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Ettelaie, R and Murray, BS (2015) Evolution of bubble size distribution in particle stabilised bubble dispersions: Competition between particle adsorption and dissolution kinetics. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 475. 27 - 36. ISSN 0927-7757

https://doi.org/10.1016/j.colsurfa.2014.10.005

Evolution of bubble size distribution in particle stabilised bubble dispersions: competition between particle adsorption and dissolution kinetics

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Keywords: Microbubbles, Particle stabilised bubbles, Disproportionation, Bubble size distribution, Hydrophobin

Submitted to: Colloids and Surfaces A: Physicochemical and Engineering Aspects

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Abstract

It is shown that in systems containing bubbles stabilised by nanoparticles, the time scales for the dissolution of small microbubbles can be comparable with those involving the transport and adsorption of the stabilising nanoparticles onto the surface of the bubbles. We have studied the evolution of model bubble size distribution functions in the light of this effect and also the competition between different sized bubbles for the finite number of available particles. It is found that for dispersions moderately rich in nanoparticles, the width of the final distribution function can become broader than the initial one, whereas for cases deficient in particles the reverse is observed. For each given bubble size, there exists a particle to bubble concentration ratio above which the final size of a bubble of this radius is no longer affected by the presence of other bubbles. In a system deficient in particles, this can still hold true for bubbles in the lower end of the size distribution range, but not the ones at the upper end. By considering simple cases consisting of just two bubbles sizes, we show that the degree of shrinkage of the bigger bubbles is significantly increased in the presence of a small amount of gas in the form of smaller bubbles. In contrast, the final bubble size of the smaller bubbles is found to be largely insensitive to the amount of gas included within larger bubbles. The implications of these results for the final fraction of retained gas, in these types of particle stabilised bubble systems, is also discussed.

1. Introduction

Many commonly encountered everyday foods own their desirable texture and mouthfeel to the presence of bubbles and foams in these products. The size and spatial distributions, colloidal stability against coalescence, drainage and disproportionation, the life time and other similar physicochemical attributes of bubbles in food systems have been the subject of many research studies, both generally [1-5] and also in the context of more specific food. Examples of the latter, underpinning the crucial role of gas bubbles in the quality of the final products, involve ice-creams [6, 7], beers and sparkling wines [8, 9], breads, cakes and dough [10, 11] and beverages and coffee drinks [12]. Bubbles can also act as possible active or inactive filler particles in gel networks consisting of aggregates of emulsion droplets. By means of theoretical work, involving Brownian dynamic simulations, Wijmans and Dickinson [13] have shown that the presence of filler particles provides an interesting possibility for the control of mechanical strength and large deformation rheology of foods containing emulsion gels. Their findings have broadly been confirmed by experimental studies on such systems [14, 15]. Indeed, one may extend the idea of using bubbles as particles even further by envisaging entire gel networks which consist of aggregates of bubbles, rather than emulsion droplets. Incorporating particulate gels of this type as food structuring agents has obvious distinct advantages. Not only can such an approach be very cost effective, it can also be useful in the design of healthier foods. Nonetheless, for the idea to be feasible in the first place, several conditions have to be met. Large bubbles are far too deformable to be used as substitutes for the emulsion droplets or replacements for the colloidal solid particles. Thus, one needs to be able to generate rather small bubbles, say of the order of a few microns, in the system. Furthermore, these bubbles have to be highly stable against coalescence, given that in the gel network they remain very close to other bubbles throughout the shelf life of the product. Finally, they should also resist the process of disproportionation and subsequent dissolution. Interestingly, out of all these requirements, it is the latter that continues to pose the greatest challenge in realising small stable microbubbles in foods and related systems.

Disproportionation is the process of diffusion of gas molecules from small bubbles to larger ones, leading to the continual coarsening of the bubbles via dissolution and disappearance of the smaller bubbles. The process is driven by the chemical potential gradients between the gas molecules in different sized bubbles, caused by the difference in the Laplace pressure inside them. Thus, in this sense disproportionation is very similar to Ostwald ripening in emulsion systems. However, there are several factors that make the time scales for disproportionation much shorter than those encountered during Ostwald ripening. Firstly, there is the higher solubility of gas molecules compared to lipids. Secondly, the interfacial tension of gas-water interfaces is somewhat higher than those for oil-water surfaces. This leads to higher Laplace pressures and larger chemical potential gradients. Finally, the molar volume of gas molecules is substantially higher than that of oils. These differences, coupled with the fact that often the bubble dispersions are open to an air surface at the top of the product effectively acting as an infinite sized bubble, all serve to make disproportionation a considerably faster process, not only limiting the long term shelf life of the bubble system, but also its short term stability. For an isolated bubble of size R in an open system, the life time of the bubble has been estimated to be τR^3 [16, 17], where

