

Recent Advances on Emulsion and Foam Stability

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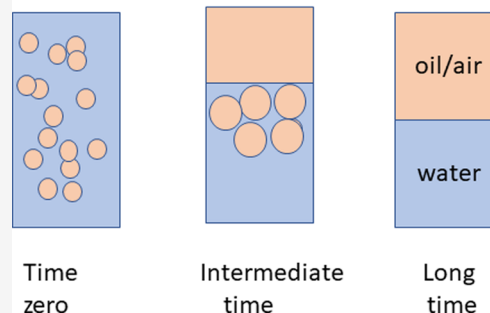
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ABSTRACT: In this perspective paper, we highlight the numerous open problems in the topic of stability of emulsions and foams, focusing on the simplest case of dispersions stabilized by surfactants. There are three main destabilization processes, gravity induced evolution, Ostwald ripening, and drops or bubble coalescence, which are analyzed separately. The discussion is restricted to the case of Newtonian fluids, deprived of microstructure, except for the presence of micelles. Thanks to continuing efforts and recent breakthroughs, we show that the understanding of emulsion and foam stability is progressing. Many problems are still open, however, and much work remains to be done along the lines outlined in the paper.

Emulsion/Foam time destabilisation



1. INTRODUCTION

Emulsions are dispersions of oil in water (O/W emulsion) or of water in oil (W/O), whereas foams are dispersions of gas in a liquid, frequently water.¹ Both emulsions and foams are stabilized by surfactants, proteins, or small particles. In some cases, for instance when particles are used, dispersions of water in gas can be obtained.² When the liquid fraction ϕ of the surrounding (continuous) liquid in emulsions and foams is large, the inner fluid is dispersed in the form of spherical drops or bubbles; in the second case, the dispersion is usually called *bubbly liquid* instead of foam. When ϕ is close to 36%, the dispersed spherical objects come in close contact (the volume fraction of a random compact assembly of monodisperse spheres is about 64%). Below $\phi \sim 36\%$, the spheres are deformed into polyhedra and the dispersions no longer flow, the surface energy cost due to the spheres' deformation being stored in the form of elastic energy. This situation is common to foams, but is also encountered in high internal phase emulsions (HIPE) such as creams. A scheme of the evolution of foam structure with increasing liquid fraction is shown on Figure 1. The evolution is similar for O/W emulsions stable enough to form HIPEs. Most emulsions however invert when the drop fraction is increased: O/W emulsions do not really transform into W/O emulsions, but rather form multiple emulsions because a surfactant used to stabilize O/W emulsions cannot stabilize W/O emulsions. This inversion was called *catastrophic* by Salager and co-workers.³

The liquid fraction of 36% corresponds to a situation where hard spheres are randomly close packed. It signals the transition between fluid and solid systems, currently called *jamming transition*. There are frequently interactions between the drops/bubbles in emulsions and foams, and the jamming transition can be significantly shifted: for instance, it can increase up to $\phi \sim$

70% in adhesive emulsions.⁴ Let us finally mention that bicontinuous structures have been discovered in particle-stabilized systems.⁵

The stability of emulsions depends on the liquid fraction ϕ as will be discussed in the following. So far, it is still very difficult to predict how stable these dispersions will be, other than empirically. Their stability is determined by an interplay between different phenomena: gravity induced motion of drops/bubbles, Ostwald ripening, and drop/bubble coalescence. Gravity decreases the external liquid fraction ϕ and hence favors ripening and coalescence; alternatively, ripening and coalescence lead to an increase of drop/bubble size and the decrease of ϕ due to gravity is then more rapid. In the following, we will summarize the recent advances in the understanding of the three different phenomena. The discussion on coalescence will be the longest, because coalescence is the less understood phenomenon.

