Physicochemical control of foam properties

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Abstract

This article summarizes our recent understanding on how various essential foam properties could be controlled (viz. modified in a desired way) using appropriate surfactants, polymers, particles and their mixtures as foaming agents. In particular, we consider the effects of these agents on the foaminess of solutions and suspensions (foam volume and bubble size after foaming); foam stability to liquid drainage, bubble coalescence and bubble Ostwald ripening; foam rheological properties and bubble size in sheared foams. We discuss multiple, often non-trivial links between these foam properties and, on this basis, we summarize the mechanisms that allow one to use appropriate foaming agents for controlling these properties. The specific roles of the surface adsorption layers and of the bulk properties of the foaming solutions are clearly separated. Multiple examples are given, and some open questions are discussed. Where appropriate, similarities with the emulsions are noticed.

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Keywords

Foam, Surfactant, Adsorption, Surfactant mixture, Foaminess, Bubble Ostwald ripening, Water drainage, Bubble coalescence, Saponin, Pickering foam.

Introduction – main types of factors affecting foam properties

It has been recognized for years that many *equilibrium* and *quasi-static* foam properties depend primarily on the *volume-surface radius*, R_{32} (called also '*Sauter mean radius*'), bubble *volume fraction*, Φ, and *surface tension* of the foamed solutions, σ. Examples of such properties are the equilibrium structure of foams in a gravity field, quasi-static foam yield stress and foam elasticity on small and slow deformations [1,2]*. As shown in the seminal papers by Princen and his collaborators [3,4]**, the effects of these three factors could be accounted for by scaling the pressures involved in the foam description (e.g. the hydrostatic and osmotic pressures in foams) by the mean capillary pressure of the bubbles, σ/R_{32}, and by a dimensionless function of the bubble volume fraction, $Y(\Phi)$. In following studies, $Y(\Phi)$ was determined by experimental measurements, theoretical modelling or computer simulations [4–9]**. This function was found later to depend on the bubble polydispersity as well — this dependence is moderate to weak for foams with low liquid fraction but becomes significant for foams approaching the bubble unjamming transition [9].

Following similar reasoning, Princen [4,5]** and other researchers after him [10–12] explained several *dynamic* properties of the foams using the so-called 'capillary number', $Ca = \mu\dot{\gamma}R_{32}/\sigma$. This number is a dimensionless measure of the applied viscous stress on the bubbles, $\mu\dot{\gamma}$, scaled with the mean bubble capillary pressure, $P_C = \sigma/R_{32}$; here μ is *viscosity* of the continuous phase and $\dot{\gamma}$ is shear rate. In the theoretical models and data interpretation Ca plays the role of dimensionless shear rate.

Such considerations were very valuable to reveal the general effects of the bubble size and volume fraction, surface tension and solution viscosity on the basic equilibrium and dynamic properties of foams. Furthermore, on this basis, plausible mechanistic explanations and related theoretical models were proposed to describe the observed effects [12,13].

Numerous recent studies, however, revealed that several other properties of the foaming solutions, such as the *surface viscoelasticity*, E_S, *yield stress* of non-Newtonian foaming solutions, τ_0, and *bubble–bubble attraction* in foams (which is also determined by the composition of the foaming solution) could affect very strongly the equilibrium and dynamic properties of the generated foams. These newly revealed effects cannot be captured directly by the approach proposed by Princen [3–5]. On the other hand, they opened novel powerful opportunities for very efficient control of the foam properties

and for pushing them into domains that had been inaccessible until recently. Examples are the ultra-stable foams and the foams with ultra-fine bubbles of micrometre size [14-16**].

The interest to the solutions with highly viscoelastic surfaces was created by the observations that they could provide higher foam stability and smaller bubbles compared with the conventional surfactant solutions [17-20**]. The particular interest to non-Newtonian foaming solutions has sparked in the last years, due to their paramount importance in several applied areas, such as the production and stability of aerated foods [21,22] and in the fabrication of porous ceramic materials via the direct foaming method [23−26].

Therefore, several research groups made systematic efforts in recent years to quantify the role of these additional 'non-Princen' factors. Somewhat unexpectedly, in the course of these studies, several remarkable and nontrivial relations between the various phenomena were revealed. Instructive examples are the relation between the foam volume and bubble size, and the relation between the final foam volume and foam rheological properties, both revealed in Ref. [27**]. Such relations allowed for first time to understand and rationalize some trends observed in the practical applications, e.g. that it is difficult to produce voluminous foams that contain small bubbles by shaking or in mixers.

The major aim of the current review is to summarize our current understanding of these 'non-Princen' factors, and of the recently revealed relations between the properties of the foaming solutions and of the foams generated by these solutions. The focus is (1) on the effects of the various ingredients in the foaming solutions: surfactants, polymers, solid particles and their mixtures used to modify the foam properties and (2) on the mechanisms involved − a consideration that we call 'the physicochemical control' of foam properties.

Electrolytes are not discussed explicitly, although they are other important ingredients used for foam control, because their effects are usually less pronounced (unless they precipitate the surfactant) compared with the other ingredients mentioned above. Due to the limited space we do not consider also the antifoam effect of hydrophobic solid particles, oily drops and their mixtures, although this effect could be very dramatic on both the foaminess and foam stability [28]. Thus, the antifoam entities appear as another efficient tool for physicochemical control of foam properties. For a general overview of the antifoam effects and their explanations, we refer to recent and comprehensive sources [29,30]* and to the literature cited therein.

We do not discuss also protein-stabilized foams because the protein molecules undergo complex transformations after their adsorption on the air−water interface. These transformations include surface denaturing, formation of covalent disulphide bonds or of physical bonds between the adsorbed molecules, etc., spanning characteristic times from fraction of a second up to hours. Therefore, the basic processes and mechanisms discussed below are more obscured in protein-stabilized foams, due to their interplay with the protein transformations, which are rather complex and system specific. Explaining how these mechanisms occur in protein-stabilized foams would require a separate review of similar size.

Figure 1 shows the main processes in foams, discussed below. In the real foams, these 'elementary' processes are often coupled very strongly. Nevertheless, analysing them separately helps to understand the various factors for their control with the mechanisms involved and, on this basis, to explain their relations and combined action.
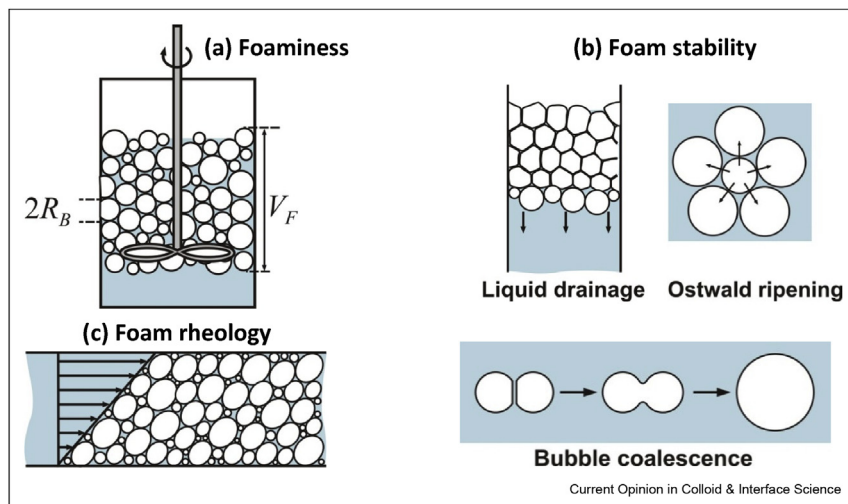
Foaminess − foam volume and bubble size

The classification of the foaming techniques distinguishes between physical, chemical and biological mechanisms [31**]. Below we focus on the most widely used in practice physical methods, which include the step of air entrapment by mechanical agitation or bubbling, using various mixers, Ross−Miles or Bikerman type of tests. We consider below separately the cases of foaming with and without bubble coalescence because the main processes and factors that govern the foam volume and bubble size in these two cases are very different.

(a) *Without bubble coalescence − role of solution viscosity and surface viscoelasticity*

Here we consider the role of solution viscosity and surface viscoelasticity under conditions of suppressed bubble coalescence. This is the case of the so-called 'surfactant-rich' regime in which the surfactant concentration is sufficiently high to provide sufficient coverage of the bubble surfaces and related complete bubble stabilization against coalescence during foaming. Hence, the bubble size does not depend on surfactant concentration in this regime, in contrast to the alternative 'surfactant-poor' regime discussed in section (b).

Systematic study on the effects of the key characteristics of Newtonian foaming solutions (viscosity, dynamic surface tension and dilatational surface modulus) on the foaming in a planetary mixer was presented in Ref. [27**]. Optical observations showed that the two main processes: (1) of air entrapment, which defines the foam growth and (2) of bubble breakup into smaller bubbles, which defines the evolution of the mean bubble size, occur in parallel and both are governed by

Figure 1

Main processes in foams that can be controlled efficiently using appropriate surfactants, polymers, particles and their mixtures: **(a)** Foaminess – foam volume and bubble size; **(b)** Foam stability to liquid drainage, bubble Ostwald ripening and bubble coalescence; and **(c)** Foam rheological properties and bubble size in sheared foams.

the evolving rheological properties of the forming foam. It was shown that the dimensionless foam shear stress, $\tau_F R_{32}/\sigma$, at the shear rate of the foaming process, is the key parameter which controls the air volume fraction and the bubble size in the final foam. For a variety of solution viscosities and surface viscoelasticities, when this dimensionless shear stress reached a critical value of

≈ 0.25 (for the planetary mixer used in Ref. [27**]) the air entrapment was blocked, due to reaching certain sufficiently high foam viscoelasticity above which no waves with large amplitude were formed on the surface of the foamed solution. As a result, the further air entrapment was completely suppressed and the foam volume did not change anymore.

