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Minireviews

Responsive Aqueous Foams

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Remarkable properties have emerged recently for aqueous foams, including ultrastability and responsiveness. Responsive aqueous foams refer to foams for which the stability can be switched between stable and unstable states with a change in environment or with external stimuli. Responsive foams have been obtained from various foam stabilizers, such as surfactants, proteins, polymers, and particles, and with various stimuli. Different strategies have been developed to design this type of soft material. We briefly review the two main approaches used to obtain responsive foams. The first approach is based on the responsiveness of the interfacial layer surrounding the gas bubbles, which leads to responsive foams. The second approach is based on modifications that occur in the aqueous phase inside the foam liquid channels to tune the foam stability. We will highlight the most sophisticated approaches, which use light, temperature, and magnetic fields and lead to switchable foam stability.

1. Introduction

Aqueous foams are widely used in cosmetics, detergents, food, fire-fighting, oil recovery, and flotation of minerals.[1] They are formed from gas bubbles dispersed in a water phase. An important parameter to describe aqueous foams is the water fraction of the foam, which corresponds to the volume of liquid dispersed in the foam volume, $\varepsilon = V_{\text{liquid}}/V_{\text{foam}}$. Foam production requires the use of stabilizing components dispersed in the aqueous phase, which can be surfactant molecules, polymers, proteins, or particles.[2] Foams are thermodynamically metastable systems that tend to separate with time into the individual components of which they are composed. The role of the foam stabilizer is to stabilize the foam by slowing down the different mechanisms of foam destabilization, that is, drainage, coarsening, and coalescence.[2] Due to gravity, the liquid inside the foams drains rapidly until an equilibrium state is reached between gravity and the capillary force, which corresponds to water fractions below 1%. In parallel, a foam evolves due to gas transfer between bubbles, called coarsening, which tends to increase the mean bubble size with time. The film separating the bubbles can rupture, which leads to bubble coalescence and results in an increase in bubble size with time. Because most of the macroscopic properties (rheological, electrical, acoustical, optical, etc.) of a foam depend on the liquid fraction and on the bubble size, it is known that most of these foam properties are, therefore, evolving with time. The control of the foam stability is a major challenge in foam science and is required for various applications of aqueous foams.[2] Recent progress in research has resulted in the creation of ultrastable foams and in understanding the mechanisms which lead to enhanced foam stability.[3] A recent review has been published on these unusual ultrastable liquid foams, that is, foams with a high degree of stability with respect to both coarsening and rupture.[4]

For some applications in industry, such as washing and material recovery processes, both the formation of a stable foam and controlled foam destabilization are required. Stable foam can be advantageous during part of the process, but at the end of the process the destabilization of the foam under control is required without changes to the system composition. For example, foams are useful for cleaning processes, but at the end of cleaning the foam needs to be destroyed in a controlled way, to recover only a small volume of contaminated liquid that is easier to handle than a large quantity of foam. The ability to rapidly destroy foam on demand is difficult to achieve. Until now, it has typically required the use of chemical agents added to break the foam, such as defoaming agents.[5] Unfortunately, with defoaming agents the foam properties cannot be finely tuned and they also prevent further re-foaming. In view of the numerous applications described, the design of responsive foams is a new and important issue.[6] A stimuli-responsive system is a system in which the behavior can be modified by changes in the solution conditions (pH, temperature, and ionic strength) or with the application of an external field (light, magnetic, or electric). The application of external stimulus is a noninvasive approach to control foam stability, whereas changes to solution conditions are an invasive approach due to the addition of extra chemical components to the formulated system. Responsive foams correspond to foams for which the stability can be tuned between stable and unstable states. There is abundant literature on responsive

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surfactants,[7] polymers,[8] emulsions,[9] and gels,[10] but only few studies exist on the on-demand control of foam stability by stimuli.

In this mini-review, we present an overview of the existing results in this area and discuss the different ways to obtain responsive foams. We describe how foam stability can be tuned by pH and ionic strength with various foam stabilizers (surfactant, proteins, and particles) but lead to irreversible changes in the system composition. We will highlight the most sophisticated approaches, which use temperature or external stimuli, such as light and magnetic fields, and lead to switchable foam stability. This mini-review is divided into two main parts because two main strategies have emerged to produce responsive foams. The first strategy acts directly on the interfacial layers adsorbed at the bubble interfaces to modify the foam stability. The second strategy is based on the modification of the bulk properties and composition of the interstitial aqueous phase surrounding the bubbles to tune the foam stability.

2. Foam Responsiveness Linked to Interfacial Phenomena

Foam is a multiscale system and the properties of the foam, such as its stability with time, result from a complex coupling between all the scales.[2] At the smallest scale (from nanometers to microns), foam stabilizers are adsorbed at the bubble interface. Changes in the solution conditions or external stimuli can act on the foam stabilizers and lead to modification of the interfacial bubble properties and consequently the foam stability.

