applied recently in the literature for various systems [75].

#### 4.3. Protein aggregates in the continuous phase

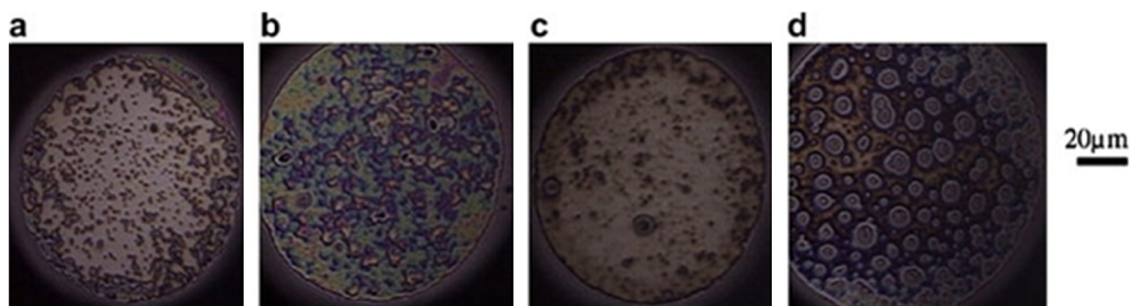
As a function of the aggregates, they can adsorb or not at the interface. When they do not adsorb to the interface, they remain in the bulk and can be confined inside the foam films and the Plateau borders. The protein aggregates can be entrapped inside the Plateau borders as a function of the structure and size of the aggregates. For various aggregated protein systems of few hundred nanometres in size, the foam drainage rate decreases in presence of aggregates due to an increase of bulk viscosity [21]. As a function of the protein aggregate size, they can play either the role of antifoaming agents or they can stabilize the foam. Small aggregates can stabilize foam films by inducing a steric repulsion between the thin liquid films due to the bulky aggregates stuck inside. In some cases, when proteins aggregates are too big, they cannot be confined inside the thin liquid films and are expelled leading to a thin film very sensitive to rupture. This destabilization phenomenon occurring in the films is similar to the one observed with solid particles [31].

The use of the thin film balance apparatus has been very useful to understand how the protein aggregates behave inside thin liquid films. In the case of fractal betalactoglobulin aggregates, the films are either fluid or gelified depending on the aggregate size [82]. When the aggregates are small (few tens of nanometres) the films are gelified and more stable than with larger aggregates (few hundreds of nanometres) leading to fluid films. In the presence of sufficient non-aggregated proteins, the mixture between non-aggregated and aggregated proteins forms a gel-like network leading to a better foam film stability (Fig. 9) [83]. In all cases, gel-like films are more stable than fluid films due to the network formation [84]. The presence of this gel-like network may rigidify the film leading to a high local surface viscosity which could limit the drainage. These stabilizing effects obtained from protein aggregates are similar to the stabilizing mechanisms observed in the case of hydrophilic non-absorbing nanoparticles (Fig. 4.d).

A useful method for the study of protein aggregates in films is the modified thin film liquid cell, where the liquid between two adsorbed layers in a thin liquid film can be exchanged [85]. Thus, the comparison of the thin film behaviour before and after exchange of the liquid provides information on the role of non-adsorbed compounds in the thin film stability. Indeed, for aggregated proteins which have no anchoring points at the film surface, they are susceptible to flow away during drainage. With this setup, useful information about the stabilizing mechanisms of aggregated proteins in the thin film can be obtained.

#### 4.4. Protein aggregates at interfaces

Non-aggregated proteins are known to adsorb to the air/water interface more rapidly than protein aggregates due to their higher mobility. For fractal betalactoglobulin aggregates the differences in surface tension observed show that the mecha-



**Fig. 9.** (Colour online.) Top view of foam films containing 94% protein aggregates with different sizes: (a)  $R_h = 35$  nm; (b)  $R_h = 71$  nm; (c)  $R_h = 117$  nm; (d)  $R_h = 197$  nm. The images were obtained for a pressure of 100 Pa (reprinted from [83], with permission).

nisms of adsorption and anchorage of protein aggregates are different from non-aggregated proteins [80]. When the protein aggregates diffuse from the bulk to the interface they tend to adsorb and need to find the proper conformation to attach at the interface. As a function of the aggregated structures and the conformation adopted at the interface, the elasticity of the adsorbed layer can increase strongly in comparison to non-aggregated proteins. In the case of protein/polysaccharide complexes, the neutron reflectivity technique has been used for various systems to determine the thickness and the structure of the interfacial films. In all cases, the presence of complexes leads to very thick films in comparison with the protein alone [81,86,87]. This thick film significantly decreases the coarsening process [88] and reduces the drainage rate [81].