Figure 2
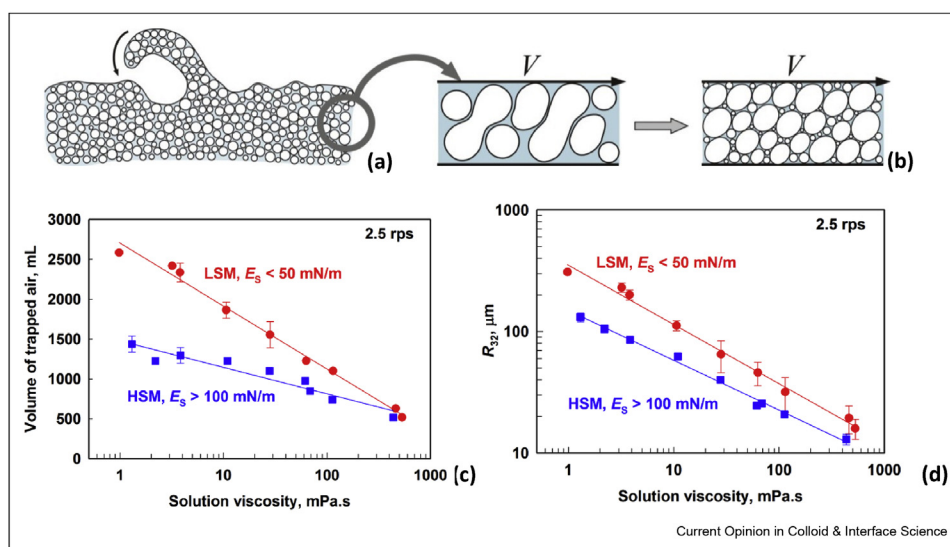
(a,b) Processes occurring during foaming at high surfactant concentration (in the so-called 'surfactant-rich regime' without bubble coalescence) using foaming methods based on mechanical mixing: **(a)** air entrapment via sloshing of surface waves and **(b)** bubble deformation and breakup into smaller bubbles **(c, d)** Effects of the surface modulus, varied using different cosurfactants, and bulk viscosity, adjusted by glycerol addition, of the foaming solution on: **(c)** volume of trapped air and **(d)** final bubble size in foams obtained in a mixer at fixed rotational speed. LSM and HSM abbreviate low surface modulus, E_S < 50 mN/m, and high surface modulus, respectively, E_S > 100 mN/m, solutions [27**].

The experiments performed in Ref. [27**] showed that increasing the solution viscosity and/or the viscoelastic surface modulus, one reaches this critical value at smaller foam volume and with smaller bubbles, under otherwise equivalent conditions; see Figure 2 for illustrative results. The explanation of both effects, of the solution viscosity and of the surface viscoelasticity, is similar. The increase of solution viscosity and/or surface viscoelasticity leads to higher viscous friction inside the sheared foam which, in its turn, leads to more extensive bubble deformation and faster bubble breakup into smaller bubbles at given shear rate [32,33]. The smaller bubbles further increase the foam viscoelasticity, thus suppressing air entrapment at lower foam volume, while facilitating the continuing process of bubble breakup in the agitated foam — the latter effect is additionally discussed in Section 4c.

The authors found [27**] that the effect of solution viscosity is gradual, whereas the effect of surface visco-elasticity is *jump-wise*, with all solutions having $E_S < 50$ mN/m behaving in the same way (negligible surface viscoelasticity), whereas all solutions with $E_S > 100$ mN/m behaved differently (high surface viscoelasticity) but without detecting any dependence on the specific value of the surface modulus, E_S. Similar jump in behaviour was reported before for the foam rheological properties under steady shear and the terms 'low surface modulus' (LSM) and 'high surface modulus' (HSM) regimes were introduced [32]. Similar qualitative differences between the systems of HSMs and LSMs were reported also for the bubble breakup in sheared foams [33].

Note that the parameter, E_S, used in the data interpretation in Ref. [27**], presents the total surface dilational modulus which includes contributions of both the storage (elastic) and loss (viscous) components, and it was measured at relatively low oscillation frequency of 0.2 Hz [27**]. Dedicated experiments showed that such HSMs, measured at low frequency, are related to the formation of condensed adsorption layers on the air–water interface [19,20]**. Such step-wise transition in the foam properties at $E_S > 100$ mN/m clearly indicates a qualitative difference in the bubble dynamics for high and low values of E_S, viz. for bubbles with 'rigid' and 'fluid' interfaces [32] — an effect that has not been clarified theoretically so far. The foams formed from solutions with intermediate values of 50 mN/m $< E_S < 100$ mN/m fell into one of these two regimes, depending on the specific values of the other governing parameters (shear rate, solution viscosity etc.).

An extensive study, aiming to clarify the effects of the molecular structure of wide range of ionic and non-ionic cosurfactants with different head groups, chain-lengths and structures of the hydrophobic tails (linear, branched, double bonded) was presented in Ref. [34].

Mixtures of two main surfactants, sodium lauryl ether sulfate and cocamidopropyl betaine — the workhorses of most current personal care formulations, with fatty acids, fatty alcohols or fragrance molecules as cosurfactants were studied [34]. The results revealed that an optimal chain-length of 8–10 carbon atoms in the cosurfactant molecules reduces significantly the dynamic surface tension at the relevant for foaming time scale (e.g. around 100 ms in Bartsch foaming test) and, thus, enhances the rate of foaming of the mixed surfactant solutions. Unexpectedly, these cosurfactants were found to increase by many orders of magnitude the viscoelasticity of the concentrated solutions of the same surfactant + cosurfactant mixtures. The explanation of these two effects (lower dynamic surface tension of the foaming solutions and higher viscoelasticity of their concentrates) was found to be similar: the medium-chain cosurfactants disturb the packing of the main surfactant molecules with longer chains in the micelles, thus increasing the demicellization rate at low surfactant concentrations and elongating the micelles into long threads at high concentrations. A hierarchy in the parameters of the cosurfactant molecules was found to govern these effects: most important is the head-group charge, then the chain-length and, finally, the presence of branching and double bonds in the hydrophobic tails [34].

Thus, two very different roles of the fatty acids and fatty alcohols as cosurfactants have emerged: (1) those with longer chain length, C14–C16 increase the surface viscoelasticity by creating condensed mixed adsorption layers with the main surfactants, while (2) the medium-chain cosurfactants with C8–C10 (including many fragrance molecules) are incorporated in mixed micelles and modify their properties, Figure 3 [20,34]**. In both cases ca. 5–10% of cosurfactant with respect to total surfactant concentration is sufficient to induce these effects.

In [27,34]** the lower dynamic surface tension was found to accelerate the foam formation in the initial stages of the foaming process, with much smaller effect on the final foam volume and bubble size at the end of the foaming process. Considering the mechanistic explanations of all effects reported above, one could expect that they are general for the mechanical type of foam generators (mixers, agitators and Ross–Miles type of devices).

The foaming of a Newtonian fluids leads to the formation of foams with highly non-Newtonian viscoelastoplastic behaviour. These specific rheological properties of the foams were successfully used to damp the sloshing waves on the surface of Newtonian fluids with important practical implications, e.g. during liquid transport in closed containers [35,36]. The authors showed experimentally that the presence of thin layer of foam on top of the sloshing fluid dramatically damps the surface waves. The mechanism of this effect was

Figure 3
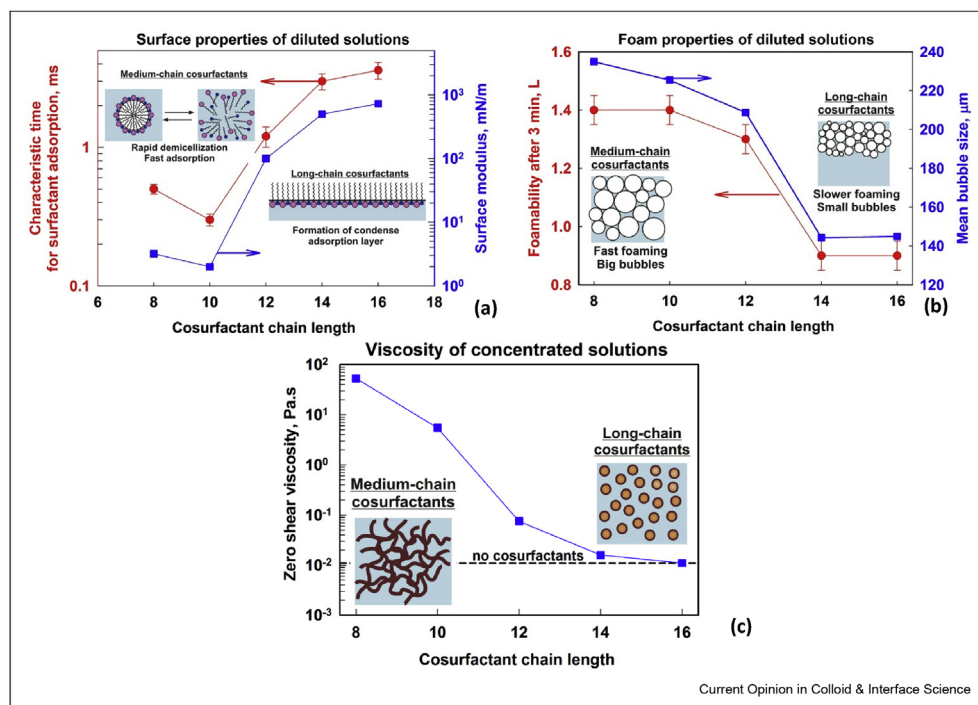
Illustrative results for the main effects of fatty acids as cosurfactants on: **(a)** Characteristic time of surfactant adsorption and on dilatational surface modulus of 0.5 wt% surfactant solutions; **(b)** Foam volume and bubble size during foaming in a planetary mixer of the same solutions; and **(c)** Zero-shear viscosity of 10 wt% concentrated surfactant solutions. The arrows in **(a)** and **(b)** are placed at the level of the respective quantity for the reference solution of the main surfactants with C12 tails, without cosurfactant. The main effect of the medium-chain cosurfactants, C6 to C10, is to disturb the micelles and to decrease the time for demicellization, reduce dynamic surface tension and enhance foaminess at low surfactant concentrations. **(c)** At higher surfactant concentration, the same C6 to C10 cosurfactants lead to the formation of worm-like micelles with strong increase of viscosity and possible gelling of the solutions. In the presence of longer-chain cosurfactants, C12 to C18, spherical or ellipsoidal micelles are formed and the solution viscosity is in the orders of lower magnitude. On the other hand, the cosurfactants with C12 to C18 create mixed condensed adsorption layers, which are highly viscoelastic, $E_S > 100$ mN/m, thus reducing the foam volume and bubble size. In all solutions the cosurfactant concentration is by 10 times lower than the concentration of the main surfactants. Figures are adapted from Ref. [34**].

clarified and described theoretically, and it is also related to the rheological properties of the foams and the friction of the foam with the container walls [35,36]. In fact, this is a very similar mechanism to the one which blocks the air entrapment in the mechanical foaming devices [27**]. Possible effect of surface viscoelasticity was mentioned in Ref. [36] but was not studied.