2.1. Surfactants at the Interface: Effect of the Adsorption/Desorption Kinetics Triggered by Stimuli on the Foam Stability

Recently, stimuli-responsive surfactants have been popularized to control self-assembled structures and to tune interfacial properties by triggers such as temperature, electric fields, magnetic fields, pH, and light.[7] Compared with other stimuli, light offers significant advantages because it can be directed precisely at a location of interest without physical contact. At ESPCI-Paris, researchers have designed photoresponsive surfactants [based on the azobenzene trimethylammonium bromide (azoTAB) molecule] with an azobenzene photochromic moiety in its hydrophobic tail, which provides rapid and reversible conversion from *cis* to *trans* conformation when the illuminating wavelength is switched from UV light ($\lambda = 365$ nm) to blue light ($\lambda = 436$ nm; Figure 1).[11] Under UV light, the solution contains 16% *trans* isomers, whereas under blue light the percentage of *trans* isomers is 66%. First, the adsorption kinetics of the two forms without UV light have been studied. The *cis* isomer adsorbs 10 times faster than the *trans* isomer but the *cis* conformation also desorbs 300 times faster. The *trans* isomer is more hydrophobic than the *cis* isomer, which is why the desorption is slower for the *trans* than for the *cis* isomer. As a result, at equilibrium, the air/water interface is almost fully covered with *trans* isomers. The authors investigated the effect of UV irradiation at the interface on the competition between the photoconversion phenomenon and the adsorption to determine the adsorption and desorption dynamics of each species (*cis* and *trans*) as a function of both the light wavelength and the intensity. When UV light is applied to the *trans*-rich interface, the adsorbed *trans* isomers convert into *cis* isomers that rapidly desorb from the interface in a few seconds. Above a critical light intensity, the *cis*–*trans* switching at the interface can become faster than the *trans* adsorption. As a result, the total number of adsorbed surfactant molecules is expected to decrease with time and light intensity. The light induces a “pumping out” of the interface and a cascade of fluxes is generated below the surface. Finally, it is found that by tuning the light intensity and the wavelength, the quantity of the surfactant molecules at the interface and consequently the surface tension can be controlled.

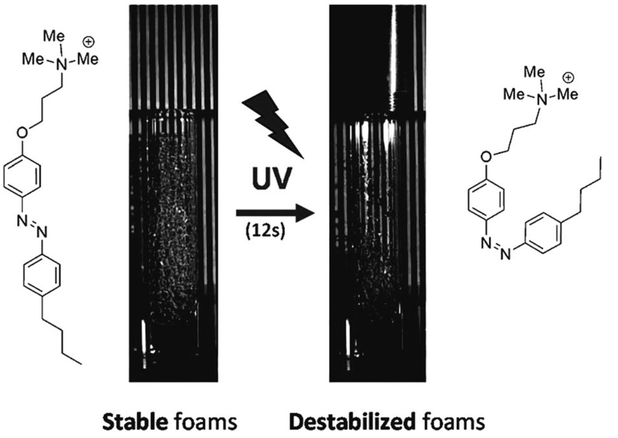

Figure 1. Illustration of the photoresponse of foams produced with the photoresponsive surfactant AzoTAB. Stable foams are produced by *trans* molecules. When UV light is shone on the top of this stable foam, the foam is destabilized quickly and all the bubbles vanish after a few seconds due to the photoconversion between the *trans* and *cis* isomers. Reproduced from Ref. [12] with permission. Copyright 2012, American Chemical Society.

Stable foams can be produced from solutions that contain high quantities of *trans* isomers, but not when *cis* isomers are predominant in the bulk. When UV light is applied to the top of a stable foam stabilized by *trans* molecules, the foam is destabilized quickly and all the bubbles vanished after few seconds (Figure 1).[12] The solution obtained after foam destabilization can again lead to the formation of stable foams just by shining blue light for several minutes on the solution to induce photoconversion between the *cis* and *trans* isomers. Under localized UV illumination, the photoconversion phenomenon at the interface from the *trans* to *cis* isomer of AzoTAB surfactants induces gradients in surface tension; such gradients lead to Marangoni flows.[13] However, these light-induced flows and the mechanisms that lead to the foam destruction are not trivial.[13] On the scale of a single wide film, it was shown that this film first gets unexpectedly thicker under UV light before rupturing.[13] This increase in thickness cannot be explained by the conformation change of the isomers at the interface but by the fluxes generated below the surface by this change. Complementary measurements on the whole foam have shown that the foam part irradiated by UV first gets wetter, that is, the water fraction increases. The foam part irradiated by UV has a higher water fraction and, therefore, is more stable. Then, the foam collapses. This behavior can be explained by the capillary suction inside the foam liquid channels towards the illuminated region, in which the interfaces of the channels have a higher surface tension. This capillary suction phenomenon initially pumps liquid towards the illuminated foam part.[13]

This system nicely illustrates that when the adsorption/desorption fluxes at the interface can be triggered by an external stimulus, the resulting foam can be easily stabilized and destabilized on demand.[12] Additionally, it provides model experimental results to better understand the coupling between the controlled flows and liquid rearrangements inside the foam liquid channels and the foam stability. A possible practical limit in the use of such photoresponsive molecules is linked to the foam's optical properties. An efficient configuration requires the illumination of a maximum of bubble interfaces; given that the reflection and transmission properties of a foam depend on its liquid fraction and mean bubble size,[14] destabilization by UV light will also depend on these parameters.