$$\tau = \frac{P_0}{6\gamma S D_g R_g T} \quad . \qquad (1)$$

Under atmospheric pressure of $P_0 = 100$ kPa and at room temperature $T = 298$ K, the value of τ is found to be $6.872 \times 10^{15}\ \mathrm{s\ m^{-3}}$ if one takes the gas-water surface tension as $\gamma = 0.07\ \mathrm{Nm^{-1}}$, gas diffusion coefficient $D_g = 2 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$, Henry's constant for gas solubility $S = 7 \times 10^{-6}\ \mathrm{mol\ N^{-1}\ m^{-1}}$. The quantity R_g appearing in Eq. (1) is the universal gas constant, 8.31 $\mathrm{J\ K^{-1}}$. Thus, for a bubble of size R = 0.1 mm the life time is estimated to be a couple of hours, while for a bubble of size 2 μm (R= 1 μm) the dissolution time can be as short as a few milliseconds.

A few techniques for stabilising small gas bubbles have been explored in the past. One such technique involves the use of highly insoluble gases such as decafluorobutane. The technique is widely used in medical imaging, with gas microbubbles of typical size 3-4 μm acting as the ultrasound contrast agents [18]. For use in food systems, such a method is not available, both due to safety related issues and also the high associated cost. Another technique is to cover the surface of the bubbles with surfactants that tend to crystalize on the surface of the bubbles once they are adsorbed [19]. Microbubbles surviving up to a year have been reported using this method [20], although the limitation in the type of surfactant used and the inevitable competitive adsorption with other amphiphilic molecules always present in foods, has meant that the method has not been pursued much further. Yet another approach to stabilising very small bubbles is the so called Pickering route [21, 22]. In this approach it is the adsorption of small nanoparticles, as oppose to molecular species, onto the surface of droplets or bubbles that is responsible for their colloidal stabilisation. Although known for quite some time, the first systematic studies of Pickering emulsions were carried out by Binks and Lumsdon in a series of studies [23-26] , and later extended to bubbles by the same and other researchers [27-29]. As with any other type of emulsion or foam, strictly speaking, droplets and bubbles stabilised by particles remain thermodynamically unstable. However, due to the considerably higher energies involved in the displacement of suitably adsorbed particles from air-water or oil-water interfaces [21, 30], for all intents and purposes the bubbles or emulsion droplets are indefinitely stable. For example, for nanoparticles of size 20 nm, possessing the appropriate surface chemistry to give a contact angle of around 90^0, the adsorption energy can easily be thousands of k_BT. For this reason, interfacial networks of such particles provide an excellent means for controlling the dissolution of microbubbles.

Experimental work involving a variety of proteins, including strong and weak film forming proteins such as β-lactoglobulin and gelatin, has shown that such biomacromolecular based interfacial films do not possess sufficient strength to withstand the Laplace pressures inside the small bubbles [16]. Consequently, the macromolecules either desorb from the surface as the bubble shrinks or, where they form cross-linked films, the interfacial layers buckle and crinkle until only a shrivelled up shell of protein is left behind. In contrast, particle stabilised bubbles, once they are generated, retain their size for periods of days with no appreciable shrinkage [29, 31] or sign of dissolution.

Whilst the adsorption of nanoparticles onto the surface of bubbles is certainly capable of arresting disproportionation, there are a few factors that have limited the use of this approach in food industry. Prominent amongst these is the availability of edible grade nanoparticles of the right size, with suitable contact angles to adsorb at the interfaces. Fat crystals are often considered as one possibility, but seem to be better suited to the stabilisation of W/O rather than O/W or bubbles [32]. Indeed in food systems, such fat particles are often thought to contribute to the destabilisation and coalescence of bubbles, as is demonstrated by the poor foaming ability of whole milk when compared to skim milk [33]. Additionally, inclusion of saturated solid fat in foods is not particularly encouraged. A different possibility involves particles of ethyl cellulose [34] or indeed complexes of ethyl cellulose with cellulose [35]. Although promising results have been reported using this method, the smallest reported bubble sizes are of the order of a few tens of microns. Given that the size of the prepared ethyl cellulous particles tends to be ~ 100nm to 200nm [34], it will be difficult to envisage stabilisation of bubbles much smaller than those already reported.

Yet another type of edible particle with potential for use in foods is based on the use of the fungal proteins, called hydrophobins. These have been the subject of much recent interest, in particular in relation to their foamability and foam stabilisation properties [36-42]. Hydrophobin is a highly globular protein with an adsorption behaviour that resembles that of very small nanoparticles. Notably, unlike more typical globular proteins, hydrophobin does not undergo any substantial unfolding upon its adsorption onto hydrophobic interfaces [38]. This property, coupled with high surface activity of hydrophobin, makes it an excellent choice for stabilising bubbles against a variety of possible colloidal instability mechanisms. For example, hydrophobin-stabilised bubbles showing no sign of disproportionation for at least four days have been reported by Cox et al. [41]. The importance of the small size of hydrophobin "particles", and hence their fast diffusion rates to newly created interfaces, has been highlighted by Green et al. [36]. This latter property is of prime importance when considering the stabilisation of small microbubbles, as we shall discuss below. Microbubbles, purely stabilised by hydrophobin, with an average size of 7 μm were reported by Tchuenbou-Magaia et al. to display only a modest degree of coarsening after 20 days [43]. At present, the difficulties in extracting hydrophobin and its high cost have limited its widespread use in foods, although only relatively low concentrations of hydrophobin are required to exert their effect [37, 38, 41] and cheaper sources of this protein are likely to become available in the future.