The yield stress and the consistency of non-Newtonian foaming solutions are reported to affect strongly the foaminess and foam stability to drainage and coarsening. However, the increase of solution yield stress and consistency to gain stability usually leads to significant decline in foamability, as explained above for Newtonian solutions and as shown in [24,25]* for non-Newtonian suspensions of particles and surfactants. The high surface viscoelasticity also suppresses strongly the foaming of such non-Newtonian suspensions — the particle adsorption layers in Pickering (particle-stabilized) foams exhibit very high surface viscoelasticity and enhance the long-term foam stability but reduce strongly the

foaminess of the respective suspensions [25]. Therefore, a compromise should be often made in the efforts to ensure both high foaminess and high foam stability in practical applications.

We do not discuss in this subsection the foaming via bubbling because the foam volume and bubble size in the systems without bubble coalescence are determined mostly by the flux of air and the size of the pores used for its incorporation. Thus, foaming can be controlled by these two factors, which are not 'physicochemical' in the sense used in the current review.

(b) *With bubble coalescence — type of surfactant and synergistic effects*.

Here we consider the foamability under conditions of significant coalescence between the bubbles during the foaming process. This bubble coalescence occurs at low surfactant concentration, which does not ensure

stabilization of the newly formed bubbles by sufficiently dense adsorption layers. As a result, the foam volume, bubble size and the other foam properties depend strongly on surfactant concentration, under otherwise equivalent conditions.

If foaming involves bubble coalescence, e.g. due to low surfactant concentration, the overall foam volume and bubble size result from the complex interplay of four processes, which occur simultaneously: bubble formation (air entrapment), bubble—atmosphere coalescence (air release from foam), bubble breakup into smaller bubbles and bubble—bubble coalescence with increase of bubble size. Two qualitatively different types of foaming should be distinguished in this context — via bubbling (relevant to froth flotation) and via mechanical agitation (most other applications).

Bubbling introduces new bubbles into the liquid phase, which float due to buoyancy, and form a foam layer, which usually starts decaying from the top. The models for the volume and stability of such foams analyse the balance of the newly generated and collapsed bubbles, as well as the balance between the hydrostatic pressure, which squeezes the liquid in the foam films, and the disjoining pressure, which stabilizes these films. The critical capillary pressure for foam film rupture was proposed as a predictor for foam stability in this case [37].

Comprehensive study was recently reported about the main surface characteristics, which control the foamability in the more complex case of mechanical agitation (Bartsch test) of surfactant solutions at low concentrations [38**]. Novel approach for description of the dynamic adsorption layers, formed during foaming, was proposed to explain the measured foam volumes. Briefly, combining dynamic surface tension data with the equilibrium surface tension isotherm for a given surfactant, the authors determined the main characteristics of the dynamic adsorption layers formed on the bubble surfaces during foaming (e.g. the transient surfactant adsorption and the related surface coverage and surface elasticity). In this way, the outcome of foaming could be related to the properties of the dynamic adsorption layers, which govern the bubble properties in foaming solution [38**].

Two master curves were observed for the ionic and non-ionic surfactants, respectively, when the foamability was plotted versus surface coverage, surface mobility or surface elasticity of dynamic adsorption layers, Figure 4 [38**]. These two master curves reflect the important role of the electrostatic repulsion, which stabilizes the foam films even at relatively low surface coverage with ionic surfactants. In contrast, surface coverage of >90% is required to stabilize the dynamic foam films for non-ionic surfactants. In addition, a very important role of the surface mobility emerged from the performed

analysis — the low surface mobility decelerates the foam film thinning, thus increasing significantly the time available for surfactant adsorption before the films thin down to their critical thickness for rupture [38**]. Thus, the surface mobility, related also to the surface elasticity, appears as a key factor for stabilization of the dynamic foam films during foaming. The observed effects closely resemble, as trends and mechanistic explanations, similar effects reported for emulsions [39].

Very often a combination of main surfactants with co-surfactants, polymers or particles is used, and *synergistic interactions* of the components are searched to increase foaminess and to obtain foams with high stability and other desired properties. The main synergistic effects in such mixtures are briefly discussed below.

The synergistic effect in the case of *surfactant mixtures* is sometimes evaluated by comparing their critical micellization concentrations (CMCs) to those of the individual surfactants and a proper mixing ratio was reported to be among the key factors [40]. In the so-called 'catanionic' mixtures (anionic + cationic surfactants) self-assembled molecular aggregates, such as vesicles and/or elongated micelles, increase the solution viscosity and thus decrease foamability, while increasing very significantly the respective foam stability, see Section 3 [18,34,41]*.

In [42] *n*-octanol with eight carbon atoms was found to act as a foamability enhancer for C_nTAB-stabilized foam at low surfactant concentrations. The authors introduced the critical synergistic concentration as a limiting parameter for the occurrence of the synergistic effect between C_nTAB and *n*-octanol [42]. This synergy allowed the use of reduced surfactant concentrations to obtain transient foams with larger volumes [42].

For *surfactant—polymer mixtures*, the two key processes that determine the final outcome of the foaming process are the formation of complexes between the surfactant and polymers molecules (1) in the bulk solution and (2) on the solution surface, respectively. Until recently, the explanations for the surfactant—polymer interactions and complex formation were based mostly on the electrostatic interactions between oppositely charged surfactant and polymer molecules.

Recent studies, however, clarified that the presence of opposite charges is not a necessary condition for boosting the foaminess and foam stability in surfactant + polymer mixtures [43**]. Strong synergy was reported for a series of weakly interacting mixtures: anionic surfactant + non-ionic polymer, cationic surfactant + cationic polymer and cationic surfactant + non-ionic polymer. This unexpected synergy was explained with the fast surfactant adsorption (which facilitates foaming and decelerates the foam film

Figure 4
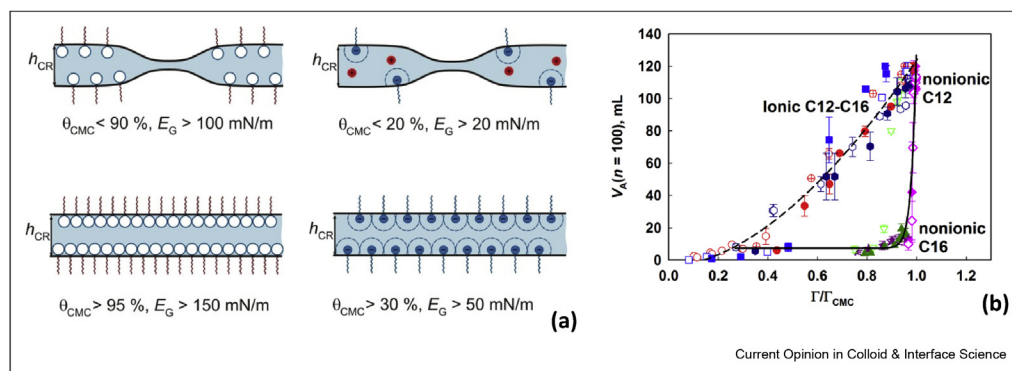
(a) Schematic presentation of the major difference between the conditions for stabilization of the dynamic foam films during foaming for non-ionic and ionic surfactants. For non-ionic surfactants, the dynamic layers should be almost complete, $\theta > 95\%$, whereas for ionic surfactants moderately populated layers with $\theta > 30\%$ are sufficient to stabilize the dynamic foam films; **(b)** Illustrative experimental results showing the correlation between the foam volume after Bartsch test and the surface coverage of the dynamic adsorption layers (related also to the mobility of the surfaces of dynamic foam films); adapted from Ref. [38**].

thinning) and the strong steric repulsion by the surface-active surfactant + polymer complex, formed in the static foams [43**]. In contrast, the mixture of strongly interacting anionic surfactant sodium dodecylsulfate (SDS) and cationic polymer polyvinylamine (PVAm) showed a significant decrease in foaming, which was explained with the decreased concentration of free SDS monomers, due to their binding to the polymer chains in the bulk solution. On the other hand, increased foam stability was measured for the same mixture (compared with the SDS solutions without polymer), explained with the formation of dense surfactant + polymer layers on the solution surface [43**]. These non-trivial effects in the mixtures of anionic surfactant + cationic polymer were further investigated to clarify the role of the surfactant head-group [44].

Surfactant + particle mixtures are usually characterized with reduced foaminess (smaller volume of the foam formed) due to the higher viscosity and higher surface viscoelasticity of the particulate suspensions, while the increase in foam stability could be very significant, see Section 3. The formed foam bubbles could be very small on foaming of viscous particulate suspensions, if the bubble coalescence is suppressed [23,24]*. Proper hydrophobization of the particles could be ensured by chemical grafting or *in situ* by surfactant adsorption. Such particles adsorb irreversibly on the water–air interface and provide efficient capillary stabilization of the bubbles if the particle adsorption layer is sufficiently dense. In this mechanism, strong synergistic effects are often observed in well-selected surfactant + particle mixtures [24,45]*. The higher particle surface coverage and inter-particle connectivity on the foam bubbles are suggested as key factors for high foamability and foam stability [45]. The morphology of the used particles is also

reported to be important for the overall foaming performance of the surfactant + particle mixtures [46].