2. GRAVITY EFFECTS

Because of the density difference between dispersed and external phases, gravity has an important effect, especially in foams for which the density difference is large. As a consequence, air bubbles rise and the liquid drains between them. The process is usually called *drainage*, whereas in emulsion, it is rather called

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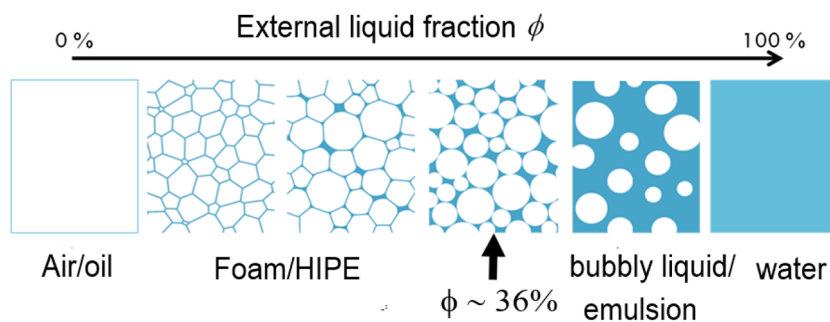


Figure 1. Scheme of the evolution of the structure of an aqueous foam when the water liquid fraction ϕ is increased. Above $\phi \sim 36\%$, a bubbly liquid is obtained. The evolution is the same for the emulsions stable enough to form HIPEs.

sedimentation if the drops are heavier than the external phase, or creaming if they are lighter.

The motion of individual bubbles or drops in the presence of gravity has received a lot of attention. When they are small, their velocity V is given by the Stokes formula

$$V_{\text{St}} = \frac{2|\rho_c - \rho_d|gR^2}{9\pi\eta_c} \quad (1)$$

where R is the radius of the drops/bubbles, ρ_c and ρ_d are respectively the density of the continuous and disperse phases, g is the acceleration of gravity, and η_c the viscosity of the continuous phase. This expression has been established for solid spheres and is valid when the surface of the drops/bubbles remains immobile during their motion.

Although this is most often the case, it was found early that when the fluids are carefully cleaned, the velocity V was larger than the Stokes velocity by a factor 3/2, as expected for spheres with mobile surfaces. Surfactants confer to the interface a resistance to deformation, characterized by viscoelastic parameters. Levich has shown that when the resistance to compression is large enough, the Stokes velocity can be used.⁶ He introduced a surface compression modulus E defined as

$$E = \frac{1}{A} \frac{d\gamma}{dA} \quad (2)$$

with γ being the surface tension and A the surface area.

The transition between the two limits, mobile and rigid surfaces, is observed when the surfactant concentration is increased and has been extensively studied.^{7,8} When the concentration is still larger, one expects that the resistance to compression will go through a maximum and then decrease to zero: at large concentration, the exchanges of surfactant between surface and bulk are fast, and the resistance to compression vanishes as also predicted by Levich. This effect has been observed during the motion of drops/bubbles in tubes under the action of a pressure drop,⁹ but not yet for gravity motion.

When the drops/bubbles are large, their velocity V is large and they can deform during their motion, changing the velocity in a complex manner. When the Reynolds number is large, instabilities can occur. These effects have received a lot of attention¹⁰ and are now reasonably well understood.

The motion of a large number of drops/bubbles is a still more difficult problem and is not fully clarified for the time being.¹¹ An empirical expression was proposed for solid spheres by Richardson and Zaki¹² and is accurate up to large drop/bubble volume fractions:

$$V = V_{\text{St}} \phi^n \quad (3)$$

The exponent n varies with the Reynolds number Re and at low Re $n = 4.5$.¹³

The extreme case of a continuous liquid fraction close to zero is surprisingly better understood, after extensive studies with foams. The liquid drains through the network of interstices between bubbles called *Plateau borders*. The velocity of drainage is proportional to V_{St} but much smaller:¹⁴

$$V = K_{\text{drain}} \frac{\rho_c g R^2}{\eta_c} \phi^\alpha \quad (4)$$

where K_{drain} is a foam permeability ($K_{\text{drain}} \sim 1/300$) and α an exponent depending on surface mobility: $\alpha = 1$ for rigid surfaces, 1/2 for mobile surfaces. Here the surface mobility is related to the surface shear viscosity. This result only applies to sufficiently dry foams, for which ϕ is equal to a few percent. A theoretical description of drainage of wetter foams is still awaiting.