In emulsions, the process of Ostwald ripening typically occurs rather slowly and as such is only of significance during storage and over longer time scales. More specifically, during the early stages of emulsification, where the freshly created surfaces are being covered by amphiphilic stabilising species, Ostwald ripening is of no particular concern. This situation is dramatically altered for small microbubbles stabilised by particles. Firstly, the diffusion coefficient of nanoparticles to the surface of bubbles will be considerably smaller than that for surfactant molecules, making the coverage of the interface a relatively slower process. Secondly, as was remarked above, the disproportionation and the dissolution of small bubbles progresses at a much faster rate than the Ostwald ripening, particularly where the bubble dispersion may also be open to the air above. Indeed in dilute bubble dispersions, the dissolution process may become the dominant short term instability mechanism, overtaking coalescence. In a recent paper [44], we have theoretically analysed the consequences of finite time durations for the transport of a sufficient number of particles onto the surface of newly created bubbles produced under quiescent conditions [44]. Examples of such processes are bubbles generated in situ as in fermentation, through ultrasound cavitation [19] or even gentle bubbling of gas into the food product. Depending on their initial size, it was shown that the bubbles can undergo a large degree of shrinkage before enough particles are gathered to prevent further dissolution. Interestingly, in a distribution of bubble sizes with enough particles present to stabilise all the bubbles at their initial size, it is the small bubbles with a radius below a characteristic value R^* that suffer the largest degree of gas loss. Bubbles much larger than R^*, although these only become completely stabilised later on, actually suffer very little shrinkage prior to doing so [44]. However, the shrinkage rates of different sized bubbles in the system occurs more of less independently. Experimental results seem to indicate the existence of such a limiting radius for a given concentration of particles, below which bubbles are no longer stabilised against dissolution [28].

The interplay between the kinetics of particle adsorption and the disproportionation process become even more complex when the system does not contain a sufficient number of particles to cover the initial surface of all bubbles. The bubbles of different sizes compete with each other for the number of available particles. Our preliminary theoretical results, for the evolution of bubble size distributions under such circumstances, indicates that the depletion of nanoparticles at the early stages of the process, due to their adsorption onto the surface of smaller bubbles, leaves the larger bubbles with very few remaining particles towards the end of the process. Consequently, even the larger bubbles which normally would have been stabilised without much shrinkage, now undergo a large degree of gas loss [44]. We have demonstrated that the final size of the bubbles becomes particle number limited rather than particle flux limited, as the initial concentration of the stabilising nanoparticles is decreased. These results also provide a preliminary indication that in the former case the spread of the bubble size distribution actually decreases compared to that for the initial distribution, whereas in the latter case it becomes broader [44]. Experimental evidence for such a behaviour in particle stabilised bubbles have been clearly reported by Stocco et al. [45], though one has to keep in mind that their experiments were carried out on relatively concentrated bubble dispersions, not prepared under quiescent conditions, as had been assumed in our calculations. In the present work we investigate this phenomenon in more detail by considering the variation in the width of the bubble size distribution with time for systems consisting of different amount of particles and bubbles. We also perform the calculations for initial bimodal distributions, where only two possible bubble sizes exist. Though of course only an idealised bubble size distribution, the results of such calculations provide a much better insight into how the dissolution of different sized bubbles becomes coupled through their competition for the finite number of particles available in the system. It is interesting to note that this remains true even where the system is open to the air above and therefore the bulk concentration of dissolved gas faraway from individual bubbles remains constant throughout the whole process. In the next section we give a brief account of our calculation methodology, already presented in more detail in a previous publication [44].