Foam stability
The main foam destabilization processes include liquid drainage, bubble Ostwald ripening (called also 'bubble coarsening') and bubble coalescence with other bubbles or with atmosphere. In real foams, these processes are usually strongly interrelated, which requires more complex approach in foam design, covering the properties of both surface layers and continuous phase, Figure 5. Therefore, the composition of the foaming solution should include ingredients, which interact on the bubble surface and/or in the bulk to ensure foam stability with respect to each of the possible destabilization mechanisms.

The main approaches for the formation of very stable and ultra-stable foams were reviewed recently by Rio et al. [16**], including the approaches for retarding or even suppressing liquid drainage, bubble coalescence and bubble coarsening. A comprehensive review of the microscale processes in aqueous foams was presented by Anazadehsayed et al. [47*] who analysed the role of the various foam elements: interior Plateau borders, exterior Plateau borders, nodes and foam films. The effect of oil droplets and particles on the main foam properties, such as liquid drainage, foam stability and interfacial mobility is also discussed in Ref. [47*].

(a) *Stability to water drainage*.

The liquid drainage occurs mainly along the Plateau channels and nodes inside the foam structure, driven by gravity and opposed by the suction capillary pressure of

Figure 5

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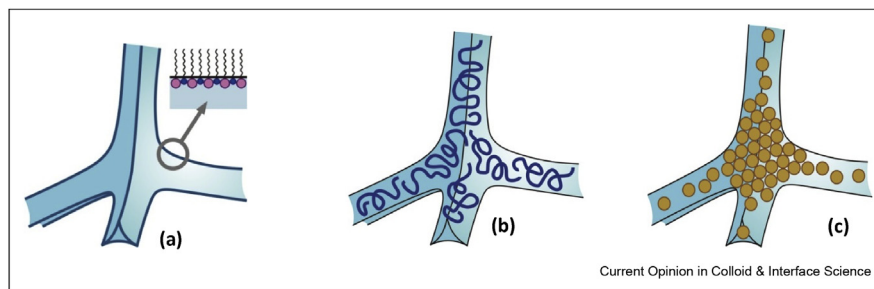
Schematic presentation of the three main mechanisms used for slowing down the foam drainage: **(a)** formation of viscoelastic surface layer on the bubbles surfaces, **(b)** addition of solutes, e.g. polymer molecules, which increase the apparent viscosity of the bulk solution and **(c)** trapping of particles or oil drops in the Plateau borders and nodes. The creation of sufficiently high yield stress of the interstitial fluid in **(b)** and **(c)** can block the liquid drainage completely.

these channels. Several types of factors and their combinations were found useful in controlling liquid drainage, as explained below (Figure 5).

- Interfacial viscoelasticity

Two drainage regimes were identified in the drainage experiments, depending on where the main hydrodynamic resistance and energy dissipation occur − in the Plateau channels or in the nodes, see the recent review in Ref. [48**]. The first regime is realized for 'rigid' liquid−gas interfaces, whereas the second one − for mobile interfaces. The characteristic time for foam drainage in these two regimes could be expressed as follows [49]:

$$t_{DR} \approx H_F \mu / K_m \rho g R_B^2 \Phi_L^m \quad m = 1 \text{ or } 1/2 \tag{1}$$

Here H_F is foam height, μ is viscosity, ρ is mass density of the continuous phase, g is gravity acceleration, R_B is bubble size and $\Phi_L = (1\text{-}\Phi)$ is liquid volume fraction. The dimensionless constants are $m = 1$ and $K_m \equiv K_1 \approx 6 \times 10^{-3}$ for immobile (rigid) interfaces, while $m = 1/2$ and $K_m \equiv K_{1/2} \approx 2 \times 10^{-3}$ for mobile interfaces. The drainage from foams with rigid interfaces is slower compared with foams with mobile interfaces, under otherwise equivalent conditions, due to the higher hydrodynamic resistance in the respective channels.

The role of interfacial mobility in foam drainage was recently reviewed by Cohen-Addad et al. [48**] with focus on the link between the processes at micro- and macroscales. Below certain interfacial mobility, the channel's resistance overwhelms the node's resistance, resulting in a switch from node-dominated to channel-dominated regime. This transition, however, depends on the bubble size [50,51]. Gauchet et al. [52] studied experimentally the transition between these two

regimes in foams characterized with different non-Newtonian surface rheological properties. The authors explained the observed transitions with the surface shear viscosity and its shear thinning, while the surface tension gradients (Marangoni effects) could not explain the experimental results [52].

The addition of long-chain fatty acids or fatty alcohols as cosurfactants and the subsequent formation of mixed adsorption layers with high surface viscoelasticity was shown to decelerate strongly the foam drainage [17,53]. Wei et al. [54] demonstrated increased foam stability to drainage (and also to bubble coarsening and coalescence) of alkyl polyglucoside−stabilized foams in the presence of isoamyl alcohol as cosurfactant. These authors introduced the so-called 'drainage composite index' and attributed the stabilization capacity of the added cosurfactant to increased surface viscoelasticity, along with the effects of reduced surface tension, formation of H-bonds and additional repulsive disjoining pressure [54]. Similar stabilization effects were seen in the presence of crude oil [54].

UV stimuli-responsive surfactants were proposed for light control of foam stability. Chevallier et al. [55]* studied trans and cis forms of azobenzene-based photo-surfactants to compare the drainage in the Plateau channels and in the foam films. The authors found that in both geometries the drainage can be slowed down using light induced gradients of the surface tensions (Marangoni effects). Light illumination can induce local variations of the capillary pressure and, hence, vertical modulation of the drainage velocity [55]*.

- Bulk viscosity of the foamed solutions

The addition of polymers is often used to increase bulk viscosity and to decelerate foam drainage, cf. Eq. (1). For example, Bureiko et al. [56] studied foams containing commercial polymers and concluded that the drainage kinetics in these foams was determined by the bulk

viscosity rather than by surface viscoelasticity. Slower drainage was attributed to higher viscosity and yield stress of foamed solutions containing surfactant aggregated in lamellar L_α phase, compared with the lower stability in the case of the less viscous L3 phase [57].

Safouane et al. [58] studied the drainage of foams made from Newtonian and non-Newtonian polymer-containing solutions with different rheological properties and noted that a transition in the drainage regime occurs as the bulk viscosity is increased, illustrating a coupling between the surface and bulk flow in the Plateau channels. They reported that foams prepared from solutions of long flexible polyethylene oxide (PEO) molecules counter-intuitively drain faster than foams made from Newtonian solutions of the same viscosity. The latter result was explained with the specific rheological properties of PEO solutions on elongation deformations in the channel network in foams.

Ferreira et al. [41]* investigated the interplay between the self-aggregation and foam properties of the catanionic surfactant mixture cetyltrimethylammonium bromide (CTAB) + sodium octyl sulfonate. They found that the foam stability is strongly affected by the molar fraction of CTAB in the mixture — an effect explained by the various types of aggregates formed at different ratios of these surfactants (micelles or vesicles). The authors concluded that the foam drainage in their systems was controlled mostly by the presence of elongated micelles, which increased solution viscosity, whereas the bubble coarsening was affected by dense adsorption layers at the gas—liquid interface [41]*.

- Structuring and creation of yield stress of the foamed solutions

Significant deceleration of drainage and even its complete arrest could be pursued by creating moderate yield stress in the foam structural elements, e.g. via confining and jamming various entities (particles, oil drops, polymer—surfactant aggregates, precipitates).

Several studies analysed the effect of the solution yield stress on the foam drainage. Lesov et al. [24,25]* adapted to foams the theory of permeation of yield-stress fluid through porous medium [59] and reached the conclusion that the liquid drainage would stop when the fluid yield stress, τ_{Y0}, exceeds a critical value:

$$\tau_{Y0} > \tau_D \approx 2\rho g R_{32} \qquad (2)$$

where τ_D is the stress to be overcome by the yield stress fluid. This prediction was verified experimentally with foams prepared from concentrated silica suspensions, in the presence of surfactants that hydrophobize the particle surface and, thus, allow one to vary the yield stress of the suspensions in wide range [24,25]*.

Non-trivial sequence of blocking and re-starting of the foam drainage was observed with foams stabilized by SDS and clay particles (laponite) [60]*. This complex foam evolution was explained with the coupled processes of liquid drainage and bubble coarsening in the foams studied. The initial drainage stopped when the clay particles jammed the confined fluid. However, with the slow increase of the bubble size due to Ostwald ripening, the yield stress of the used laponite suspension fell below the critical value needed to stop drainage in the foam with increased bubbles, cf. Eq. (2), and the liquid drainage re-started.

The role of particle size in the collective particle jamming in Plateau channels was analysed by Haffner et al. [61]*. For spherical particles, the jamming transition occurs at rather high particle volume fraction and is very sensitive to particle size. To account for this effect, geometrical confinement parameter, λ, was introduced, which compares the particle size to the size of the constrictions in the foam channels [62]. Effective confinement parameter, λ_{eff}, was introduced in Ref. [63] to generalize the theory by accounting for the effect of particle hydrophobicity on liquid drainage.

Besides particle—surfactant mixtures, other compositions were suggested in literature to create yield-stress foaming fluids. For example, glycyrrhizic acid (GA) was shown to form ultra-stable, thermosensitive 'superfoam' via the self-assembly of supramolecular GA nanofibrils at the air—water interface and in the continuous phase [64]**. The rapid adsorption of the GA nanofibrils on the bubble surface, forming a multilayer interfacial network, combined with the build-up of a viscoelastic fibrillar network in the continuous phase, resulted in foams, which remained stable for months and years without drainage [64]**. Melting of the fibrillar network by mild heating led to loss of foam stability, due to reversible gel—sol transition of the supramolecular GA network [64]**.