Two recent studies have shown how the liquid drainage at the origin of the foam collapse could be tuned by a temperature gradient[15] or an electric field[16] in a real 3D foam. The drainage of a 2D microfoam produced from the anionic surfactant sodium dodecyl sulfate (SDS) mixed with glycerol has been controlled by applying a constant temperature gradient that generates Marangoni stress at the air/water interface.[15] This thermocapillary Marangoni effect corresponds to a mass transfer along the air/water interface due to a temperature-induced surface tension gradient. This effect can accurately counterbalance the effect of gravity or overcome it, which results in drainage of the liquid in the opposite direction. This approach to controlling the drainage could be pursued to control the drainage in more complex 3D foams. In the same way, reverse drainage has been induced by an electric field in a model soap film produced from a mixture of a cationic surfactant (tetradecyltrimethylammonium bromide) and potassium chloride.[16] An electric field was generated inside the soap film and has been shown to induce an electro-osmotic hydrodynamic flow in the film. These electrokinetics properties take their origins from the air/water interfaces, at which hydrodynamic flow is coupled to ion repartition, and are strongly sensitive to the molecules at interfaces. As a result, the films can be up to ten times thicker under an applied electric field. This study needs to be adapted to real 3D foam structures and not only thin films so that this electrokinetic phenomenon can be used to control liquid drainage in real systems.

2.2. Macromolecules at the Interface: Effect of Changes in Solution Conditions on the Interfacial Rheological Properties and on the Foam Stability

Some macromolecules, such as proteins and polymers, can be foam stabilizers. They are amphiphilic molecules that can adsorb at the air/water interface.[17] In bulk, the hydrophobic part tends to be shielded from the aqueous phase by the more hydrophilic part, which makes the macromolecules water-soluble. The main difference from low-molecular-weight surfactants is the strong increase in interfacial viscoelasticity for layers with adsorbed macromolecules at the air/water interface. The compression elastic modulus is defined by Equation (1):

$$E = A\frac{d\gamma}{dA} \tag{1}$$

in which A is the interfacial area and γ is the surface tension. For sinusoidal deformations at frequency ω, there can be a phase shift φ between surface tension and area variations, which leads to a dilational viscosity k [Eq. (2)]:

$$k = \frac{E\sin\phi}{\omega} \tag{2}$$

To reduce the coarsening process, one possibility is that the interfacial layer exhibits a high surface elastic modulus and a resistance to compression.[18] In the case of low-molecular-weight surfactant monolayers, rapid exchange of such surfactants can occur between the bulk and the interface due to the easy desorption and adsorption of the monomers at the interface, which leads to no resistance of the monolayer to compression at moderate frequencies (values of the compression elastic modulus close to zero).[19] As a result, interfacial layers with low elastic modulus cannot efficiently prevent coarsening. In this case, the layer at the interface is described as being in a fluid-like state. In contrast, proteins or polymers can give a strong viscoelastic layer at the interface.[20] Moreover, they also develop a resistance to shear deformation and can have both high dilatational and shear viscoelastic moduli.[21] An interfacial layer with high viscoelasticity (in compression or shear) can then counteract coarsening and drainage, and prevent film rupture. In this case, the interfacial layer is described as being in a solid-like state. As a consequence, foams stabilized by proteins, polymers, etc. provide enhanced stability in comparison to low-molecular-weight surfactants.[18a,21]

For proteins, all the environmental changes that lead to the higher exposure of hydrophobic parts to the aqueous phase will increase the surface activity. Ionic strength and pH are two examples of such environmental changes. Both the structure of the proteins and the adsorbed interfacial films formed are modified by varying pH or ionic strength.[22] The resulting foam stability can be tuned as a function of the parameter used to modify the bulk solution composition before foam production. However, the only examples in the literature, in which in situ rapidly switchable foam stability is described after foam production, concerned synthetically designed peptides.[23] The development of specific peptides to switch the foam stability has been done by the group of Middelberg. In their first studies, this group has designed a peptide that contains 21 residues in total. At positions 9 and 20, two metal-binding histidine residues are present. When the peptide molecule is at the air/water interface, the two metal binding histidine residues are in contact with the bulk aqueous phase and oriented towards neighboring peptide molecules. Under acidic pH conditions, the histidine residues are in their protonated forms. In the absence of metal ions or at acidic pH in bulk solution, the authors have shown that the peptides form an interfacial layer with very low elasticity (interfacial elastic modulus of 7 mN m^{-1}) similar to the interfacial properties obtained with low-molecular-weight surfactants. The interfacial layer of adsorbed peptides is in a fluid-like state. In the presence of metal ions, such as zinc, the interfacial elastic modulus drastically increases to reach values close to 120 mN m^{-1}, which is comparable to values obtained for interfacial layers formed by proteins.[20] Under these conditions, the peptides adsorb to form a mechanically strong resistant solid-like layer. In the fluid-like and solid-like states, the same surface tension of around 52 mN m^{-1} is reached, which means that peptides are not removed from the interface. By using a neutron reflectivity technique, the authors have shown that in both cases, solid-like and fluid-like states, the structure of the interfacial layer formed by the peptides is a monolayer with almost the same structural characteristics.[24] The difference between the solid-like and the fluid-like states is due to the changes in the interactions between the peptide molecules at the interface by the binding of zinc ions by histidine residues. In the presence of binding ions, the solid-like interfacial layer can be tuned to a fluid-like state by adding ethylene diamine tetraacetic acid (EDTA) to the solution, which removes the ions from the peptide layer. In the same way, acidification of the bulk solution leads to protonation of the histidine residues and disruption of the metal–histidine binding. As a result, the acidification leads to a transition between the two interfacial states. The properties of the interfacial layer can be switched reversibly from the fluid-like to the solid-like state by modifying the bulk composition.