When drainage is completed, the liquid fraction vertical profile remains constant, with a dry foam at the top, and a wetter one in contact with the drained liquid. This profile has been determined theoretically and found in agreement not only with experiments with foams, but also with emulsions.¹⁵

3. OSTWALD RIPENING

The internal pressure in drops/bubbles exceeds the external pressure by a quantity equal to the capillary pressure, equal to $2\gamma/R$ for spherical drops/bubbles. Due to this excess pressure, the internal fluid is transferred by diffusion through the continuous phase, from the small drops/bubbles to the larger ones. The problem is the same than in alloys and a theory was established by Lifchitz, Slyozov, and Wagner (LSW theory) in the limit $\phi \rightarrow 1$.¹⁶ This theory predicts that the radius increases with time as $R \sim t^{1/3}$ with a rate $\Omega_3 = dR^3/dt$ given by

$$\Omega_3 = \frac{8}{9} \frac{\gamma D_m S V_m}{k_B T} \quad (5)$$

where D_m is the diffusion coefficient of molecules of the dispersed phase into the continuous phase, V_m their molecular volume, S the solubility of the dispersed phase in the continuous phase, k_B the Boltzmann constant and T the absolute temperature. For bubbly liquids, the solubility S is generally expressed in terms of Henry constant He :

$$\Omega_3 = \frac{8}{9} \gamma D_m He V_m \quad (6)$$

with He being expressed in $\text{mol m}^{-3} \text{Pa}^{-1}$.

Measurements of the Ostwald ripening rate in alloys with φ between 80 and 40%, showed that the experimental rates vary only by a factor three.¹⁷

Experiments with emulsions however rarely fitted with the theory, and deviations by factors of order 10 are currently observed. For instance, the ripening rate depends on the amount of surfactant in excess in the continuous phase, but no rational explanation was yet found.¹⁸ A mechanism specific to emulsions was recently identified: exchange of disperse phase during contact between drops.¹⁹ The exchange is facilitated when the surfactant molecules are small. However, and although the coarsening rate can be reasonably estimated by the LSW theory, its exact value cannot yet be predicted.

In dry foams, the gas transfer occurs mainly through the thin liquid films formed between bubbles, instead of the larger spaces between bubbles, that scale with the bubble radius. As a result, the bubbles radius increases more rapidly: $R \sim t^{1/2}$. The ripening rate Ω_3 such as $dR^2/dt = \Omega_2 f(\varphi)$, $f(\varphi)$ being the fraction of bubble surfaces covered by films, is given by

$$\Omega_2 = k \frac{\gamma D_m \text{He} V_m}{h} \quad (7)$$

where k is a geometrical coefficient related to bubble shape ($k \sim 1.37$ for Kelvin tetradecahedra) and h the film thickness.²⁰

As in Ostwald ripening of emulsions, the experimental determinations of the rate Ω_3 differ from the predictions by factors of order 10.²¹ This is probably because drainage produces rapid changes of liquid fraction, difficult to control. Indeed, a good agreement was obtained in experiments in which the coupling of drainage and coarsening has been modeled.²⁰ However, experiments with relatively dry foams $\varphi < 15\%$, where the liquid fraction was maintained constant thanks to a rotation of the foam samples led to rates significantly different from the predicted ones.²² It is possible that residual drainage affected these measurements.

Recent experiments performed in microgravity conditions in the International Space Station²³ were found in good agreement with eq 7 and allowed to determine the function $f(\varphi)$. In turn the rates measured in bubbly liquids are much larger than those predicted, possibly because of gas exchanges through transiently formed films as found in emulsions.¹⁹

4. COALESCENCE

Coalescence is the rupture of the liquid films formed between drops/bubbles, either during collisions, or at rest in HIPES or foams. Coalescence is the less well understood destabilization process in emulsions and foams. One of the reasons is the large number of different coalescence scenarios. For instance, hydrophobic particles can bridge aqueous films and rupture them through a dewetting process. This is one of the mechanism of action of antifoams.²⁴ In the following, we will focus on dispersions containing only surfactants and distinguish between dispersions with high and low stability, which destabilize in a very different manner.²⁵

4.1. Dispersions with Low Stability. Some emulsions and foams destabilize a few minutes after being formed. This happens in general when the surfactant concentration is low, below the critical micellar concentration (cmc) for nonionic surfactants and about 2 orders of magnitude below for ionic surfactants.²⁶ Exerowa proposed that these concentrations correspond to the onset of formation of stable liquid films between drops and bubbles.²⁷ Such films are in equilibrium under the action of forces between film surfaces, attractive van

der Waals forces and repulsive forces, electrostatic for ionic surfactants, and steric for nonionic ones. Figure 2 shows the