The catanionic vesicles of CTAC + myristic acid also form a gel-like phase and slow down foam drainage [18]*. The vesicles act as stable elastic micro-spheres, which jam the Plateau channels and nodes at sufficiently high concentration [18]*. Crystals of precipitated SDS in the presence of salts were also shown to decelerate drainage via blocking the Plateau channels, thus leading to ultra-stable and temperature-responsive foams [65].

Blocking the Plateau channels and increasing foam stability, while preserving very good foamability, was reported for solutions containing multilamellar tubes, formed from 12 hydroxy stearic acid and ethanolamine or hexanolamine [66]*.

The oil drops could also act as stabilizing agents against drainage, if densely packed and jammed in the Plateau

channels [67*]. Oil drop accumulation increases the local viscosity and slows down channel shrinking and the foam film thinning. In these systems the drainage process could be arrested as in the case of foamed suspensions [60,67]*. While the yield stress of the interstitial fluid stabilizes the foam at rest, rapid drainage could be induced by foam shear [68]. These effects were explained by considering the shear-induced flow of interstitial material in the transient foam films and its coupling with the flow in the foam channels [68].

(b) *Stability to bubble Ostwald ripening*.

Bubble Ostwald ripening (bubble coarsening) changes the bubble size distribution in foams via molecular gas transfer across the foam films from the smaller to the bigger bubbles. While the average bubble size steadily increases, the process occurs through subtle local events in which the bubbles smaller than the mean surface-length radius, R_{21}, diminish with time while the bigger bubbles grow [69].

A review of the coarsening process in foams containing various surfactants and gases was presented by Briceño-Ahumada and Langevin [70]. The crucial physico-chemical parameters that can be used to control this process are highlighted, with a special account for the effects of the local liquid fraction in the foam and of the foam film permeability, which depends on the used surfactant. As explained in Ref. [70], Ostwald ripening and foam drainage are strongly coupled because the rate of Ostwald ripening is approximately proportional to the area of the foam films between the neighbouring bubbles (which increases with drainage). On the other hand, foam drainage is faster for bigger bubbles and, thus, the bubble ripening enhances drainage [51,71]*.

We note that, due to geometrical constraints, bubbles in foams are compressed against each other, forming thin foam films across which the most intensive gas transfer occurs. Hence, the gas permeability across these foam films is considered in the detailed models of bubble Ostwald ripening in foams. This specific mode of gas transfer leads to different time dependence of the mean bubble size, compared with the classical Ostwald ripening in diluted dispersions, containing separated entities [71]*.

The driving force of the bubble Ostwald ripening in foams is the difference in the chemical potentials of the gases captured in different bubbles. For bubbles containing single gas, this chemical potential increases with the bubble capillary pressure, which is inversely proportional to bubble size. The rate of ripening increases also with the gas solubility and gas diffusivity in the continuous phase. For a single gas in the foam (or for mixture of gases with similar solubility and diffusivity which is the case of atmospheric oxygen and nitrogen in water), the above factors are captured well by the

following expression for the flux of gas molecules across the foam film separating two neighbouring bubbles (proposed years ago by Princen and Mason [72]):

$$J_{ij} = \frac{dn_{ij}}{dt} \approx \frac{A_{ij} H D}{k_B T} \left(\frac{\sigma_i}{R_i} - \frac{\sigma_j}{R_j} \right) \bigg/ (h + 2D / K_{al}) \qquad (3)$$

Here J_{ij} is gas flux across the foam film separating two bubbles in the foam (denoted as bubbles i and j, respectively) per unit time, A_{ij} is the area and h is the thickness of this foam film, H is gas solubility and D is gas diffusion coefficient in the continuous medium, $k_B T$ is thermal energy, $\sigma_{i,j}$ and $R_{i,j}$ are surface tensions and radii of the contacting bubbles (in the general case the surface tensions of the shrinking and expanding bubbles could be very different), and K_{al} is the gas permeability of the surfactant adsorption layer.

Based on the above concepts, several physicochemical approaches have been proposed in literature to slow down Ostwald ripening in foams, Figure 6. One approach is to introduce ingredients (e.g. glycerol) in the continuous phase, which reduces the gas solubility and diffusivity in the aqueous core of the foam films [73]*. Another approach is to use appropriate surfactants or cosurfactants, which form compact (dense) adsorption layer, thus reducing the gas permeability of these layers and creating surface elasticity [73]*. Increase of the foam film thickness using appropriate polymer layers or solid particles also reduces the bubble Ostwald ripening significantly [18,73–79]*. Complete arrest of Oswald ripening could be achieved by forming an irreversibly adsorbed layer of solid particles on bubbles surfaces (bubble armouring) [25,80] or by building a yield stress/ elasticity in the continuous phase [24,25]*. Completely different, but also very efficient, approach is the use of gas mixture, which contains a fraction of poorly soluble gas [81]*. In these systems, the ripening leads to accumulation of the poorly soluble gas in the shrinking bubbles and dilution of this gas in the expanding bubbles. The 'osmotic' pressure created by this difference in the concentration of the poorly soluble gas counteracts the Laplace pressure difference between bubbles, thus decelerating significantly the Ostwald ripening [81]*.
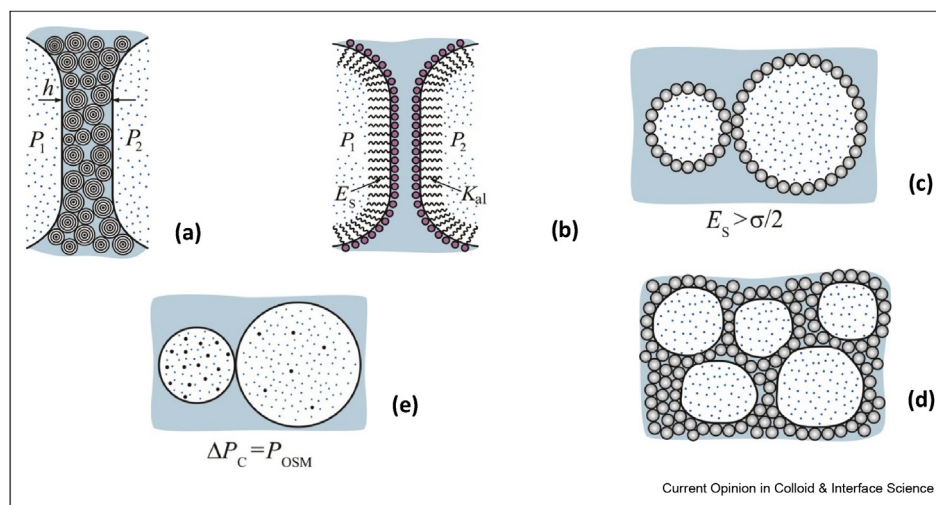
Examples of these approaches are briefly presented below with the basic ideas for their theoretical description.

- *Surface elasticity and reduced gas permeability of surfactant adsorption layers*

The effect of surface elasticity was described in [18,75] * using the Gibbs stability criterion, $E_S > \sigma/2$, where E_S

Figure 6

Schematic presentation of the main mechanisms used to slow down the bubble Ostwald ripening in foams: **(a)** formation of thicker foam films by trapping dispersed entities, **(b)** formation of highly viscoelastic layers on the bubbles surface, which reduces the gas permeability across the foam film and increases surface elasticity, **(c)** assembly of armouring coat of irreversibly adsorbed jammed particles on the bubble surface, thus creating a mechanical resistance to bubble shrinkage; **(d)** creation of yield stress in the bulk fluid; **(e)** use of gas mixture in foaming with at least one of the gases being of low solubility in the continuous phase, thus creating osmotic pressure between the shrinking and expanding bubbles, which opposes the difference in their capillary pressures.

is the dilatational viscoelasticity and σ is the dynamic surface tension in the time scale of the bubble ripening, typically minutes to hours. Extending this approach, Salonen et al. [82] modelled their experimental results about the evolution of two neighbouring bubbles with surface elasticity and analysed the relationship between the initial sizes of the bubbles, initial surface tension, surface elasticity and the conditions for mechanical equilibrium. On this basis, a modified and more complex Gibbs criterion was introduced [82].

Increase of surface viscoelasticity was achieved experimentally by adding long-chain cosurfactants like fatty acids or alcohols, or using large well-packing molecules in the adsorption layers, such as some triterpenoid saponins [73,75−77]*. One should note, however, that the formation of viscoelastic adsorption layers reduces also the gas permeability across these layers [73]*. From practical viewpoint, these are all beneficial effects. However, from scientific viewpoint, one needs an in-depth analysis to decouple the effects of surface elasticity from the effects of reduced gas permeability and, thus, to reveal the actual reasons for the reduced rate of Ostwald ripening in foams stabilized by low-molecular-mass surfactants.

For this purpose, a detailed theoretical model was developed in [73,77]*, combining Eq. (3) with an approach, developed by Lemlich [69] to account for the various gas fluxes between the bubbles. This model defines a series of differential equations, which

describe explicitly the time evolution of the bubble size distribution in coarsening foam, starting from a given initial distribution and accounting for all effects incorporated in Eq. (3). Other theoretical approaches to describe Ostwald ripening are briefly summarized in Refs. [70].

Using this theoretical model, it was shown in Ref. [73]* that the Ostwald ripening was controlled by reduced gas permeability through the condensed adsorption layers in the foams containing long-chain fatty acids and fatty alcohols as cosurfactants. The effect of surface elasticity turned out to be negligible in these systems because the surface deformation is very slow and, hence, the adsorption layers relax by surfactant adsorption and desorption, leading to negligible surface elasticity at the characteristic long time-scale of minutes and hours. The same theoretical approach, however, showed that the adsorption layers of triterpenoid saponins are much more efficient in suppressing Ostwald ripening because they create substantial surface elasticity even at very low rates of surface deformation − the saponin molecules are bigger and their desorption from the bubble surfaces is suppressed by strong intermolecular attraction inside the adsorption layer [77,83]*.