Recently, the interfacial properties of fibre aggregates from various proteins have been studied [89,90]. Similar adsorption kinetics is measured in the presence of rigid or flexible fibril aggregates from betalactoglobulin proteins. In the two cases, they are able to form interfaces with a high interfacial modulus, the highest modulus being achieved with long flexible fibres and the lowest one with the non-aggregated betalactoglobulin proteins. Similar results have been obtained in the case of lysozyme fibres [89]. An important point to notice here is that the structure and rheological properties of protein fibre stabilized interfaces are modified not only by the length and stiffness but also by their polydispersity [90]. The impact on the foaming properties has not been studied yet. In the same way, the formation of complexes between proteins and polysaccharides has shown a drastic increase of the viscoelastic properties of the air/water interface in various systems [22]. For example, in the case of betalactoglobulin/acacia gum complexes, the surface tension of the complexes is the same as that for the pure protein, but the complexes form much stronger viscoelastic films [88]. In all cases, the presence of a viscoelastic layer at the interface from protein aggregates or protein/polysaccharide complexes can lead to an increase of the foam stability by decreasing the coalescence and coarsening processes.

## 5. Conclusion

We have shown how the presence of particles, whether solid or composed of surfactants, proteins and polymers can influence foam stability. They can be used to destroy foams, but we have focused on the cases where they enhance foam stability. The objects can adsorb onto the gas/liquid interfaces to create thick solid films which can be sufficiently rigid to arrest coarsening. They can remain in the liquid phase, where they can slow down drainage either by blocking in the Plateau borders or simply by changing the viscosity of the fluid. It is even possible to create foams which are stable for months if not years by choosing correctly the stabilizing agents.

Many open questions remain on the stability and ageing of foams, independently of the stabilizing objects or processes present. The use of particles, proteins, amphiphilic aggregates, or polymers also adds complexity to the study of foams. The objects used can have a specific structure of their own over several length-scales and relaxation time-scales over several decades. This makes the study of these foams particularly difficult and requires specific experimental approaches spanning the whole structures and time-scales. We can also invert the question and ask what is the influence of the gas/water interfaces and in particular the potential confinement in the foam liquid channel on the assembly of these objects? We can use foams as confining media providing us with macroscopic samples of micro-objects confined by soft walls.

The complexity of the objects can also be tuned to an advantage; they can be specially designed to understand specific foam ageing behaviour. Studies have been carried out using light-sensitive surfactants to probe interfacial adsorption and film stability [91,92]. These specific objects can also be used to produce smart foams for which the foam aging mechanisms can be controlled on demand by external stimuli such as temperature, UV and magnetic field. Indeed all these stimuli can be used to trigger a change in the incorporated objects, making them more or less efficient for foam stabilization [17], or allowing the foam to be completely destabilized using the chosen stimulus [62,93–95]. It is also possible to place other types of functional objects inside the foam, such as polymerisable emulsion droplets leading to the creation of solid foams [96].

The organization and behaviour of aggregated structures in foams still holds open questions, which will allow us both to further understand the mechanisms of foam ageing and to achieve even finer control over the foams.

## Acknowledgements

We would like to thank COST (MP 1106) for support. Dominique Langevin and Emmanuelle Rio are gratefully acknowledged for the careful reading of the manuscript.