2. Theory and method

For an isolated bubble of initial size R(0), not stabilised by any surface active species, the dissolution and shrinkage of bubble is described by the rather well known theory of Epstein and Plesset (EP) [46]. This is based on the diffusion of gas from the vicinity of a bubble to the surrounding bulk solution, resulting from the concentration gradients between the two, caused by the higher excess Laplace pressure inside the bubble. There are many reported experimental results which have supported the EP theory [47, 48] . In the literature concerning bubbles in foods alternative theories have also been considered [49]. One such example is the theory of de Vries [50], where the diffusion of gas only occurs over a thin layer close to the surface. The thickness of this layer is not easily determined but rather is dependent on the conditions encountered by the bubble. As such, the layer thickness often appears as an adjustable parameter in the theory. Both the theory of de Vries, as well as a slightly simpler form of Epstein and Plesset analysis (which ignores the very short lived initial transients) have been extended by Kloek et al. [51] and by ourselves [16, 17] respectively, to included cases involving the presence of viscoelastic interfacial films on the surface of bubbles. Furthermore, we have considered a modification of EP theory to account for the shrinkage of bubbles trapped just beneth a flat air-water interface. The experimental data for the variation of radius with time for such bubbles, stabilised by a variety of different proteins, have been found to agree very well with the predictions of this theory [16]. Consequently, we shall take the rate of dissolution of a bubble to be that governed by the staedy state form of the EP theory. For a bubble far from the flat air-water surface this becomes

$$R(t) = \left(R(0)^3 - t\right)^{1/3} \quad , \qquad (2)$$

where R(t) is the radius of the bubble at time t. In writing the above equation, and from now on, we take the unit of length as that of the average initial radius, <R(0)> , and that of time as $<R(0)>^3 \tau$, where τ is given by Eq. (1). Nonetheless, we stress that it is relatively easy to substitute other alternative forms for the relation between R(t) and t in the analysis presented below, if these are found to be more appropriate for a given system.

As more particles arrive on the surface of a bubble, while it also shrinks, the coverage of the surface of the bubble by nanoparticles, λ, increases with time. At some point, when the surface coverage reaches a threshold value, λ^*, the network of adsorbed particles at the interface develops an interfacial yield stress and therefore starts to resist compaction. With further dissolution leading to a higher particle surface coverage, the value of this interfacial yield stress increases until it can withstand the stresses in the “2D” particle network which result from the Laplace pressure inside the bubble. The situation envisaged is somewhat analogous to that for the compaction of three dimensional networks as for example can occur during the sedimentation process [52] . The exact nature of the variation of the interfacial yield stress with λ and the exact value of λ^*, are sensitive functions of the shape of the nanoparticles, their polydispersity and more crucially, the type of colloidal interactions that may exist between them [53-55]. To our knowledge no generally accepted expressions for the λ dependence of the interfacial yield stress for such a particle network, adsorbed on a surface has been proposed so far [56]. Nonetheless, in line with the predictions of the 2D percolation theory, it is expected that such a function will be a rapidly increasingly one for particle surface coverage values beyond λ^*. Therefore, to a first approximation, it is reasonable to take this function to be a simple stepwise function, with the interfacial yield stress being zero below λ^* and sufficiently high above so as to arrest the shrinkage of the bubbles. This was also the approach which was adopted previously [44]. Thus, in such a model, a bubble will continue to shrink unhindered until its particle surface coverage attains the threshold value, whereupon it is stabilised by the network of adsorbed particles and ceases to shrink further. In reality, the abrupt halt to the dissolution of the bubbles is expected to take the form of a relatively fast slowing down of the shrinkage once λ exceeds λ^*, before the dissolution process is completely arrested.

It is useful at this stage to define two dimensionless numbers as follows

$$\nu = \frac{\lambda^*}{\pi \, \mathrm{D_p n_0} < \mathrm{R}(0) >^2 \, \mathrm{R_p^2} \tau} \tag{3}$$

and

$$\beta = \frac{\mathrm{n_0 R_p^2}}{4\mathrm{N_b} < \mathrm{R}(0) >^2 \, \lambda^*} \quad , \tag{4}$$

where R_p is the radius of the nanoparticles, D_p their diffusion coefficient, given by Stokes-Einstein equation $k_BT/(6\pi\eta R_p)$, n_0 their number density and η the viscosity of the dispersion medium. The number density of bubbles in the system, having an initial average radius <R(0)>, is denoted by N_b. The first of these numbers, ν in Eq. (3), is the ratio of two time scales as follows. The first is the time for a typical bubble (i.e., one with a radius ~ <R(0)>) to reach the threshold particle surface coverage λ^*, assuming no shrinkage. The second is the life time of the bubble if it was not stabilised and thus shrank and disappeared completely. Following others, we have taken the movement of the nanoparticles to be essentially a diffusive one under the quiescent conditions studies here [57-60]. It is clear that in systems with a large value of ν there will be a high degree of gas loss and a substantial decrease in the size of bubbles before they are stabilised. The second dimensionless number β, as defined by Eq. (4), provides an estimate of the maximum total surface area that can potentially be stabilised by the nanoparticles, expressed roughly as the ratio of the total initial surface area of the bubbles. For simplicity, we have taken the contact angle for the adsorbed nanoparticles on the surface of the bubbles as 90^0 here and throughout the paper. The generalisation to other angles though is relatively straightforward. Small values of β in a system indicate that the dispersion is deficient in particles. Once again, in such cases a high level of bubble shrinkage is expected. However, note that on this occasion the size of the bubbles becomes limited by the number of particles available in the system rather than the rate of their arrival onto the surface of the bubbles. The transition from "adsorption controlled" to "particle number controlled" regimes were predicted in our previous analysis [44] but will be highlighted more clearly here.