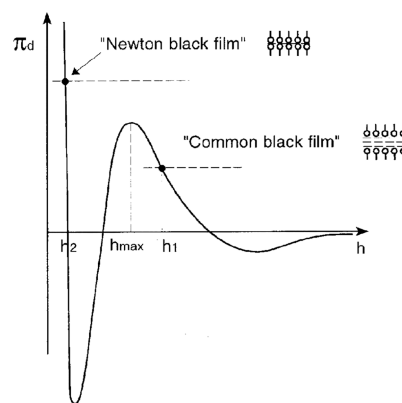


Figure 2. Schematic representation of the variation of the disjoining pressure π_d with film thickness h , including contributions of van der Waals attraction and electrostatic and short-range repulsion. The horizontal dashed lines correspond to different applied pressures ΔP and the vertical ones show the pressures at which the film has reached its equilibrium thickness.

schematic variation with film thickness of the force per unit area, called *disjoining pressure* π_d (Figure 2). In unstable emulsion and foams, only van der Waals forces are present, and the films never reach an equilibrium thickness.

When two drops or bubbles approach at a velocity V and when the distance h between their surfaces becomes small, these surfaces may deform and flatten out. Flattening occurs when the hydrodynamic pressure P_{hyd} at the film center exceeds the capillary pressure P_{cap} in the drops/bubbles. It is only then that films form strictly speaking. For drops/bubbles of radius R with immobile surface boundary conditions, when $P_{\text{hyd}} > P_{\text{cap}}$ and $h < h_{\text{flat}}$, the surfaces flatten:

$$h_{\text{flat}} = \frac{R}{2} \sqrt{\frac{3\eta_c V}{\gamma}} \quad (8)$$

4.1.1. Film Thinning and Rupture. Shortly after film formation, the flattened regions deforms and dimples form²⁸ (see Figure 3). This occurs when the film thickness is about twice smaller than h_{flat} . After the formation of the dimple, the surfaces continue to approach until coalescence occurs.

The problem of film rupture was extensively investigated. A model was proposed early by Sheludko and Vrij, in which rupture is due to the amplification of capillary waves at the film surfaces when the film thickness becomes small enough.^{29,30} The Vrij's model predicts a critical film thickness for rupture of a few tens of nanometers, although recent experiments showed that the films studied rupture at much smaller thicknesses, a few angstroms.³¹ A hydrodynamic model, with no adjustable parameters accounted very well for the rupture times. Although the fluids used were surfactant-free, the surface was assumed to be immobile. As discussed earlier, this can arise from residual contamination. It should be noted that the effect of residual contamination depends on the type of experiment performed: the same interface can behave as mobile or rigid, depending of the type of applied constraint.

Evidence of coalescence induced by fluctuations were reported in solutions containing particles and polymers.³² However, in these systems, the surface tension was ultralow and

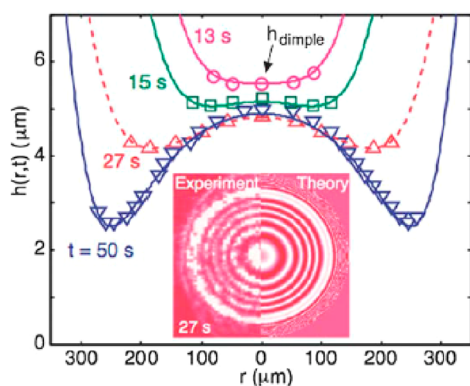


Figure 3. Vertical profile of a silicone oil film between glycerol drops at various times after dimple formation: experiments (symbols) and theory (lines). The inset shows interference fringes observed when illuminating the film perpendicularly to its surfaces. Reproduced with permission from ref 28. Copyright 2011, Royal Society of Chemistry.

the surface fluctuations were present all along the drop surfaces, not only in the regions where two drops were approaching as assumed in the Vrij-Sheludko model. Studies of films with mobile surfaces were performed recently and evidence of surface fluctuations was found when the film thinning velocity was small. However, although the films ruptured when they were 30 nm thick, the observations were not consistent with the Vrij's model.³³

In the experiments of ref³¹ the films remained centrosymmetric during thinning. In ref,³³ an asymmetry developed when the fluctuations appeared. Asymmetrical film thinning was reported early, but attributed to a hydrodynamic instability occurring when the surface rheological parameters are small.³⁴ This instability causes the films to rupture when they are still quite thick.