## References

- [1] I. Cantat, et al., *Les Mousses: Structure et Dynamique*, Collection "Échelles", Belin, Paris, 2010.
- [2] D. Weaire, S. Hutzler, *The Physics of Foams*, Oxford University Press, Oxford, UK, 1999.
- [3] A. Saint-Jalmes, Physical chemistry in foam drainage and coarsening, *Soft Matter* 2 (2006) 836–849.
- [4] D. Langevin, E. Rio, Coalescence in foams and emulsions, in: P. Somasundaran (Ed.), *Encyclopedia of Surface and Colloid Science*, second edition, Taylor and Francis, New York, 2006, pp. 1–15.
- [5] S. Hilgenfeldt, S.A. Koehler, H.A. Stone, Dynamics of coarsening foams: accelerated and self-limiting drainage, *Phys. Rev. Lett.* 86 (20) (2001) 4704.
- [6] V. Carrier, A. Colin, Coalescence in draining foams, *Langmuir* 19 (11) (2003) 4535–4538.
- [7] P. Garrett, Recent developments in the understanding of foam generation and stability, *Chem. Eng. Sci.* 48 (2) (1993) 367–392.
- [8] D. Weaire, V. Pegeron, Frustrated froth: evolution of foam inhibited by an insoluble gaseous component, *Philos. Mag. Lett.* 62 (6) (1990) 417–421.
- [9] A. Webster, M. Cates, Osmotic stabilization of concentrated emulsions and foams, *Langmuir* 17 (3) (2001) 595–608.
- [10] M. Safouane, et al., Aqueous foam drainage. Role of the rheology of the foaming fluid, *J. Phys. IV* 11 (PR6) (2001) 275–280.
- [11] M. Safouane, et al., Viscosity effects in foam drainage: Newtonian and non-Newtonian foaming fluids, *Eur. Phys. J. E* 19 (2) (2006) 195–202.
- [12] R. Tuinier, et al., Transient foaming behavior of aqueous alcohol solutions as related to their dilational surface properties, *J. Colloid Interface Sci.* 179 (2) (1996) 327–334.
- [13] D. Langevin, Influence of interfacial rheology on foam and emulsion properties, *Adv. Colloid Interface Sci.* 88 (1–2) (2000) 209–222.
- [14] N.D. Denkov, et al., The role of surfactant type and bubble surface mobility in foam rheology, *Soft Matter* 5 (18) (2009) 3389–3408.
- [15] S. Tcholakova, et al., Control of Ostwald ripening by using surfactants with high surface modulus, *Langmuir* 27 (24) (2011) 14807–14819.
- [16] B.S. Murray, Stabilization of bubbles and foams, *Curr. Opin. Colloid Interface Sci.* 12 (4) (2007) 232–241.
- [17] A.-L. Fameau, et al., Smart foams: switching reversibly between ultrastable and unstable foams, *Angew. Chem., Int. Ed. Engl.* 50 (36) (2011) 8264–8269.
- [18] A. Salonen, et al., Solutions of surfactant oligomers: a model system for tuning foam stability by the surfactant structure, *Soft Matter* 6 (10) (2010) 2271–2281.
- [19] P. Wierenga, H. Gruppen, New views on foams from protein solutions, *Curr. Opin. Colloid Interface Sci.* 15 (5) (2010) 365–373.
- [20] B.S. Murray, R. Ettelaie, Foam stability: proteins and nanoparticles, *Curr. Opin. Colloid Interface Sci.* 9 (5) (2004) 314–320.
- [21] T. Nicolai, M. Britten, C. Schmitt,  $\beta$ -Lactoglobulin and WPI aggregates: formation, structure and applications, *Food Hydrocoll.* 25 (8) (2011) 1945–1962.
- [22] C. Schmitt, S.L. Turgeon, Protein/polysaccharide complexes and coacervates in food systems, *Adv. Colloid Interface Sci.* 167 (1) (2011) 63–70.
- [23] A. Stocco, et al., Aqueous foams stabilized solely by particles, *Soft Matter* 7 (4) (2011) 1260–1267.
- [24] W. Kloek, T. van Vliet, M. Meinders, Effect of bulk and interfacial rheological properties on bubble dissolution, *J. Colloid Interface Sci.* 237 (2) (2001) 158–166.
- [25] S. Tcholakova, N. Denkov, A. Lips, Comparison of solid particles, globular proteins and surfactants as emulsifiers, *Phys. Chem. Chem. Phys.* 10 (12) (2008) 1608–1627.
- [26] C.A. Miller, Antifoaming in aqueous foams, *Curr. Opin. Colloid Interface Sci.* 13 (3) (2008) 177–182.
- [27] N.D. Denkov, Mechanisms of foam destruction by oil-based antifoams, *Langmuir* 20 (22) (2004) 9463–9505.