The dimensionless numbers ν and β between them specify the evolution of the bubble size distribution function in our model. The value of the particle surface coverage on a bubble increases both as a result of its shrinkage and also the arrival of new particles onto its surface.

Taking both of these terms into account, the time dependence of λ in our chosen units of length and time, <R(0)> and τ<R(0)>^{3}, is described by the following equation

$$\frac{d\lambda}{dt} = \frac{2\lambda}{R(t)}\frac{dR}{dt} + \frac{\lambda^*}{vR(t)}\frac{n(t)}{n_0} \quad , \tag{5}$$

where n_0 and n(t) represent the number density of the particles remaining in the bulk (i.e., still not adsorbed) initially and at a later time t. For values of $\lambda < \lambda^*$ the rate of shrinkage dR/dt is obtained from Eq. (2), whereas for $\lambda > \lambda^*$ it is zero. The second term on the right hand side of the Eq. (5) may similarly become zero at some stage when $\lambda = \lambda_{max}$, representing the maximum degree of packing of particles on the surface of the bubble. The values of λ^* and λ_{max} are generally not the same, though for particles solely interacting through a hard sphere type potential that only form adsorbed monolayer of particles, they are expected to be quite close. It is interesting to note that if the particles form multilayers then the value of λ can become larger than one. For such systems, the ratio n(t)/n0 in Eq. (5) has been shown [44] to fall according to

$$\frac{n(t)}{n_0} = \exp\left(-\frac{1}{\nu\beta}\int_0^t < R(t') > dt' \right) \tag{6}$$

With time, as the bulk becomes increasingly depleted of nanoparticles. The set of equations (2), (5) and (6) can now be integrated together to obtain the distribution of bubble sizes at any given time. For some special cases this can be achieved analytically [44], though in more general cases resort to numerical solutions has to be made. We presented and used one such possible scheme in a previous publication [44]. In such a scheme the bubbles are divided into a large number of size intervals. Using the discretised form of equations (2) and (5), the size and the degree of coverage, λ, for bubbles in each size range is updated over a short time period. Similarly equation (6) is used to update the number of remaining particles, after the same time interval. The process is repeated over many such time intervals until bubbles of all sizes in the distribution are found to be stable (i.e. have $\lambda > \lambda^*$). As the initial size ranges tend to become broader with time, it is necessary to split the intervals into two at appropriate stages, in order to ensure that the numerical accuracy of the scheme is maintained. The details of how this is achieved can be found in a previous publication [44] and therefore will not be repeated here.

In next section we examine the numerical solution to the set of equations (2),(5) and (6), obtained through the procedure above, to study the evolution of bubble size distribution under a variety of different initial conditions.

3. Results and discussion

3.1 Results for cases involving an initial normal size distribution

The size of the globular protein, hydrophobin, is known to be 2 - 3 nm [61, 62]. However, in aqueous solutions hydrophobin molecules tend to associate to form at least dimers so as to protect the hydrophobic patch on their surface from contact with water. Wang et al. report a hydrodynamic radius of ~ 3.5 nm for such hydrophobin oligomers [63], obtained using dynamic light scattering. Therefore, in this work also we also take the radius of our "hydrophobin-like" nanoparticles to be 3.5 nm. Typical concentrations of hydrophobin used in a number of recent experimental studies [37, 38, 41] to stabilise foams have been in the range 0.001% to 0.1% w/w (or around 0.00075% to 0.075% v/v). To our knowledge no accurate results regarding the "effective contact angle" or the critical threshold coverage required to stabilise the foams have so far been reported for hydrophobin in the literature. However, without any significant loss of generality, one may take these to be 90^0 and $\lambda^* = 0.5$, respectively. In particular, we note from Eqs. (3) and (4) that a different set of values for these parameters will only imply a slightly different set of concentrations of particles and bubbles in the system if the same dimensionless numbers ν and β are used in the calculations.

The graphs in Fig. 1 display the bubble size distribution function at different stages during its evolution. The initial distribution (short dashed line) was chosen to be a normal distribution with a standard deviation of 0.15 <R(0)>, while the final one, when all the bubbles are stable, is represented by the solid line. Two other curves show the size distribution function at intermediate stages, t=0.5 and t=1.0, prior to the complete arrest of dissolution. The results were generated for bubbles of initial mean radius 3.5 μm at an initial gas volume fraction of 40%. The concentration of "hydrophobin-like" particles was set at 0.04% v/v. As expected, the distribution shifts as a whole towards lower bubble size values with time. It also broadens at first since the small bubbles shrink more rapidly than larger ones. It is these smaller bubbles that reach the critical threshold particle surface coverage earlier on during the process, whilst still suffering a larger degree of overall gas loss. It is also clear that the distribution function breaks up into two distinct parts in the intermediate stages. One part, at the lower end of the size range, represents the bubbles stabilised already. The other involves bubbles that as yet have not gathered the required number of particles on their surface to prevent them from shrinking. The sharp discontinuity between the two parts is the consequence of the approximation made in our model whereby disproportionation ceases abruptly as soon as the particle surface coverage for the bubble reaches λ^*. In practice, arrest of the dissolution will be a more gradual process, as λ approaches and then exceeds λ^*. If this is taken into account, it leads to a degree of the rounding of the sharp discontinuity in our calculated results. Nonetheless, a bimodal type size distribution function would still be predicted at intermediate times, before all the bubbles become fully stable.