For this system, the foamability (quantity of foam produced) remains the same regardless of the bulk system composition, in contrast to the foam stability, which is drastically different. In presence of ions, foams are relatively stable for a few tens of minutes. However, in acidic conditions or in the absence of ions, foams are unstable and collapse within one minute after foam production (Figure 2). When a stable foam is formed, the addition of a small volume of EDTA to the top of the foam causes rapid collapse in a few seconds.[25] The foam can be easily destroyed just by removing the ions from the interfacial layer surrounding the foam bubbles, which leads to a transition in situ between the fluid-like to the solid-like state. All these results suggest that the differences observed in foam stability do not result from changes in the affinity of the peptides for the interface or to changes in surface excess, but are directly linked to the mechanical properties of the interfacial layer formed by the peptides. This approach has been pursued by the same group to develop other peptide systems that lead to switchable foam stability.[23b] In the systems described herein, the foam stability is tuned by environmental changes that occur in the bulk system composition and lead to disadvantages in comparison to an external stimulus for which no change in the system composition is needed to obtain full reversibility. Because it is not easy to change the foam composition after its production, modification of the foam stability can only be achieved by injecting liquid within the foam, which cannot be performed in a controlled manner. This process is coupled to the gravitational drainage and might also induce convective instabilities.[2] A more elegant way would be to induce a change in pH in situ by using external stimuli, such as light.[26]

In the same way, a thermoresponsive polymer (PNiPam) has been shown to adsorb at interfaces and transit from a fluid-like to solid-like state at a well-defined temperature.[27] This transition temperature corresponds to the lower critical solubility temperature, which means that below this temperature water is a good solvent for the PNiPam chains but they collapse above this temperature. This transition is reversible both in bulk and at the interfaces. At all temperatures, the foaming properties of the PNiPam are low and the foams produced are unstable.[28] As a result, it is impossible to produce thermoresponsive foams from PNiPam alone. To overcome this problem, a small amount of surfactant (SDS) has been mixed with PNiPam to improve the foaming properties. Indeed, the foamability and the foam stability have been greatly improved by adding the surfactant but the thermal responsiveness of the

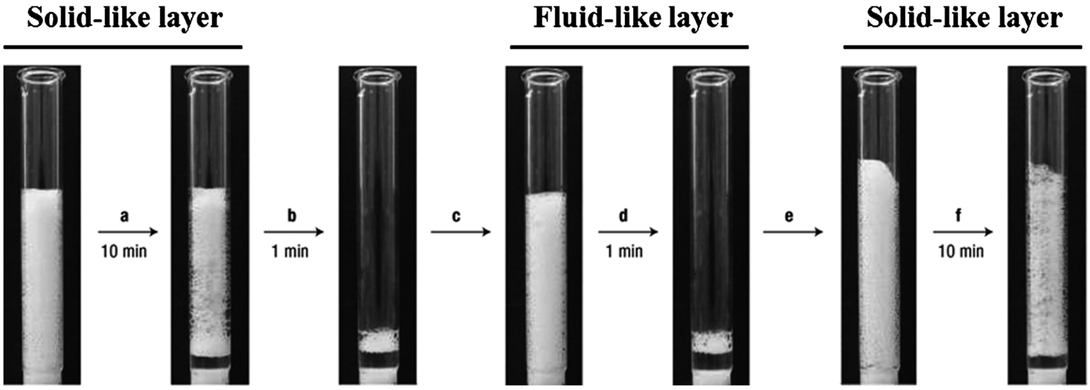

Figure 2. Illustration of the response of foams produced with peptides responsive to changes in pH. a, b) Stable foams produced at pH 7.4 when peptides form a solid-like interfacial layer, but c) can be destroyed in 1 min after decreasing the pH of the foam, which leads to a fluid-like layer. d) The foam produced after acidification is unstable because all the bubbles disappear in 1 min. e) After neutralization of the solution, a new stable foam can be produced (f). Reproduced from Ref. [23a] with permission. Copyright 2006, American Chemical Society.

interfacial layer has been lost.[28] Until now, there has been no example in the literature of responsive foams produced from PNiPam, whereas many examples of responsive emulsions have been obtained from this thermoresponsive polymer.[29]

2.3. Solid Particles at the Interface: Effect of Contact Angle on the Foam Stability

Particles are used in foam stabilization for industrial applications, such as flotation[30] and food processing.[31] However, the mechanisms for preventing foam destabilization, and especially coarsening, are far from understood.[4,32] Solid particles can be used either to stabilize foams or to suppress foaming as antifoams do. Recently, these foams have attracted more attention to understand the key mechanisms that prevent foam destabilization.[4] The adsorption of particles at an air/water surface depends on the hydrophobicity of the particles, which is described by the contact angle (θ) that the particles make with the air/water interface measured through the water (Figure 3a).[33] The energy (ΔG) required to remove a particle from the interface is linked to the contact angle and the particle size.[34] For spherical homogeneous particles, ΔG is maximum when $\theta = 90^\circ$ and is about $10^4\,k_BT$ for a particle with a radius of 10 nm (k_B is the Boltzmann constant and T is the absolute temperature). Thus, ΔG is several orders of magnitude higher than the thermal energy, which leads to irreversible adsorption of particles at the interface.[34] To produce such foams, foaming techniques with high energy input are usually required.[2]