- [28] S.I. Karakashev, M.V. Grozdanova, Foams and antifoams, *Adv. Colloid Interface Sci.* 176 (2012) 1–17.
- [29] B.P. Binks, Particles as surfactants—similarities and differences, *Curr. Opin. Colloid Interface Sci.* 7 (1–2) (2002) 21–41.
- [30] T.N. Hunter, et al., The role of particles in stabilising foams and emulsions, *Adv. Colloid Interface Sci.* 137 (2) (2008) 57–81.
- [31] T.S. Horozov, Foams and foam films stabilised by solid particles, *Curr. Opin. Colloid Interface Sci.* 13 (3) (2008) 134–140.
- [32] F.-Q. Tang, et al., The effect of SiO<sub>2</sub> particles upon stabilization of foam, *J. Colloid Interface Sci.* 131 (2) (1989) 498–502.
- [33] S. Fujii, et al., Aqueous particulate foams stabilized solely with polymer latex particles, *Langmuir* 22 (18) (2006) 7512–7520.
- [34] R.G. Alargova, et al., Foam superstabilization by polymer microrods, *Langmuir* 20 (24) (2004) 10371–10374.
- [35] R.M. Guillermic, et al., Surfactant foams doped with laponite: unusual behaviors induced by aging and confinement, *Soft Matter* 5 (24) (2009) 4975–4982.
- [36] J.S. Guevara, et al., Stabilization of Pickering foams by high-aspect-ratio nano-sheets, *Soft Matter* 9 (4) (2013) 1327–1336.
- [37] E. Vignati, R. Piazza, T.P. Lockhart, Pickering emulsions: interfacial tension, colloidal layer morphology, and trapped-particle motion, *Langmuir* 19 (17) (2003) 6650–6656.
- [38] D. Wasan, A. Nikolov, Thin liquid films containing micelles or nanoparticles, *Curr. Opin. Colloid Interface Sci.* 13 (3) (2008) 128–133.
- [39] G. Sethumadhavan, A. Nikolov, D. Wasan, Stability of films with nanoparticles, *J. Colloid Interface Sci.* 272 (1) (2004) 167–171.
- [40] C. Stubenrauch, R. von Klitzing, Disjoining pressure in thin liquid foam and emulsion films—new concepts and perspectives, *J. Phys. Condens. Matter* 15 (27) (2003) R1197.
- [41] F. Carn, et al., Foam drainage in the presence of nanoparticle–surfactant mixtures, *Langmuir* 25 (14) (2009) 7847–7856.
- [42] E. Dickinson, et al., Factors controlling the formation and stability of air bubbles stabilized by partially hydrophobic silica nanoparticles, *Langmuir* 20 (20) (2004) 8517–8525.
- [43] T. Kostakis, R. Ettelaie, B.S. Murray, Effect of high salt concentrations on the stabilization of bubbles by silica particles, *Langmuir* 22 (3) (2006) 1273–1280.
- [44] L.R. Arriaga, et al., On the long-term stability of foams stabilised by mixtures of nano-particles and oppositely charged short chain surfactants, *Soft Matter* 8 (43) (2012) 11085–11097.
- [45] U.T. Gonzenbach, et al., Ultrastable particle-stabilized foams, *Angew. Chem., Int. Ed. Engl.* 45 (21) (2006) 3526–3530.
- [46] U.T. Gonzenbach, et al., Processing of particle-stabilized wet foams into porous ceramics, *J. Amer. Ceram. Soc.* 90 (11) (2007) 3407–3414.
- [47] I. Lesov, S. Tcholakova, N. Denkov, Drying of particle-loaded foams for production of porous materials: mechanism and theoretical modeling, *RSC Adv.* 4 (2) (2014) 811–823.
- [48] F. Krauss Juillerat, U.T. Gonzenbach, L.J. Gauckler, Tailoring the hierarchical pore structures in self-setting particle-stabilized foams made from calcium aluminate cement, *Mater. Lett.* 70 (2012) 152–154.
- [49] K. Koczo, L. Lobo, D. Wasan, Effect of oil on foam stability: aqueous foams stabilized by emulsions, *J. Colloid Interface Sci.* 150 (2) (1992) 492–506.
- [50] S. Cohen-Addad, et al., Rigidity percolation in particle-laden foams, *Phys. Rev. Lett.* 99 (16) (2007) 168001.
- [51] F. Rouyer, et al., Transport of coarse particles in liquid foams: coupling of confinement and buoyancy effects, *Soft Matter* 7 (10) (2011) 4812–4820.
- [52] N. Louvet, R. Höhler, O. Pitois, Capture of particles in soft porous media, *Phys. Rev. E* 82 (4) (2010) 041405.
- [53] S. Guignot, et al., Liquid and particles retention in foamed suspensions, *Chem. Eng. Sci.* 65 (8) (2010) 2579–2585.