Early rupture was also observed in emulsions with large concentrations of surfactant. This happens when the partition coefficient of the surfactant between oil and water is close to one. When the surface is compressed, the surfactant can dissolve very rapidly in both oil and in water, and the resistance to compression vanishes, leading to very rapid film thinning: the surface tension gradients produced during film thinning cannot be sustained and no Marangoni force is present to slow down film thinning, the film surfaces are mobile.³⁵ This is likely also the mechanism behind the action of demulsifiers which are surfactants equally partitioned between oil and water.³⁶

4.1.2. Coalescence without Film Formation. When the velocity V is very small, and/or if the drops/bubbles are very small, no films are formed, with P_{hyd} remaining smaller than P_{cap} . At small gap thickness and under the influence of van der Waals attraction, the surfaces bend outward (protrude toward each other), and two *pimples* are created.²⁸ Pimples form because the van der Waals disjoining pressure increases faster than the hydrodynamic pressure when the gap thickness decreases. Pimples spontaneously grow until the surfaces touch each other and drops/bubbles coalesce. In the opposite case of very high velocities, drops or bubbles approaching an interface may rebound after the collision.

Experiments were performed recently by Politova et al., who measured the lifetimes of water drops of dilute aqueous surfactant solutions pressed by gravity onto a flat oil–water interface.³⁷ The data for small drops has been analyzed assuming that the lifetime was controlled by the velocity of approach, and

that coalescence occurs when h reaches the value at which the van der Waals disjoining pressure equals the capillary pressure. The agreement between calculated lifetimes and measured ones was rather good for small drops (for which films are not expected to form).

Politova et al. also made experiments with larger drops, for which flat films should form between the drops and the oil–water interface. Coalescence was assumed to occur when the film thickness reaches the critical thickness in Vrij's model. The agreement with the experiments is not as good as for the small drops, probable because of the inadequacy of Vrij's model in this case.³⁷

In summary, when the surfactant concentration is not sufficient for equilibrium films to form, emulsions and foams are very unstable and destabilize after only a few minutes. Only attractive van der Waals forces are present between drops/bubbles surfaces and accelerate the drops/bubbles approach when they are close enough. Instabilities may lead to asymmetric deformations, rapidly followed by rupture when the distance between drops/bubbles is still large. The surface fluctuations recently observed might be precursors of this instability, explaining why the Vrij-Sheludko model that assumes centrosymmetry is not appropriate.³³

The lifetime of drops/bubbles is controlled by their velocity of approach, the coalescence itself being very rapid (typically of the order of milliseconds). It should be noted that the lifetime then depends of the type of experiment performed: it is different for instance when coalescence is observed during the creaming of an emulsion or by looking at the collision between a single drop and a microscopic oil–water interface.³⁸ The trends can even be opposite, when for instance a polymer is added: on one hand, the polymer can lead to flocculation and accelerate coalescence during emulsion creaming, and on another hand increase the viscosity of the continuous phase, slowing down film thinning in single drop experiments, thus slowing down coalescence.³⁹

4.2. Dispersions with High Stability. When the surfactant concentration is large enough, stable equilibrium films can form. In the case of emulsions, the surfactant should be present in the continuous phase of the emulsion (Bancroft rule), in order for the surface tension gradients produced during film thinning to remain active and slow down thinning. There is indeed not enough surfactant in the thin films to replenish the depleted surfaces.⁴⁰

The lifetime of the films is then larger than the film thinning time, because the time of film rupture becomes important and dominates in the very stable films. Figure 4 shows the evolution of film lifetime with surfactant concentration before and after the onset of stable film formation (black spot in the figures on the right).⁴¹