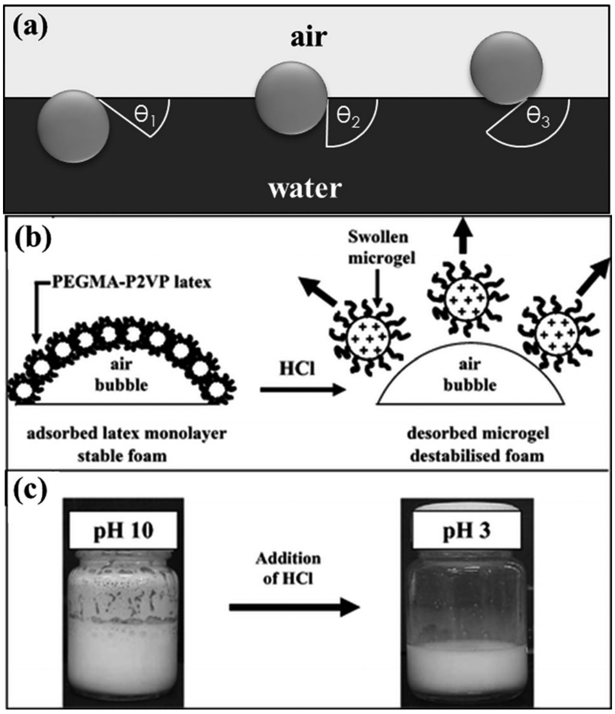

Figure 3. a) Schematic of a spherical particles at a planar air/water interface for contact angles of less than 90° (left), equal to 90° (center), and greater than 90° (right). For $\theta < 90^\circ$, aqueous foams may form. b) Illustration of the pH-responsive nature of the foams prepared by using 380 nm PEGMA-P2VP latex. The foam is stable at pH 10, but becomes destabilized at pH 3 because the PEGMA-P2VP particles undergo a latex-to-microgel transition at low pH due to protonation of the 2-vinylpyridine residues. This leads to desorption of the cationic microgel particles from the bubble surface, which destroys the foam. c) Picture of a stable foam at pH 10, which is quickly destabilized by adding HCl. Reproduced from Ref. [38] with permission. Copyright 2008, The Royal Society of Chemistry

The contact angle increases with the hydrophobicity of the particle. By adjusting the hydrophobicity of the particles before foam production, it is possible to control the adsorption of particles at the air/water interface and consequently the resulting foam stability. In the literature, the hydrophobicity of the particles has been modified either by silanization[35] or by the adsorption of oppositely charged amphiphilic molecules.[36] This second method is becoming more popular to produce foams due to do the simpler preparation and its applicability to various types of particles and amphiphilic molecules.[4]

The charge of the particles is another parameter to control the particle adsorption at the interface and the subsequent foam stability, as illustrated by Armes and co-workers. The effect of particle charge on foam stability has been shown by using latex particles with diameters of around 700 to 900 nm and stabilized by poly(acrylic acid) as steric stabilizer.[37] The charges of the particles can be tuned by changing the pH. At low pH, the latex particles are positively charged and they adsorb at the air/water interface, which is known to exhibit anionic character. In the presence of these cationic particles, stable foams are obtained. At high pH, above the isoelectric point, the same latex particles are negatively charged. The anionic latex particles cannot adsorb at the air/water interface. Therefore, they cannot act as a foam stabilizer. Cationic particles adsorb much more strongly at the air/water interface than anionic latexes particles. The authors also studied this pH effect in situ by adjusting the pH of a stable foam that contained positively charged latex particles.[37a] After adjustment of the pH from low to high, the foam was gently shaken; large bubbles disappeared and the smaller ones remained intact. This result suggests that the initially positively charged particles become negatively charged in situ, which leads to their detachment from the air/water interface and results in partial foam destruction. The foam stability can be adjusted by modifying the pH in situ, which in turn tunes the particles charge. The same group developed smaller pH-responsive latex particles with a mean diameter of 380 nm, which undergoes a latex-to-microgel transition at low pH (Figure 3b).[38] These pH-responsive latex particles give stable foams at high pH values. Upon decreasing the pH in situ, the swelling leads to catastrophic destabilization of the foam due to microgel desorption from the air/water interface (Figure 3c). In the same way, by using polystyrene latex particles stabilized by using a polybase rather than by a polyacid, pH-responsive aqueous foams can be obtained for different pH values.[39] In this case, at high pH the particles are relatively hydrophobic, they adsorb at the air/water interface and stabilize the aqueous foams. At low pH values, the hairy latex particles have cationic water-soluble hairs with hydrophilic character and no foam can be produced. Rapid defoamation can be induced by decreasing the pH of an initial stable foam, which induces the desorption of the particles from the air/water interface. These studies have shown that by tuning the charge or/and hydrophobicity of particles, it is possible to finely modify in situ the foam stability from ultrastable to unstable. However, in a recent study it has been noted that the contact angle and the charge of the particles are not the only key parameters to control the foam properties, but the flocculation state and the shear energy applied to produce the foam are important too.[40] An interesting way to explore the production of responsive foams would be to exploit this new finding by tuning the aggregation state of the particles by stimuli.