As the small bubbles become stable and cease to shrink further, whilst the large bubbles continue to decrease in size, it is clear that the bubble size distribution function will stop broadening at some point and will begin to become narrower once again. This indeed is the case for the system considered in Fig. 1. The effect is even more clearly displayed in the graphs of Fig. 2, where we have tracked the time variation of the average radius, $<R(t)>$, and its standard deviation, $(<R(t)^2>-<R(t)>^2)^{1/2}$, for the system of Fig. 1. Two other systems with smaller concentrations of nanoparticles, at 0.02% (dashed line) and 0.01% (solid line), are also included for comparison. The initial bubble size distribution function and the volume fraction of bubbles (at 40% v/v) were kept the same for all three systems. The initial broadening of the distribution function, followed by its narrowing, is evident in Fig. 2b. It is interesting to note that the variation of the standard deviation of bubble radii is more extreme for the system with the smallest amount of particles, i.e., with 0.01% v/v (the solid line). The reasons for this will be discussed in more detail in the next section. It suffices for now to say that in systems devoid of a sufficient number of particles, the presence of small bubbles has a much stronger influence on the degree of the shrinkage of the bigger bubbles. The effect diminishes as the concentration of the nanoparticles is increased, with bubbles of different sizes evolving more or less independently of each other in such particle rich dispersions.

Both sets of graphs in Fig. 2a and Fig. 2b, showing the temporal variation of the average bubble radius and its standard deviation respectively, display an initial period in which all three systems evolve in an identical manner. This is the time period during which none of the bubbles, whether large or small, have yet become stable. Although the amount of particle surface coverage at any given time, for bubbles of the same size in each of the three systems, would clearly be different, since the particles have not formed a network on the surfaces to resist dissolution, the rate of shrinkage of the bubbles is identical. The curves do start to diverge as soon as the smallest bubbles begin to stabilise. This of course should occur sooner in a system with a larger concentration of nanoparticles, in line with the results of Fig. 2. Similarly, the average radius does not drop quite as much (see Fig. 3a) in systems containing a larger number of particles, as may be expected. However, it is important to note that even when there are a sufficient number of available nanoparticles to eventually stabilise all the bubbles, the average radius still decreases to a final value smaller than the initial one. In such systems, it is not the availability of particles that governs the final average size but the rate at which such particles arrive at the fresh gas-water interfaces. This gradual switch from a final bubble radius that is "particle number density controlled" to "particle adsorption rate controlled" is best demonstrated by considering a slightly different situation. In the next set of graphs in Fig. 3, we have kept the number of particles fixed and instead have varied the volume fraction of the gas bubbles. By keeping the concentration of available nanoparticles the same, we ensure that the rate of diffusion of these to the surface of the bubbles remains, at least initially, identical in the three systems considered. The gas volume fractions were set at 40% (dashed line), 10% (dash-dotted line) and 2% (solid line). The average initial bubble radius was set at 7 μm this time, with that of the particles at 3.5 nm, same as before. In all cases the volume fraction of stabilising nanoparticles was 0.01% and the starting bubble size distribution function was a normal distribution, the same as the one shown in Fig. 1. The graphs in Fig. 3a demonstrate the changes occurring in the average radius of the bubbles with time, while those in Fig. 3b show the variation in the standard deviation of the bubble radii over the same time period. Once again, it is clear that the largest variation in the standard deviation, $\sigma(t)$, occurs for the case with the smaller ratio of particles to gas bubbles (Fig. 3b). It is also worth noting that in such cases the final bubble size distribution is narrower than the original starting one (0.07 as compared to 0.15). The opposite is true when the dispersion is rich in nanoparticles, as seen from the graph for the 2% v/v of gas bubbles (0.164 as compared to 0.15). There is some tentative experimental evidence supporting this prediction, albeit obtained under somewhat different conditions than those for which our calculations are strictly valid [45]. The experimental data suggest that a broader bubble size distribution results when the concentration of the stabilising nanoparticles is increased. For the system with an initial gas volume fraction of 40% the final average bubble radius is 0.48<R(0)>, less than half its original value (Fig. 3a, the dashed line). Starting with a perfectly monodisperse bubble size distribution, it is a trivial matter to show that the final size ratio of the bubbles would be ~ $\sqrt{\beta}$, if the final size was purely limited by the number of available particles in the system [44]. For a system with a starting 40% v/v of gas, the value of β as defined by Eq. (4) is 0.2. This then suggests a final size ratio of 0.5. This is in good agreement with the value 0.48 obtained in Fig. 3a, considering that our starting bubble size distribution function here was not a monodisperse one. The final average bubble radius increases as the initial amount of the gas is reduced to 10% and then further down to 2% (Fig. 3a, dash-dotted and solid lines, respectively). Furthermore, the final value is achieved quicker in systems with a lower initial volume of bubbles. However, this scenario only holds true down to a certain volume fraction of gas. Our calculations performed for even more dilute gas dispersions, indicate that there are no substantial changes in the final average radius of the bubbles once the initial volume fraction of these is below ~ 2%. For example, the curves for 0.5% v/v of gas (not shown here) were almost indistinguishable from the 2% (the solid line) in figures 3a and 3b. Clearly then, for these very dilute bubble systems, it is not so much the availability of nanoparticles relative to the gas bubbles that governs the final bubble size, but rather their rate of arrival and adsorption onto the surface of the bubbles. By keeping the number of particles at 0.01% v/v, while only altering the number of bubbles, we keep the initial rate of diffusion of the particles to the surface of the bubbles the same in all cases. Thus, in the "particle adsorption rate controlled" regime the starting volume fraction of the bubbles is seen to be of no relevance in determining the final size ratio at which the bubbles are eventually stabilised.