Investigation of the shear rheological properties of the adsorption layers at the surface of the dispersion containing CTAC and myristic acid mixtures was performed by Arriaga et al. [74]. Liquid-condensed domains in liquid-expanded layer were observed.

Sequential layers of vesicles were jammed next to the adsorption layer, yielding a very thick surface layers, which stabilized the foams against coarsening and coalescence [74]. Melting temperature was reported above which the surface layers became fluid and the foam stability decreased [74]. Similar conclusions were reached by Varade et al. [18]* who emphasized the strong synergy between the viscoelastic surfactant layers and the presence of vesicles in the bulk solution. In a separate study, viscoelastic aqueous phase containing entangled worm-like micelles was shown to preserve the foam films thicker and, thus, to decelerate the Oswald ripening in foams even at high bubble fraction [78].

The role of H-bond formation between the head groups of the adsorbed surfactant molecules was speculated to create short-range attraction, which could increase the rigidity and the elasticity of the surfactant adsorption layers and, thus, to enhance the foam stability against coarsening and coalescence [84]. Indeed, H-bonds were found to play very important role for the high viscoelasticity of adsorption layers of triterpenoid saponins, but only in combination with several other important effects, such as the rigid hydrophobic scaffold of the saponin molecules and strong dipole—dipole interactions which jam the adsorption layers, reinforce the molecular packing and suppress molecular desorption, thus maintaining high surface elasticity even at very slow surface deformations [77,85]*. The combination of all these effects reduces the bubble Ostwald ripening in saponin-stabilized foams by several orders of magnitude, compared with the other low-molecular-mass surfactants. Therefore, the role of hydrogen bonding in adsorption layers of various types of surfactants deserve further systematic studies with dedicated experiments.

- *Particle-armoured bubble surfaces and yield-stress bulk fluids*

The relation between foam coarsening and bubble shrinkage in the presence of mixture of silica nanoparticles and oppositely charged surfactant was investigated by Maestro et al. [76]*. The authors showed that the particles jam on the surface of the bubbles upon bubble shrinkage, followed by interfacial buckling on further compression of the surfaces. The particle adsorption at which jamming and buckling occur was independent of surfactant concentration, suggesting that the main role of surfactant was to assist particle adsorption, without affecting noticeably the rheological properties of particle adsorption layer. The authors discussed also that the surface of the growing bubbles could be insufficiently covered and protected by particles. Therefore, coalescence first occurred between the bigger bubbles in the foam and later between these bubbles and the surrounding air. As a result, only the smaller bubbles survived the aging process in their system. The authors suggested that such two-step

scenario, including (1) foam coarsening via growing and coalescence of the bigger bubbles and (2) seized coarsening of the armoured smaller bubbles could be relevant to emulsions as well [76]*.

Beltramo et al. [86]* also presented a strategy to arrest the dissolution of particle-coated bubbles in water, controlling the interfacial particle interactions. The authors showed that a percolated network of particles with a sufficiently high yield stress on the bubble surface could stop the bubble dissolution. Thus, foam and emulsion materials could be created with stable microstructures and controllable textures [86]*.

Mixtures of cationic and zwitterionic surfactants, sometimes in combination with nanoparticles were shown to form viscoelastic particle-micelle network in the Plateau channels and/or in the foam films [78,79]. The role of surfactant aggregates and particles in these mechanisms for decelerating Ostwald ripening was verified by cryo-SEM images [79].

The presence of solid particles or liquid drops in the continuous phase can change significantly its rheological properties. The bulk elasticity or yield stress of a viscoelastic medium could also lead to complete arrest of the bubble Oswald ripening if they are sufficiently large [24,25]*. Both the suspension yield stress and suspension elasticity are governed by the particle—particle attraction and, therefore, they could be finely tuned by selecting the surfactant type and concentration in the particle suspension [25].

To quantify the effect of yield-stress fluids on Ostwald ripening, two quantities were suggested in the literature. Lesov et al. [24,25]* proposed that the Ostwald ripening would be arrested when the yield stress of the fluid phase, τ_{Y0}, is higher than the mean capillary pressure, $P_C = \sigma/R_{32}$, of the bubbles, viz. $\tau_{Y0} > \sigma/R_{32}$. Alternatively, the bulk elasticity of the surrounding medium was proposed in Ref. [87] to be compared with P_C. The rationale behind the latter suggestion is that any small change of the bubble size in a viscoelastic medium would require deformation of this medium. It is rather possible that these two estimates, which differ by a factor of ≈ 10, might account for different aspects of the bubble coarsening process. Small changes in the bubble size would, indeed, require small elastic deformations of the surrounding. However, the real foams usually contain bubbles of many different sizes. Although the bigger bubbles may be arrested by moderate viscoelasticity of the medium, the smaller bubbles with higher capillary pressure can shrink, thus creating large, non-linear local deformations and related capillary stresses in the foam. The yield stress of the fluid in the Plateau channels seems to be more relevant quantity to oppose the capillary stresses appearing in such non-linear deformations.

(c) *Stability to bubble coalescence.*

The coalescence is the least understood among the various destabilization processes in foams. It is realized via rupture of the foam films between neighbouring bubbles. The various effects discussed in the literature in relation to film stability could be grouped around the following types of factors: (1) surface forces including the possible gelling of the foam films [88], (2) surface elasticity [89] and (3) perturbation of surfactant layers and of (brittle) adsorption layers of particles or proteins on foam shear, which could induce forced bubble coalescence [90], Figure 7.

Recently, Langevin [91]** presented a comprehensive review on the coalescence in foams and emulsions. The close similarities between these two types of systems along with some subtle differences were outlined. Different contributions to the coalescence events were discussed, including the role of hydrodynamic forces, surface rheology, surface forces and thermal fluctuations in the thin foam or emulsion films. The role of the surfactant type and concentration are analysed, and the main coalescence scenarios are discussed.

Below we briefly summarize the main conclusions of several recent studies, which propose new mechanistic insights and make a link with the physicochemical approaches to stabilize foams and foam films.

Biance et al. [92] studied the dynamic effects appearing when the bubbles in foams undergo rearrangements (so-called 'T1 events'). Bubble coalescence was observed when the bubbles were subject to T1 events, and the liquid fraction in the foam was below a given critical value. This result was attributed to the observed dynamic thickening of the freshly formed foam films, which appear after each T1 event. According to the authors, if no sufficient liquid is present to ensure this film thickening, the dynamic foam films are destabilized

and the neighbouring bubbles coalesce. Two mechanisms were reported for the formation of new films after bubble rearrangement, depending on the rheological properties of the liquid and on surface viscoelasticity [93]. In a following study, Briceno-Ahumada et al. [94] proposed that, for very small bubbles, the newly formed films after T1 events could thin very rapidly and rupture before their surfaces are covered and protected by surfactants.

The coalescence in foams is often modelled by experiments with single-foam films. The main results from these studies are summarized in a recent review [95]. The contribution of the DLVO and non-DLVO forces is discussed, and the role of surfactant concentration is explained in terms of the critical concentration, C_{bl}, at which black spots start to occur in the foam films before their rupture. The latter parameter was introduced by Sheludko and Exerowa years ago [96], and it separates two regions with different film rupture mechanisms. At lower surfactant concentrations, the film lifetime is governed by the hydrodynamics of film thinning down to the critical thickness of film rupture, whereas at higher surfactant concentrations flat equilibrium films are formed, stabilized by repulsive forces and the films lifetime increases substantially. The viscoelasticity of the film surfaces also affects the film thinning process, as well as the stochastic process of equilibrium film rupture [95]. Similar conclusions were drawn recently from experiments with emulsion films [97].

For years it was proposed that the bubble coalescence in foams should occur when the capillary pressure, defined mostly by the size and volume fraction of the bubbles, exceeds a certain critical value [98]. Direct comparison between the critical pressures for single-foam films and the respective foams was made by Khristov et al. [98] who found somewhat lower critical pressure in foams. The authors referred this effect to the bigger foam films and to the avalanche-type bubble collapse in foams, both facilitating foam destruction at lower pressures.

Figure 7
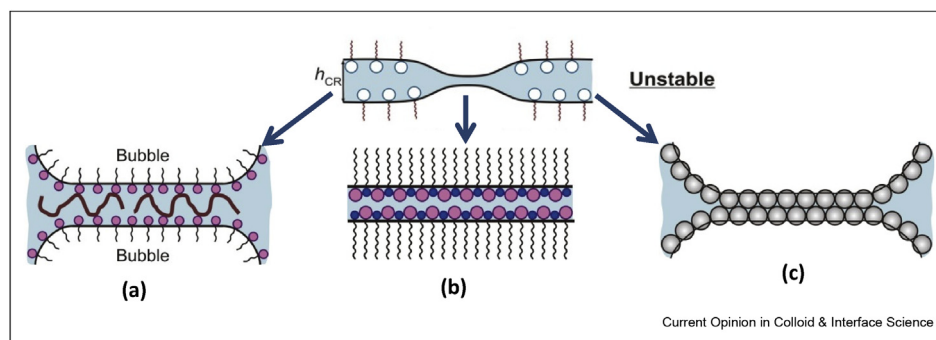
Schematic presentation of the main approaches for enhancing the stability of foam films: **(a)** enhancing the repulsive surface forces, e.g. the steric repulsion by adsorbed polymers as shown here; **(b)** creating dense adsorption layers with high surface viscoelasticity, which reduces the lateral fluctuations creating film instabilities; **(c)** adsorption of solid particles or molecular aggregates (e.g. vesicles), which create structured ultra-stable films.

Recently, similar trends were observed in Ref. [99] — the measured critical capillary pressures in two-dimensional foams was of the right order of magnitude, but significantly lower than the critical pressures measured by Khristov et al. [98]. Therefore, it was proposed that the critical capillary pressure indicates the transition to rapid bubble collapse, whereas film rupture and bubble coalescence are still possible below this pressure, although they are less frequent and stochastic [99]. Similar trends were reported for the critical capillary pressures for drop coalescence in emulsions [97,100].