In all cases, pH as stimulus has some disadvantages in comparison with external stimuli, such as light or magnetic fields, because pH modification is an invasive approach that requires the addition of extra chemical components to modify the chemical composition of the system. To overcome this problem, magnetic particles have been used to stabilize foams to control the foam stability with non-contact stimulation by the application of a magnetic field.[41] Foams have been produced from nanometer-size magnetic particles that are adsorbed very strongly at the interface and lead to ultrastable foams at room temperature. These foams cannot be destroyed under even strong magnetic fields ($65\,\mathrm{T\,m^{-1}}$). To detach particles from the interface, a capillary force needs to be overcome. This capillary force is linked to the contact angle and the size of the particles. Under these conditions (magnetic field strength and contact angle of the particles), the authors have demonstrated that the particles can be detached from the interface only if their size is of the order of 10 to 100 μm. The foam stability could not be controlled in the presence of nanometer-sized magnetic particles in these conditions. Campbell et al. developed food-grade anisotropic magnetic polymeric microrods by incorporation of magnetite nanoparticles within the microrod interior.[42] These magnetic microrods lead to stable foams by adsorption at the air/water interface. The authors also did not succeed in triggering the destruction of the foam by using an external magnet due to the nanometer size of magnetic particles. These two studies highlight the fact that when magnetic particles in the nanometer range are strongly attached to the interface, it is almost impossible to detach them from the interface by using a magnetic field. The advantage of the particles remaining attached at the interface is that the foam can be heated quickly and in a homogeneous manner by applying an oscillating magnetic field. The irreversible attachment of the magnetic particles at the interface leads to control of the foam temperature without direct contact.[41]

3. Foam Responsiveness Linked to Phenomena that Occur in the Foam Liquid Channels

Aqueous foams contain packed gas bubbles, which are separated by thin films that join to create the liquid channels, called plateau borders.[2] The water phase present in the network of films and plateau borders can contain various objects, such as particles, surfactant self-assembly, and emulsion droplets. External stimuli or environmental changes can modify these objects and tune the bulk properties of the water phase inside the films and the plateau borders and consequently the foam stability.

3.1. Effect of Magnetic Particles within the Foam Liquid Network

In the last section, we described how nanometer-size magnetic particles could not be removed from the air/water interface by applying a magnetic field.[41] However, in the case of emulsions stabilized by spherical paramagnetic carbonyl iron micron-sized particles, the emulsions can be destroyed by removing the magnetic particles from the oil/water interface.[43] These carbonyl iron micron-sized particles have been successfully used by Lam et al. to produce magnetically responsive foams.[44] These foams are stabilized by modified cellulose (hypromellose phthalate HP-55) particles. The partially hydrophobic and anisotropic HP-55 particles are the major foam-stabilizing component, forming stable structures around the air bubbles and leading to the stabilization of the foam. The micron-sized carbonyl iron magnetic particles are entrapped inside the gel-like matrix of percolated HP-55 particles and captured in the foam liquid channels (Figure 4a). These foams drain slowly by gravity over several days, which leads to various water fractions as a function of time. For fresh foams, the water fraction is high (around 50%) and for old foams (7 days after foam formation), the water fraction is around 15%. These foams are

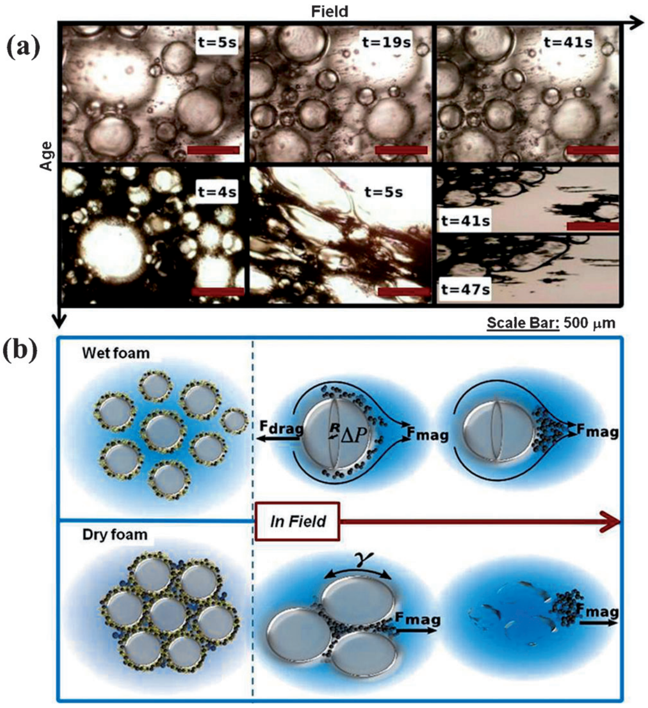

Figure 4. Foams stabilized by a mixture of HP-55 particles and micron-sized carbonyl iron magnetic particles. a) Snapshots of the collapse process of microscopic bubbles for wet foam (top row) and dry foam (bottom row). Upon application of the magnetic field, for dry foams, films become stretched and bubble coalescence occurs but this destabilization mechanism did not occur for wet foams. b) Illustration of the mechanism of foam collapse for wet (top row) and dry foam (bottom row). Reproduced from Ref. [44a] with permission. Copyright 2013, American Chemical Society.

stable for weeks at room temperature in the absence of magnetic fields, but they can be destroyed rapidly on demand with the use of a magnetic field.