Films form even between small drops when repulsive interactions are present: when the distance h between drops/bubbles becomes comparable to the range of surface forces and when these forces are repulsive, the capillary pressure is opposed by the disjoining pressure and drops/bubbles surfaces flatten. It was observed that the films form only close to their equilibrium thickness when they are very small (diameters of the order of 10 μm).⁴²

For fully immobile surfaces, the velocity of film thinning is given by the Reynolds expression:

$$V_{\text{Re}} = -\frac{dh}{dt} = \frac{2h^3}{3\eta_c R^2} \{ \Delta P - \pi_a(h) \} \quad (9)$$

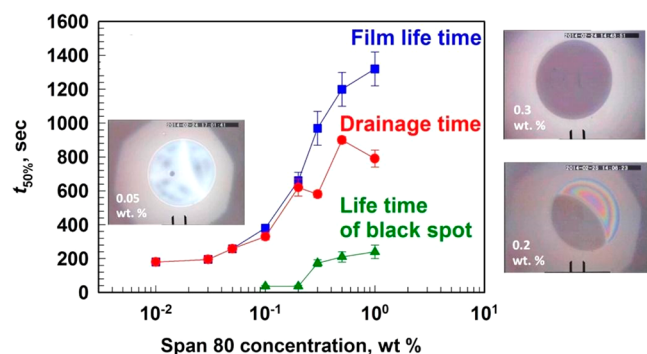


Figure 4. Measured lifetimes of films formed by water drops pressed by gravity onto a flat oil–water interface (time required for 50% of films to break after their formation) versus surfactant concentration together with film images. Hexadecane films, stabilized by Span 80, in contact with an aqueous phase, 150 mM NaCl. The distance between the dark vertical bars is 50 μm . Reproduced with permission from ref 41. Copyright 2017, Elsevier.

where ΔP is the pressure difference between film center and border. This pressure contains contributions of the capillary pressure (always present and due to film border curvature), gravity when the film is not horizontal, and eventual externally applied forces. In general, the surface tension gradients are not sufficient to ensure that the surfaces are immobile, and the thinning velocity is larger than V_{Re} . It is sometimes assumed that eq 9 can be used by introducing a smaller viscosity $\eta_{\text{eff}} = n^2 \eta$, the index n being a mobility factor: $0 < n < 1$. This is not correct, because n is not constant: the thinning velocity decreases faster than h^3 when h decreases⁴⁰ and tends toward the Reynolds velocity when the film thickness approaches its equilibrium value.⁴³ This value depends on the applied pressure and is such that $\Delta P = \pi_d(h) (V_{\text{Re}} = 0)$.

When repulsive forces are present, the equilibrium films should never rupture. Models such as the Vrij model are inappropriate, because it assumes that the force is attractive (van der Waals). However, the film surfaces being partly mobile, surface concentration fluctuations are possible and if the local concentration is small enough, the repulsive forces may disappear, allowing the film to rupture. De Gennes estimated the corresponding activation energy:⁴⁴ $U^* = k_B T \delta \Gamma^2 / \langle \delta \Gamma^2 \rangle$ where Γ is the surface concentration, $\delta \Gamma$ its variation, and $\langle \delta \Gamma^2 \rangle$

the mean square amplitude of surface concentration fluctuations:⁴⁵

$$\langle \delta \Gamma^2 \rangle = \frac{k_B T \Gamma^2}{E A_{\text{hole}}} \quad (10)$$

where E is the surface compression elastic modulus (see eq 2) and A_{hole} the area of the region depleted in surfactant. When a film ruptures, the critical hole radius is half the film thickness.⁴⁶ Taking $\delta \Gamma \sim \Gamma$, $E \sim 40 \text{ mN/m}$, $h \sim 10 \text{ nm}$, U^* is about a few hundred $k_B T$. De Gennes then quoted that intrinsic film rupture is extremely difficult and can only occur with external agents such as antifoam particles are present. However, for a film to rupture, $\delta \Gamma$ only needs to be about $\Gamma/10$, concentration at which films are no longer stable.²⁷

De Gennes related the activation energy U^* to the compression elastic energy and estimated the coalescence frequency:

$$\frac{1}{\tau} = \frac{1}{\tau_0} \frac{A}{A_{\text{hole}}} \exp\left(-\frac{U^*}{k_B T}\right) = \frac{1}{\tau_0} \frac{A}{A_{\text{hole}}} \exp\left(-\frac{\delta \Gamma^2 E A_{\text{hole}}}{\Gamma^2 k_B T}\right) \quad (11)$$

where τ_0 is a molecular time, equal to the hole dimension divided by the velocity of compression waves and A is the contact area of two emulsion drops/bubbles [de Gennes, unpublished, see ref 1 page 113, for details]. This relation shows that the stability of emulsions and foams frequently appears correlated with the surface compression modulus E , at least for surfactants irreversibly adsorbed, for which the modulus is not affected by exchanges between surface and bulk.