In a system deficient in nanoparticles and having a polydisperse distribution of bubble sizes, the impact of the low number of particles is more acutely felt by the larger bubbles. To see why this is the case, consider the graphs in Fig. 4. These provide the value of the bubble radius below which the bubbles are no longer shrinking, plotted as a function of time. The results are obtained for the same systems as those in Fig. 3. It is obvious that irrespective of the initial amount of gas, the small bubbles in all three systems are the ones that are stabilised first, with the larger ones taking a longer time to achieve the required particle surface coverage. However, the difference in the stabilisation time between the large and small bubbles is far more pronounced in the system most deficient in particles (Fig. 4, dashed line). Secondly, the stabilisation time for very small bubbles, in all three cases, are more or less identical as can be observed by the overlap of the curves at small values of R and t. This indicates that for these smaller bubbles, the final radius is "particle adsorption rate controlled". For the bigger bubbles, the final predicted size and the stabilisation times are quite different and both strongly dependent on the initial volume of the bubbles present in each system, because they are in the "number of particles controlled" regime. It is also instructive to consider the variation of the amount of remaining particles in the bulk solution as a function of time, and to contrast these for the three cases studied in Fig. 3. This has been done in Fig. 5, where the concentration of the non-adsorbed particles is expressed a fraction of its original value at t = 0. Not surprisingly the drop is most rapid for the 40% v/v gas system, whilst for the 2% v/v case the concentration of particles in the solution remains fairly uniform throughout the whole process, up to and including complete arrest of dissolution of all bubbles. For a small bubble which stabilises after a time period of say t = 0.1 to 0.2 (in our normalised time units), the rapid drop or otherwise of the concentration of available particles in the bulk solution is not of great importance. Even for the 40% bubble system, it can be seen from Fig. 5 that the value of $n(t)/n_0 \sim 0.7$ at the time of stabilisation. In contrast, for a large bubble with a stabilisation time of 3.0, for example, the bulk solution is almost devoid of any nanoparticles by the time this bubble stops shrinking, in a 40% v/v gas system. Thus, larger bubbles in the particle deficient systems (i.e. low values of β) undergo a relatively greater degree of shrinkage compared to those in a particle rich dispersion (large β). This explains the significantly narrower final size distribution function predicted to arise in the latter cases. Different final size distribution functions for each of the three systems considered in Fig. 3 are presented for comparison in Fig. 6.

3.2. Cases with an initial bimodal bubble size distribution

As seen in the previous section, the final size ratio for the bubbles in the lower end of the size distribution range was "particle adsorption limited". As such the presence of the larger bubbles had little influence on the final degree of shrinkage of these smaller bubbles. In contrast, the bigger bubbles have their final radii largely governed by the number of available particles. Therefore, the value of the final size ratio for these is much more sensitive to the presence of other bubbles. In particular smaller bubbles, whilst only containing a modest fraction of the total gas in the system, present a disproportionately larger surface area onto which the nanoparticles will be adsorbed. Hence, by depleting the concentration of the particles in the bulk solution more rapidly, their presence can significantly alter the final size of the larger bubbles and as such the total amount of the gas that is retained in the dispersion.