Upon the application of a magnetic field, the rate and mechanism of foam collapse were shown to be dependent upon the water fraction, which is linked to the age of the foam.[44b] When exposed to a magnetic field, the magnetic particles trapped in the HP-55 matrix are magnetized; they are attracted and pulled by a lateral force in the direction of the magnetic field gradient. For fresh foams, the particles can move freely within the foam liquid channels that contain water as a free liquid medium toward the source of the magnetic field without bubble rupture (Figure 4a). For aged foam, the films between the bubbles are present due to a lower water fraction and are very sensitive to disturbances. Bubbles are tightly packed. When the particles move due to the application of the magnetic field they pull on the rigid thin films between bubbles, which leads to film rupture and rapid foam destabilization (Figure 4b). Moreover, in aged foams, the magnetic particles are close to each other due to the small quantity of water in the foam films, which leads to a stronger collective response to the applied magnetic field.[44a] The amount of time necessary to destabilize the foams by using a magnetic field decreased as the age of the foam increased. This system perfectly illustrates how the presence of particles trapped inside the foam liquid films and channels and responsive to an external stimulus, such as a magnetic field, can lead to responsive foams in a simple way.

3.2 Effect of Thermoresponsive Surfactant Self-Assembly in the Foam Liquid Channels

Recently, ultrastable foams have been produced by exploiting the self-assembly behavior of fatty acids combined with suitable organic counterions.[3a] Fatty acids act as anionic surfactants because they are composed of an aliphatic alkyl tail and a polar carboxylic acid headgroup. The crucial parameter that determines the self-assembly of the fatty acids is their packing parameter. Consequently, changing the packing parameter can trigger a change in the self-assembled structure. For self-assembled fatty acid structures, it has been found that the aliphatic tail can be in either a crystalline or a liquid state.[45] The transition between both states is induced by a change in temperature and is called the chain-melting transition.[45] Therefore, fatty acids are thermoresponsive surfactants. The chain-melting transition leads to modifications of the self-assembled structure in the aqueous phase. The macroscopic properties of the solution, like viscosity[46] or interfacial properties,[47] can also change in response to the temperature-induced change in the self-assembled surfactant structure.

Specifically, the combination of 12-hydroxystearic acid (12-HSA) and hexanolamine self-assembles to form tubes of micron length in aqueous solution at room temperature.[48] At room temperature, the aliphatic chains are in the crystalline state. At 60 °C, the chain-melting process occurs and the surfactants rearrange to form spherical micelles of nanometer size. It was also found that the system forms a very dense monolayer of fatty acid molecules at the interface. This layer leads to low surface tension and shows high compression rigidity and high interfacial elasticity.[46] At room temperature, the fatty acid tubes adsorb below the dense monolayer.[47a] When foamed, the tubes form a gel-like network within the foam lamellas and in the plateau borders.[3a] 12-HSA-based foams formed below 60 °C are ultrastable due to the presence of tubes, whereas above 60 °C the spherical micelle solutions form foams with weak stability. Below the chain-melting temperature of 60 °C, the foam volume remains constant for months. When heated above the chain-melting temperature, the tubes convert to spherical micelles inside foam liquid channels and desorb from the interface, and the gel-like network is destroyed. In response to the change in the self-assembled structures, the foam is destabilized and the foam volume decreases quickly. As soon as the system is cooled to below 60 °C, the fatty acid tubes are recovered and the foam becomes ultrastable again within a few seconds (Figure 5a).

The reversible switchability between ultrastable and unstable foam depends solely on the temperature of the foam. Instead of heating the foam externally, internal heat sources can

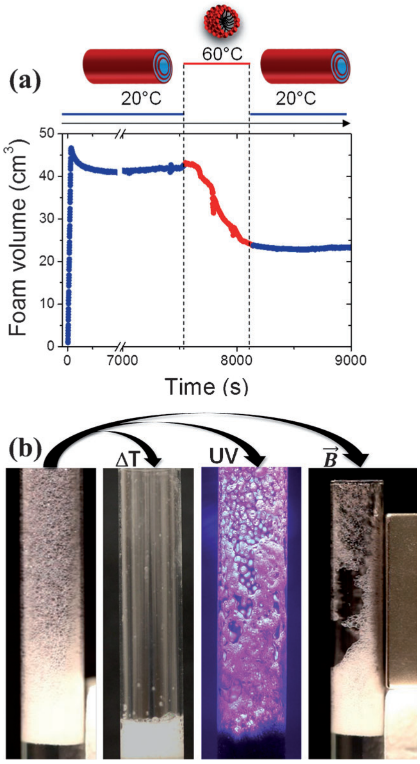

Figure 5. a) Evolution of the foam volume as a function of both temperature and time for foam produced with 12-HSA tubes, which shows the thermoresponse of the foam. At 20 °C, foams are ultrastable due to the presence of 12-HSA tubes inside the foam liquid channels. At 60 °C the tubes reassemble into spherical micelles, which leads to a drastic decrease in the foam volume. By decreasing the temperature to 20 °C, tubes are reformed in the foam liquid channels and the foam volume remains constant again with time. Reproduced from Ref. [3a] with permission. Copyright 2011, Wiley-VCH. b) Illustration of the ability of 12-HSA foam with micron-sized magnetic particles to respond to three different external stimuli: temperature, UV irradiation, and a magnetic field. Reproduced from Ref. [49] with permission. Copyright 2013, The Royal Society of Chemistry.

be incorporated. Carbon black particles can absorb UV light and dissipate the absorbed energy as heat. It has been shown that 12-HSA-based foams mixed with carbon black particles are stable in the dark but readily collapse upon UV or solar irradiation.[49] The collapse is temperature induced, as explained earlier. Another approach was to mix 12-HSA-based foams with micron-sized carbonyl iron particles to produce foams responsive to multiple stimuli. Combining the 12-HSA system with carbonyl iron particles produces foams that are responsive to temperature, light, and magnetic fields (Figure 5b).