Kabalnov and Wennerstrom proposed an alternative model to relate emulsion stability to the surfactant layer curvature energy and applied the model to nonionic surfactant near the temperature at which the tension is minimum.²⁵ They found an activation energy given by $U^*/k_B T = 0.43 + 30.9 \Delta T$, ΔT being the temperature difference with respect to the temperature at which the tension is minimum. The change of the activation energy with temperature is thus drastic and compatible with experimental observations. There are however many drawbacks in the model. Kabalnov and Wennerstrom used an expression of the curvature energy that is not valid for the very thin equilibrium films formed by nonionic surfactants: the radius of curvature of the hole is comparable to the surfactant molecular

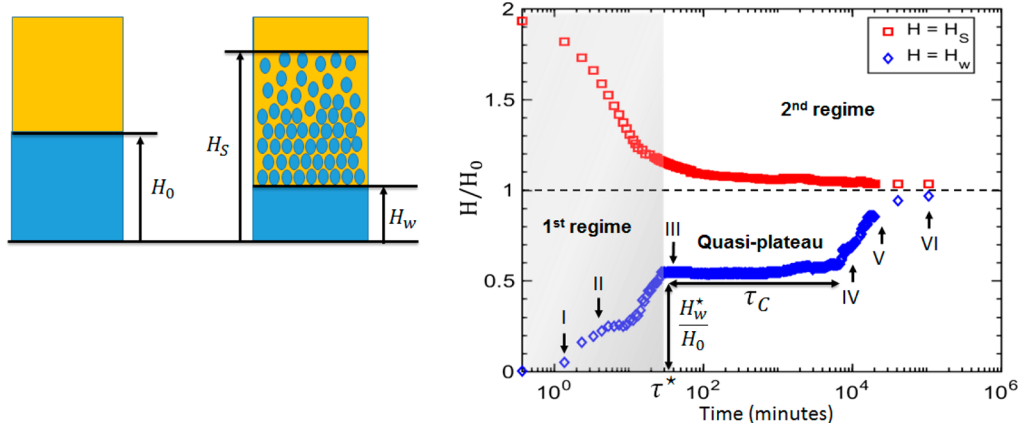


Figure 5. Left: Definition of interface positions measured in the bottle test; before mixing, the water and oil heights are equal. Right: position of the oil-emulsion interface (red circles) and of the water-emulsion interface (blue circles). The first regime corresponds to the creaming of the emulsion. After a quasi-plateau, coalescence starts in the second regime. Reproduced with permission from ref 48. Copyright 2020, Royal Society of Chemistry.

length. In addition, they used a surface tension expression that neglects the variation of the elastic constants with temperature and the contribution of dispersion entropy. They also used a positive Gaussian bending elastic modulus, whereas a careful analysis of surface tension data led later to a negative modulus.⁴⁷ The activation energy calculated with the data of ref 47 becomes $U^*/k_B T = 11.5 + 66.6 \Delta T$, and the predicted change in activation energy with temperature is no longer drastic as observed in the experiments. The model could apply to ionic surfactants, for which the equilibrium films are thicker and the expression of the curvature energy more appropriate. However, this energy becomes negligible compared to the other surface energy contributions in systems with larger surface tension.