The modification of foam film surfaces is one of the main approaches for control of the thin film drainage and stability against coalescence. Loose and mobile surfactant layers lead to faster film thinning and easier rupture, whereas adsorption layers with higher density and elasticity decelerate the film drainage and suppress coalescence. Therefore, the type of the surfactant that stabilizes the foam is of significant importance. If nonionic surfactants are used, high surface coverage is needed to suppress the surface mobility and to decelerate the foam film thinning via steric stabilization [38] **. In contrast, the foam films are stabilized by electrostatic forces at much lower surface coverage with ionic surfactants [38]**. Appropriate surfactants and cosurfactants are, therefore, selected to provide surface charges and high surface elasticity [17,64,83,101]**.

Particles are also combined with surfactants and/or polymers to improve foam stability against coalescence, due to the armouring effect, which ensures capillary stabilization of the bubbles [25,102]. Recent study [103] focused on linking the process of anionic surfactant (SDS) precipitation in the presence of divalent Mg^{2+} counter ions to the foam formation and stability. Surfactant crystals partitioning was observed between the bulk solution and bubble surfaces. At low crystal adsorption, unstable foams were obtained due to coarsening and coalescence in the surfactant-coated film areas. In contrast, long-term stability was observed in foams with closely packed surfactant crystals on bubble surfaces, and optimal foam stability and foamability were observed at intermediate in size crystallites [103].

The film thinning and coalescence could be affected by modifications of the liquid phase as well. The increase of solution viscosity in the presence of vesicles, wormlike micelles, polymers, etc., decelerates and could even stop the foam film thinning, thus, giving more time for building complete surfactant adsorption layers and for suppressing coalescence.

The importance of surface rheology and confinement effects in foams and foam films was analysed also in relation to foam experiments under microgravity [104]. Some unexpected results from the experimental studies at the International Space Station (ISS) are reviewed in Refs. [104] and plausible explanations are proposed. The theoretical aspects of drainage in low gravity are discussed and it is described in the limiting cases of high and low interfacial mobility [105]. Note that drainage is strongly related to coalescence stability in foams and emulsions, as drainage increases (1) the capillary pressure which squeezes the liquid from the foam films and (2) the size of the foam films, both effects facilitating the film rupture.

Foam rheological properties and bubble size in sheared foams

Foam rheological properties were recently reviewed by Cohen-Addad et al. [48]** and by Denkov et al. [2]. On steady shear, the dependence of the total shear stress, τ_F on the shear rate, $\dot{\gamma}$, is usually represented by the Herschel—Bulkley model:

$$\tau_F = \tau_0 + \tau_V = \tau_0 + k\dot{\gamma}^n \qquad (4)$$

where τ_0 is the foam yield stress, τ_V is the viscous (shear-rate dependent) stress; k is the foam consistency and n is the power-low index. The physicochemical approaches to modify these rheological properties of the foams are briefly summarized below.

(a) *Foam yield stress*.

Beside the well-studied effects of bubble size, polydispersity and volume fraction, the foam yield stress could be affected by several other factors. The bubble—bubble attraction was shown to affect significantly the foam yield stress (and the foam-wall yield stress as well) without changing noticeably the viscous term, τ_V in steadily sheared foams [106]. Strong bubble—bubble adhesion was induced using appropriate cationic polymers [106]. For foams containing bubbles with HSM, the authors measured much higher foam yield stress and foam-wall yield stress, resulting in atypical $\tilde{\tau}$ vs. Ca curves that cannot be described by Herschel—Bulkley model. These effects were explained with the formation of polymeric bridges between the neighbouring bubbles (or between the bubbles and the solid wall in the foam-wall friction experiments) for static or slowly sheared foams. These bridges break when the shear rates increases, because the thickness of the transient dynamic foam films formed between the colliding bubbles in sheared foams becomes larger than the doubled thickness of the polymer adsorption layers, Figure 8.

Not all cationic polymers create such effects and subsequent study [107]* clarified the key molecular characteristics of the polymers, which lead to bridging or non-bridging of the bubble surfaces. The overall conclusion of this study was that two types of

phenomena are governing the effect of polymers on the shear rheology of surfactant-stabilized foams: (1) the competition between the polymer co-adsorption onto the surfactant adsorption layer at the bubble surface and the surfactant binding to the dissolved polymer molecules in the bulk solution and (2) the thickness of the formed polymer–surfactant adsorption layers, which determines whether the polymer chains are able to protrude sufficiently deep into the solution to bridge the foam film surfaces [107]*. For example, strongly charged linear polymers (e.g. Merquat 100) were found not to bridge the foam films surfaces even in still foams when the films are the thinnest, while moderately charged and/or branched polymers (e.g. Jaguars) bridged the bubble surfaces and increased strongly the foam yield stress.

The effect of solid particles and oil drops, dispersed in the foaming medium, on foam rheological properties is also studied [108–110]*, and some general trends have emerged. The yield stress of the particle-containing foams depends strongly on the ratio between the particle and bubble sizes [110]. The yield stress of foams containing small solid particles or small oil drops was governed by the Bingham-capillary number, $B = \tau_{Y0}R/\sigma$, where τ_{Y0} is the yield stress of the foamed medium, R_B is the bubble size and σ is the surface tension. For foams containing large particles, the yield stress was described by a model developed for description of the micro-mechanics of particle-loaded yield-stress materials, considering the foam as a continuous matrix. In the range of intermediate sizes, the scaled foam yield stress was shown to undergo an exponential decay, which is related to the number of bubbles separating the neighbouring particles [110]. These authors investigated also the yield stress of foams made from concentrated emulsions possessing their intrinsic yield stress. They found that both the Bingham-capillary number and the volume fraction of the interstitial emulsion are governing factors for the resulting foam yields stress [110].

A detailed review summarizing the properties of various types of yield stress materials and the theoretical approaches for their description was presented recently [111]. Numerous aspects are reviewed, including the relaxation time scales, interplay between shear flow and aging, existence of inhomogeneous shear flows and shear bands, wall slip, and non-local effects in confined geometries, many of them relevant to foams and emulsions.

(b) *Foam consistency and power-law index.*

The power-law index, n, in the Herschel–Bulkley equation characterizes the shear-thinning behaviour of the system. For Newtonian liquids $n = 1$, whereas for foams and concentrated emulsions with $\Phi > \Phi_{CP}$ values of n between 0.2 and 0.5 are usually reported [32]. The consistency, k, is more complex for direct interpretation because its dimension is Pa.s^n and the values of k can be compared only for fluids with the same power-law index, n.

In a recent study, Nelson and Ewoldt [112] introduced an alternative parameter to the foam consistency by re-defining the Herschel–Bulkley equation in the following way:

Figure 8
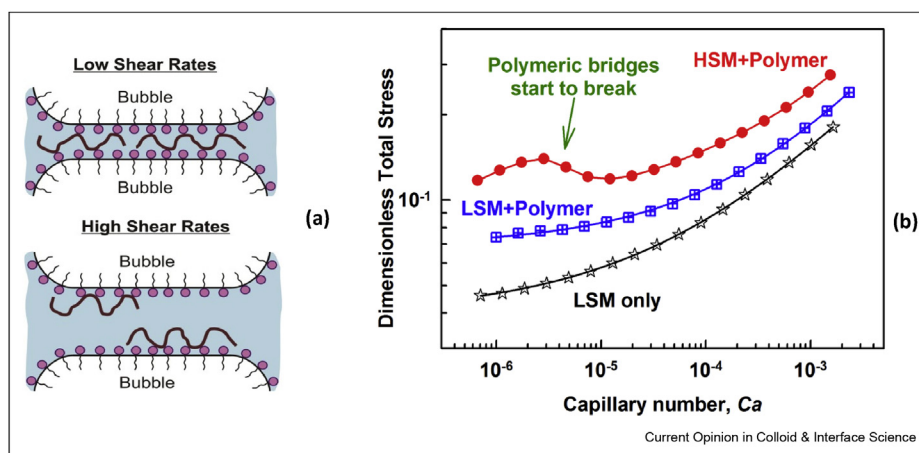
(a) Schematic presentation of the bubble–bubble adhesion at low shear rates due to the formation of polymer bridges between the foam film surfaces; these bridges brake at high shear rates because the dynamic foam films in sheared foams are much thicker than the equilibrium foam films in still foams [107]*. (b) Experimental results illustrating this effect – foam rheological curves in the cases of HSM and LSM adsorption layers. The higher stress at low shear rates in the presence of polymer reflects the resistance to the shear deformation of the polymer bridges formed between the neighbouring bubbles, while the maximum in the curve for HSM + Polymer system reflects the breakage of these bridges with concomitant decrease of the foam shear stress; adapted from Ref. [107]*.

$$\tau = \tau_0[1 + (\dot{\gamma}/\dot{\gamma}_{critical})^n] \qquad (5)$$

In the latter equation $\dot{\gamma}_{critical}$ is the shear rate at which the flow stress becomes twice bigger than the yield stress. Thus, the inconvenient dependence of k on n is avoided. The critical shear rate in some approximate way separates the two recognized regimes of bubble dynamics in sheared foams − 'diffusive' (non-affine) at low shear rates and 'convective' (ordered in lanes) at high shear rates, respectively [113]. This approach was expanded to some other non-Newtonian fluids [114].

The value of n for foams was found to depend significantly on the surface viscoelasticity, Figure 9. Two regimes were identified experimentally for adsorption layers with low and high surface moduli, respectively (LSM and HSM). The experiments showed that the viscous stress is much higher for bubbles covered with HSM adsorption layers, under otherwise equivalent conditions. For HSM layers the power-law index for inside-foam friction, n, was in the range $0.20-0.25$, while the power-law index for foam-wall friction $m \approx 1/2$. In contrast, the viscous friction was significantly lower and the measured power-law indexes were $n \approx 1/2$ and $m \approx 2/3$ for foams with LSM adsorption layers [32]. Other research groups also reported qualitatively different behaviours of foams or bubbles covered with HSM and LSM adsorption layers, respectively [115]. Detailed theoretical models were proposed to describe these differences [12,13].