- [54] J. Goyon, et al., Shear induced drainage in foamy yield-stress fluids, *Phys. Rev. Lett.* 104 (12) (2010) 128301.
- [55] A. Salonen, et al., Dual gas and oil dispersions in water: production and stability of foamulsion, *Soft Matter* 8 (3) (2012) 699–706.
- [56] P.R. Garrett, P.R. Moore, Foam and dynamic surface properties of micellar alkyl benzene sulphonates, *J. Colloid Interface Sci.* 159 (1) (1993) 214–225.
- [57] J. Israelachvili, *Intermolecular and Surface Forces*, Second Edition, London Academic Press limited, 1992, 450 p.
- [58] S.G. Oh, D.O. Shah, Relationship between micellar lifetime and foamability of sodium dodecyl-sulfate and sodium dodecyl-sulfate 1-hexanol mixtures, *Langmuir* 7 (7) (1991) 1316–1318.
- [59] D. Varade, et al., On the origin of the stability of foams made from cationic surfactant mixtures, *Soft Matter* 7 (14) (2011) 6557–6570.
- [60] A.-L. Fameau, et al., Self-assembly, foaming, and emulsifying properties of sodium alkyl carboxylate/guanidine hydrochloride aqueous mixtures, *Langmuir* 27 (8) (2011) 4505–4513.
- [61] B. Novales, et al., Self-assembly of fatty acids and hydroxyl derivative salts, *Langmuir* 24 (1) (2008) 62–68.
- [62] A.-L. Fameau, S. Lam, O.D. Velez, Multi-stimuli responsive foams combining particles and self-assembling fatty acids, *Chem. Sci.* 4 (10) (2013) 3874–3881.
- [63] A.-L. Fameau, et al., Foaming and emulsifying properties of fatty acids neutralized by tetrabutylammonium hydroxide, *Colloids Surf. A, Physicochem. Eng. Asp.* 403 (2012) 87–95.
- [64] C. Micheau, et al., Specific salt and pH effects on foam film of a pH sensitive surfactant, *Langmuir* 29 (27) (2013) 8472–8481.
- [65] M.A.V. Axelos, F. Boue, Foams as viewed by small-angle neutron scattering, *Langmuir* 19 (17) (2003) 6598–6604.
- [66] C. Curschellas, et al., Foams stabilized by multilamellar polyglycerol ester self-assemblies, *Langmuir* 29 (1) (2012) 38–49.
- [67] D. Varade, et al., On the origin of the stability of foams made from cationic surfactant mixtures, *Soft Matter* 7 (14) (2011) 6557–6570.
- [68] E. Mileva, D. Exerowa, Amphiphilic nanostructures in foam films, *Curr. Opin. Colloid Interface Sci.* 13 (3) (2008) 120–127.
- [69] A.-L. Fameau, et al., Adsorption of multilamellar tubes with a temperature tunable diameter at the air/water interface, *J. Colloid Interface Sci.* 362 (2) (2011) 397–405.
- [70] D.J. McGillivray, et al., Ordered structures of dichain cationic surfactants at interfaces, *Langmuir* 19 (19) (2003) 7719–7726.
- [71] L.R. Arriaga, et al., Adsorption, organization and rheology of cationic layers at the air/water interface, *Langmuir* 29 (10) (2013) 3214–3222.
- [72] A. Stocco, et al., Interfacial behavior of cationic surfactants, *Langmuir* 26 (13) (2010) 10663–10669.
- [73] C. Curschellas, et al., Interfacial aspects of the stability of polyglycerol ester covered bubbles against coalescence, *Soft Matter* 8 (46) (2012) 11620–11631.
- [74] A.-L. Fameau, A. Saint-Jalmes, Yielding and flow of solutions of thermoresponsive surfactant tubes: tuning macroscopic rheology by supramolecular assemblies, *Soft Matter* 10 (20) (2014) 3622–3632.
- [75] T. Nicolai, D. Durand, Controlled food protein aggregation for new functionality, *Curr. Opin. Colloid Interface Sci.* 18 (4) (2013) 249–256.
- [76] D. Oboroceanu, et al., Fibrillization of whey proteins improves foaming capacity and foam stability at low protein concentrations, *J. Food Eng.* 121 (2014) 102–111.