Equation 11 predicts that the film lifetime is inversely proportional to film area. It has been recognized early that coalescence begins when emulsion drops reach a critical size, for instance, during their growth due to Ostwald ripening.⁴⁹ In other studies, it was claimed that coalescence occurs above a critical capillary pressure.^{50,51} In these experiments, however, both the size and the capillary pressure vary, and it is not easy to disentangle their role. An experiment with 2D foams was designed to control both parameters independently. It was then shown that at constant film area, the film lifetime does not depend on capillary pressure and that at constant capillary pressure, the film lifetime is proportional to film area as predicted by eq 11.⁵²

The role of the capillary pressure was recently clarified using simple bottle tests in which the creaming of emulsions is monitored. Changing the oil fraction allows to obtain a larger height of the creamed emulsion H , and to vary the pressure (Figure 5). The results are in excellent agreement with a model based on the fact that the film lifetime is proportional to film area: increasing H increases the contact area between drops.⁴⁸ The results have been used to compare the coalescence probability with the model of Wennerstrom and Kabalnov, despite the drawbacks of this model.^{53,54}

5. CONCLUSIONS AND PERSPECTIVES

The discussion presented highlights the numerous open problems in the topic of stability of emulsions and foams stabilized by surfactants. The discussion was restricted to surfactant solutions without microstructures, except for the presence of micelles. In practice, these dispersions can be stabilized by polymers, particles or their mixtures including with surfactants. The constitutive fluids can also be viscoelastic, which bring additional complexity.

We have tried to list the recent advances, together with the still open problems and considered separately the processes involved in the destabilization: gravity effects, ripening, and coalescence. Because none of them are yet fully described, we did not attempt to discuss the interplay between them.

Gravity effects are perhaps the better understood ones, the phenomena at play being well identified. It is now recognized that the question of interface mobility is specific to the type of hydrodynamic flow considered and that the same interface could well behave as mobile or immobile in different situations. The rheological parameters characterizing this mobility can be different, for instance, the compression modulus in the motion of isolated drops/bubbles and the surface shear viscosity in foam drainage. The description of the gravity effects is now satisfactory for very dilute dispersions, even when the drops or bubbles are large and deformed. The gravity drainage of dry foams is also well described. The intermediate cases where the

continuous or the disperse liquid fractions are larger than a few% remains to be improved.

Ostwald ripening is less well understood, although the ripening rates are seldom larger or smaller than the theoretical predictions by a factor 10. The role of free surfactant is still not clear, despite numerous studies. The exchange of dispersed phase during collisions recently evidenced might help to clarify the issue. Studies of wet foams (or HIPEs) are in progress and will fill the missing liquid fraction gap.

Numerous recent coalescence studies improved the understanding of this process, the most complex in emulsion and foam destabilization. It is now clear that coalescence mechanisms in unstable emulsions and foams are completely different than the mechanisms at play in more stable dispersions. The lifetime of unstable dispersions is fully determined by the time of approach of drops/bubbles. When the drops/bubbles are sufficiently large, films may form between them. In some cases, the film surfaces do not remain flat and dimples are formed; when the dimples remain centrosymmetric, coalescence was reported to occur only when the surfaces are very close (a few Å). In other cases, an instability occurs, the dimple loses its axisymmetry, and the film ruptures when it is still thick (a few tens of nanometers). Asymmetrical thickness fluctuations have also been observed when the approach is sufficiently slow. When the drops are very small, films do not form between them and coalescence possibly occurs via pimple formation. The question of what drives the rupture and of the critical distance at which coalescence occurs are therefore still unclear.

The stable dispersions destabilize after a time that can be long, hours for foams, months for emulsions. Destabilization occurs once the drop/bubble size has reached a critical value, for instance, during the ripening process. The probability of film rupture is indeed proportional to the contact area between drops/bubbles if one assumes that coalescence is caused by thermally activated holes in the surfactant layer. With this assumption, coalescence is predicted to be stochastic, as observed in practice. Recent bottle tests experiments showed that it is possible to measure the coalescence probability, and comparisons with models are in progress.

To summarize, thanks to continuing efforts and recent breakthroughs, our understanding of emulsion and foam stability is progressing. Many problems remain open, however, and much work is still to be done along the lines outlined in this paper.

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Notes

The author declares no competing financial interest.

Biography

Dominique LANGEVIN studied at Ecole Normale Supérieure Paris and became afterwards CNRS research scientist, being presently directeur de recherche emeritus. She began her research at the Physics laboratory of Ecole Normale Supérieure, she was postdoc at P.G.de Gennes' laboratory, Collège de France, she directed later the Centre de

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