(c) *Bubble size in sheared foams*.

In sheared foams the bubbles deform and can break into smaller bubbles, under the action of the viscoelastic stresses created by velocity gradients. It was shown experimentally that one can describe the bubble breakup in foams by a well-defined critical dimensionless stress, $\tilde{\tau}_{CR} \equiv (\tau_{CR}R/\sigma) \approx 0.40$. The bubbles with radius R in flowing foam with stress, τ, would rapidly break if the respective dimensionless ratio $(\tau R/\sigma) > 0.40$, while the smaller bubbles corresponding to $(\tau R/\sigma) < 0.40$ survive the flow in the same foam without breakage, because they are less deformed [33]. Thus, smaller bubbles could be obtained using all factors, which increase the friction inside sheared foam, including higher solution viscosity, higher surface elasticity, higher shear rate, higher yield stress, higher bubble volume fraction etc. Qualitative similarity was observed with the oil-in-water emulsions for which lower value of the critical dimensionless stress for drop breakup was measured, $\tilde{\tau}_{CR} \approx 0.15$ [33]. The kinetics of bubble breakup was found to depend very significantly on the bubble polydispersity − faster breakup was observed in more polydisperse foams, compared with the monodisperse ones [33].

Importantly, the critical dimensionless stress for bubble breakup in foams was found to be two orders of magnitude lower than the known critical stress for breakup of single bubbles in sheared Newtonian liquids, $\tilde{\tau}_{CR} \approx 25$ [33]. Similarly, the critical stress in concentrated emulsions was by an order of magnitude lower than that for breakage of single drops in sheared unbound Newtonian fluids (at the same viscosity ratio) [33]. Thus, much smaller bubbles and drops are obtained in foams and concentrated emulsions than those predicted by the Grace plot designed for single drops and bubbles [33,116]. These results indicate the very efficient breakup of the densely packed bubbles (drops) in foams (emulsions). This effect was explained by the strong particle−particle interaction between the neighbouring bubbles (drops) in these systems [33]. The so-called 'microstructure-induced capillary instability' of the breaking bubbles was directly observed in

Figure 9
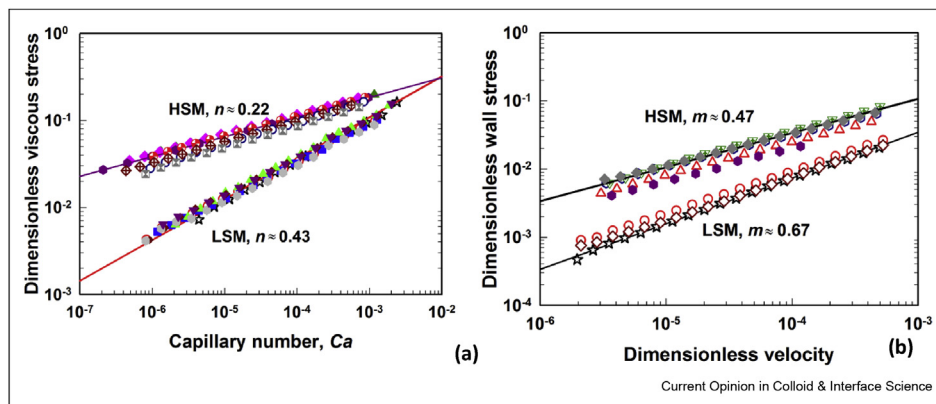
(a) Dimensionless viscous stress $\tilde{\tau}_V$, vs. capillary number, Ca, and (b) Dimensionless foam-wall stress $\tilde{\tau}_W$, vs. dimensionless wall velocity, Ca^*, for foams stabilized by surfactant with low surface modulus and high surface modulus; adapted from Ref. [32].

foams, Figure 10, and similar effects were proposed to explain the results with concentrated emulsions [33].

Outlook

Several new approaches have been developed recently for efficient control of foam properties using appropriate surfactants, polymers, solid particles and their mixtures. The most significant effects were observed with foaming solutions which exhibit non-Newtonian behaviour, high surface viscoelasticity and/or strong bubble—bubble adhesion. These effects are not captured by the classical approach developed by Princen in which the foam properties are described in terms of the mean capillary pressure of the bubbles, σ/R_{32}, the dimensionless function of the bubble volume fraction, $Y(\Phi)$, and the capillary number, Ca, only.

The overview of the various effects shows that the rheological properties of the foaming solutions and of the formed foams play a central role in the explanations of the various phenomena when the bubble coalescence is negligible. For example, the foam volume and the bubble size in the conventional foaming methods, based on mechanical agitation of the foaming solution, are determined by the rheological properties of the generated foam. Other examples are the effects of the yield stress of the foamed fluid on the liquid drainage and bubble Ostwald ripening. Using yield-stress foaming fluids turned out to be a powerful and useful approach to create ultra-stable foams. These effects are relatively well understood and could be described quantitatively using the basic rheological properties (yield stress, apparent viscosity at the relevant shear rate etc.) of the foaming solution or of the foam formed.

Surface viscoelasticity and bubble—bubble adhesion turned out to be two other powerful factors for controlling foam properties. Much smaller bubbles and higher viscous friction are observed when foaming solutions with surface modulus higher than ca. 100 mN/m are used. Appropriate surfactant mixtures and some natural surfactants (e.g. the triterpenoid saponins) form adsorption layers with such high viscoelasticities. Furthermore, such viscoelastic layers are able to increase tremendously the foam stability with respect to bubble Ostwald ripening (coarsening) and moderately with respect to liquid drainage. Such stable foams, containing very small bubbles, are highly desired in some applications, e.g. in the personal care foams (face-wash, hand-wash, shaving, etc.) and as ultrasound contrast agents.

Cationic polymers and solid particles are able to bridge the surfaces of the neighbouring bubbles, thus strengthening the foam structure and increasing foam viscoelasticity with subsequent increase of its stability to liquid drainage and bubble Ostwald ripening. All these latter effects are very significant and their mechanistic explanations are clear, but theoretical models to describe them quantitatively are still missing in many cases. Therefore, one could expect further systematic experimental, theoretical and computer modelling efforts to quantify and describe these effects. While preparing this review we realized that the effect of bubble—bubble adhesion has been studied systematically in relation to foam rheology. However, we did not see similar systematic studies in the context of foaminess, Ostwald ripening and foam stability, although the bubble adhesion could affect strongly these foam properties as well. Therefore, one could expect such studies to appear in the next years.

Figure 10
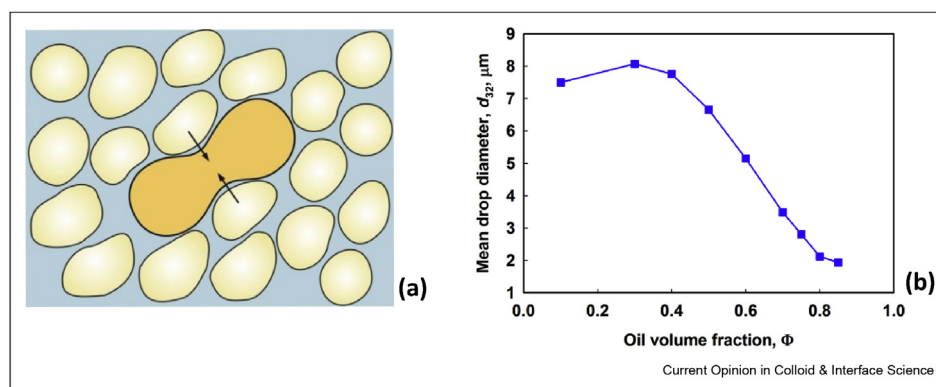
(a) Schematic presentation of the breakage process in sheared foams and concentrated emulsions due to the so-called 'structure-induced capillary instability', which leads to orders of magnitude smaller bubbles and drops compared with the predictions of the Grace plot. The smaller bubbles facilitate the deformation of the bigger ones, thus reducing the critical deformation and the related critical capillary number leading to breakage of the bigger bubbles in the sheared foam. **(b)** Manifestation of this effect in sheared emulsions – the drop size decreases strongly with the increase of drop volume fraction [33].

The phenomena involving bubble—bubble coalescence are much less understood. There are still uncertainties about the main mechanisms of foam film rupture and on the specific roles of the various types of foam stabilizers in this process. One observes a slow but steady progress in this area, based on the understanding that several different mechanisms of film rupture occur in the real foams (e.g. during foaming, upon foam shear and in still foams) and that the various foaming agents could play very different roles in these mechanisms.

The specific strength of the 'physicochemical approach', advocated in this review, is that one could explain the complex effects of the various components (surfactants, polymers, solid particles) on the properties of the produced foams via several, much better understood modifications of the basic properties of the foaming solutions. Examples of such modifications are the surfactants, which create highly viscoelastic surfaces, polymers and/or particles which create strong bridging attraction between the neighbouring bubbles, and polymers or particles leading to non-Newtonian properties of the foaming solutions. In this way, one could classify and rationalize the effects of the countless number of ingredients into a very limited number of their possible effects on the properties of the foaming solutions, thus simplifying tremendously the analysis of these complex systems. For many of these phenomena, one could see clear analogues in emulsion systems.

Due to the very strong interest of the pharma, food, cosmetic and chemical industries in the applications of foam-based and emulsion-based products, this research area will remain a hot topic in the coming years. Due to the structural and dynamic complexity of these systems, only a combination of systematic experiments with rigorous theoretical approaches (starting from simple scaling rationalized by plausible mechanisms) and computer modelling give a chance for deeper understanding and, on this basis, for a full exploitation of the opportunities created by the countless combinations of various foaming and emulsification ingredients.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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