To our knowledge, this is the only example in the literature of foams for which the stability can be switched reversibly between stable and unstable states under multiple external stimuli: temperature, light, and magnetic fields. However, other surfactant self-assembled structures could efficiently produce similar foams.[3b,50] It is important to highlight that the origin of the foam responsiveness at macroscopic scale is directly linked to the structural transitions of self-assembly inside the foam liquid channels from micron-sized objects to nanometer-sized objects, which is in turn controlled by the alkyl chain state at the molecular level triggered by temperature.[51]

3.3. Effect of Responsive Emulsion Droplets inside the Foam Liquid Channels

In many cosmetic and food product, a mixture of air bubbles and oil droplets are found. These systems are called foamulsions or foamed emulsions.[52] Stable foamulsions can be produced when emulsion droplets are trapped and jammed between the bubbles.[4] The presence of emulsion droplets in both the plateau borders and the film slows down drainage and coalescence as in the case of solid particles.[53] Oil droplets are also known to be very effective antifoam agents.[5] Whether oil droplet acts as antifoam or not is linked to the interfacial tensions between the three phases of the system: air, oil, and water. Various coefficients are used to describe the antifoam potential of oil, such as spreading, entering, and bridging.[5] The entry coefficient is linked to the potential of the oil droplets to penetrate into the air/water interface, that is, how easily the droplets can have access to air by rupturing the initial air/water interface, and is defined by Equation (3):

$$E = \gamma_{\mathrm{aw}} + \gamma_{\mathrm{ow}} - \gamma_{\mathrm{ao}} \tag{3}$$

in which γ is the surface tension and *a*, *o*, and *w* refer to the three phases (air, oil, and water, respectively). The value of this coefficient should be positive to have oil droplets acting as an antifoam. The oil droplets that cannot enter the film surface can act as a foam stabilizer by being trapped in the foam liquid channels.[53] The size of the droplets have been shown to play a role on the antifoaming behavior.[5] These two different roles of emulsion droplets, as foam stabilizers or antifoaming components, have been used to produce responsive foams.

This duality has been used first in the literature to control the foamability of a foamulsion produced from an oil/water emulsion that included both a light-responsive polymer (azobenzene-modified poly(acrylate)) and a thermoresponsive surfactant (tetraethylene glycol monodecyl ether). By modifying the temperature, the foamability is lost due to interfacial reorganization. The temperature induces a change in the partitioning of the surfactant at the oil/water interface due to the temperature response of the surfactant. Because of this interfacial reorganization, the droplets can more easily enter into the air/water interface and destroy the foam. Under UV irradiation, the emulsion is known to be destabilized due to a change in the conformation of the polymer. By applying UV light to the foamulsion, the foamability can be almost completely stopped due to a decrease in the emulsion stability, which leads to a growth in droplet size induced by coalescence. This coalescence phenomenon seems to be at the origin of foam breaking because larger droplets are known to have smaller entry barrier coefficients.[5]

A similar approach has been used to destabilize surfactant-free foamulsions by using temperature changes.[54] In this case, the emulsion is stabilized by methycellulose and tannic acid complexes. The methycellulose gels at 65 °C, which leads to coalescence of the emulsion droplets. Foams produced from these emulsions are stable for days at room temperature due to the close packing of oil droplets around the gas bubbles. Foamulsions are stable below 65 °C, but above 65 °C foamulsions quickly collapse due to the coalescence of the oil droplets that cover the air bubbles, which no longer act as foam stabilizers but as defoamers. These two examples highlight how the presence of emulsion droplets, which are responsive to external stimuli, inside the foam liquid channels can lead to responsive foams.

4. Summary and Outlook

Responsive foams for which the stability can be tuned from unstable to stable state can be achieved by external stimuli or environmental changes and by using various foam stabilizers: surfactants, proteins, solid particles, and emulsion droplets. This review explains how responsive foams can be designed. The responsiveness at the macroscopic scale of the whole foam is linked to the responsiveness of the foam stabilizer either at the air/water interface or in the bulk inside the foam liquid channels. Various triggers have been used to tune the foam stability: pH, ionic strength, light, temperature, and magnetic fields. To date, only two examples based on surfactants have shown reversible switching between stable and unstable foams by using light or/and temperature as a stimulus.[12,49] The main limitation to design switchable responsive foams is to find an appropriate foam stabilizer that provides both good foaming properties (foamability and foam stability) and responsiveness at the air/water interface or in the bulk liquid channels. For example, PNiPam is a thermoresponsive polymer that adsorbs at the air/water interface but is a poor foam stabilizer. As a consequence, it cannot be used alone to produce responsive foams.[28]

In view of the recent progress in the fields of synthetic stimuli-responsive polymers,[8] surfactants,[7] and particles,[55] the development of new types of highly functional soft materials based on aqueous foams will be pursued. From our point of view, in the near future, a simple approach to develop new responsive foams would be to use systems that have already been used to produce responsive emulsions to adapt them to produce responsive aqueous foams. For example, thermoresponsive PNiPam colloidal microgels are known to produce thermoresponsive emulsions and they could be used to produce foams.[29,56] Moreover, a major part of the research into responsive foams for the future will focus on use of the properties of these types of foams for the development of responsive porous materials.[57] Finally, from an applied point of view, the systems described in this review can find potential applications in diverse industries in which both stabilization and on-demand destabilization of foam is required, such as textile, petrochemical, washing, environmental cleanup, and material recovery processes.

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