- [77] A. Bals, U. Kulozik, Effect of pre-heating on the foaming properties of whey protein isolate using a membrane foaming apparatus, *Int. Dairy J.* 13 (11) (2003) 903–908.
- [78] J. Davis, E.A. Foegeding, Foaming and interfacial properties of polymerized whey protein isolate, *J. Food Sci.* 69 (5) (2004) C404–C410.
- [79] P.A. Wierenga, L. van Norél, E.S. Basheva, Reconsidering the importance of interfacial properties in foam stability, *Colloids Surf. A, Physicochem. Eng. Asp.* 344 (1) (2009) 72–78.
- [80] B. Rullier, B. Novales, M.A. Axelos, Effect of protein aggregates on foaming properties of  $\beta$ -lactoglobulin, *Colloids Surf. A, Physicochem. Eng. Asp.* 330 (2) (2008) 96–102.
- [81] I. Schmidt, et al., Foaming properties of protein/pectin electrostatic complexes and foam structure at nanoscale, *J. Colloid Interface Sci.* 345 (2) (2010) 316–324.
- [82] B. Rullier, et al.,  $\beta$ -Lactoglobulin aggregates in foam films: correlation between foam films and foaming properties, *J. Colloid Interface Sci.* 336 (2) (2009) 750–755.
- [83] B. Rullier, et al.,  $\beta$ -Lactoglobulin aggregates in foam films: effect of the concentration and size of the protein aggregates, *J. Colloid Interface Sci.* 343 (1) (2010) 330–337.
- [84] R. Zuniga, et al., Kinetics of formation and physicochemical characterization of thermally-induced  $\beta$ -lactoglobulin aggregates, *J. Food Sci.* 75 (5) (2010) E261–E268.
- [85] P.A. Wierenga, E.S. Basheva, N.D. Denkov, Modified capillary cell for foam film studies allowing exchange of the film-forming liquid, *Langmuir* 25 (11) (2009) 6035–6039.
- [86] R.A. Ganzevles, et al., Modulating surface rheology by electrostatic protein/polysaccharide interactions, *Langmuir* 22 (24) (2006) 10089–10096.
- [87] R.A. Ganzevles, et al., Structure of mixed  $\beta$ -lactoglobulin/pectin adsorbed layers at air/water interfaces, a spectroscopy study, *J. Colloid Interface Sci.* 317 (1) (2008) 137–147.
- [88] C. Schmitt, et al., Effect of time on the interfacial and foaming properties of  $\beta$ -lactoglobulin/acacia gum electrostatic complexes and coacervates at pH 4.2, *Langmuir* 21 (17) (2005) 7786–7795.
- [89] N.-P.K. Humblet-Hua, E. van der Linden, L.M. Sagis, Surface rheological properties of liquid–liquid interfaces stabilized by protein fibrillar aggregates and protein–polysaccharide complexes, *Soft Matter* 9 (7) (2013) 2154–2165.
- [90] J.-M. Jung, D.Z. Gunes, R. Mezzenga, Interfacial activity and interfacial shear rheology of native  $\beta$ -lactoglobulin monomers and their heat-induced fibers, *Langmuir* 26 (19) (2010) 15366–15375.
- [91] E. Chevallier, et al., Photofoams: remote control of foam destabilization by exposure to light using an azobenzene surfactant, *Langmuir* 28 (5) (2012) 2308–2312.
- [92] E. Chevallier, et al., Light induced flows opposing drainage in foams and thin-films using photosurfactants, *Soft Matter* 9 (29) (2013) 7054–7060.
- [93] A. Salonen, D. Langevin, P. Perrin, Light and temperature bi-responsive emulsion foams, *Soft Matter* 6 (21) (2010) 5308–5311.
- [94] S. Lam, et al., Magnetically responsive pickering foams, *J. Amer. Chem. Soc.* 133 (35) (2011) 13856–13859.
- [95] A.R. Patel, et al., Stable and temperature-responsive surfactant-free foamulsions with high oil-volume fraction, *ChemPhysChem* 13 (17) (2012) 3777–3781.
- [96] F. Schüller, et al., Synthesis of macroporous polystyrene by the polymerization of foamed emulsions, *Angew. Chem., Int. Ed. Engl.* 51 (9) (2012) 2213–2217.