To study the above effect in more detail, in this section we shall consider a somewhat hypothetical initial bubble size distribution function, consisting only of two bubbles sizes; a larger bubble size of radius 10.5 μm and a smaller one with radius 3.5 μm. It would be useful to make the size difference between the two sets of bubbles in the study even larger. However, this makes the numerical calculations very time consuming indeed. Fortunately, with the values of 10.5 and 3.5 μm used for the radii here, it is still possible to clearly demonstrate the effect we wish to discuss here. We shall keep the total initial concentration of the gas at 30%, but vary the portion of this gas that is contained in the larger bubbles by a relatively small amount from 100% down to 90%, in different systems. The concentration of the nanoparticles is likewise set to a fixed value of 0.01% and as before these have a size 7 nm in all the cases we consider. Figure 7 displays the final bubble radius attained by the larger bubbles, plotted against the fraction of the gas initially contained within such bubbles. The stable radius for these bubbles changes by around 14% from ~ 7.1 μm in the absence of the smaller bubbles, down to 6.1 μm when 10% of the initial gas is contained in the smaller bubbles. At the same time, the final radius of the smaller bubbles remains almost constant, around 1.4 μm for all the systems in Fig. 7. Thus, while the small bubbles do undergo a considerable degree of shrinkage and gas loss, their final size ratio of ~ 0.4 is more or less independent of the choice of our starting size distribution function. These findings are quite consistent with the fact that the final radius of the smaller bubbles is “particle adsorption limited” here, whereas that of the larger ones is essentially determined by the degree of availability or the lack of nanoparticles. The same calculations were also repeated at a considerably higher nanoparticle concentration. As expected, the level of shrinkage for both sets of bubbles was less. However, this time no significant variations between the stable radii of the bigger bubbles from one system to another were noticed. With the system rich in the stabilising nanoparticles, the final radius of the bigger bubbles is also now “particle adsorption controlled” and therefore no longer effected by the presence of other bubbles.

The more extensive shrinkage of the larger bubbles due to the presence of smaller ones, in the particle deficient systems, clearly impacts the final fraction of gas that is retained in these cases. In Fig. 8 we display the percentage of the retained gas relative to that present at the beginning, plotted against the fraction of the gas contained in the large bubbles. The percentage of the retained gas in the dispersion containing 10% of small bubbles is only two thirds of its value when all the gas incorporated was done so as large bubbles. In particular, had the large bubbles not been affected by the depletion of particles adsorbed onto the smaller bubbles, the expected final radius would have been 7.1 μm. This means that the fraction of the retained gas would have been around 27%, rather than ~ 20% for the system with 10% of small bubbles (Fig. 8). It could be that it in some applications the inclusion of a broad bubble size distribution may be of some interest. However, more generally, if the aim is to stabilise the larger bubbles and to retain the largest possible portion of the gas in the system, then the presence of the smaller bubbles seems to be undesirable.

4. Summary and Conclusions

We have considered the manner in which an initial bubble size distribution function evolves with time, in systems where the bubbles become stabilised against disproportionation as a result of adsorption of a sufficient number of nanoparticles onto their surface. The combination of rapid dissolution and the slow particle transport and adsorption, coupled with the competition of bubbles of different sizes for capturing the limited number of the nanoparticles, gives rise to a rich variety of behaviour. It has been shown that the spread of the bubble size distribution function increases at first, as the smaller bubbles tend to shrink more rapidly than the larger ones. Later on in the process, the distribution begins to narrow again, before the full stabilisation of all bubbles is achieved. The magnitude of the variation in the spread of the size distribution function during these intermediate stages is sensitive to the number of available particles. Indeed, the distribution function can end up being broader than the original starting one if the system has a sufficient, but not too large an excess of nanoparticles. For dispersions deficient in particles the opposite is true. Stocco et al. [45] have recently reported experimental results involving particle stabilised bubbles that seem to follow this predicted trend. This effect arises as a result of the competition between different sized bubbles for the adsorption of nanoparticles and the speed with which the bulk solution becomes depleted from these particles. One possible application for which a narrow distribution of bubble sizes may prove useful includes refractive index enhancer agents as for example in paints and coatings. Here it is rather desirable to have a tight bubble size distribution of ~ 0.5 μm, the same as the wavelength midway in the visible light spectra. The same is also true of ultrasound imaging contrast agents, based on the presence of microbubbles. Again the optimal bubble size for such agents is well defined and a narrow spread around this size can considerably improve the efficiency of the agent. By examining the behaviour of simpler systems, consisting of only two different bubble sizes, we have demonstrated the strong influence that the presence of the smaller bubbles exerts on the final size for the larger bubbles. Interestingly, the reverse does not hold and the degree of shrinkage of the small bubbles remains independent of the amount of larger bubbles. The effect is significantly more prominent when the system lacks a sufficient number of particles to cover the initial surface of all bubbles, but diminishes for dispersions rich in particles, whereupon the final radii of large bubbles also become independent of the initial starting distribution. The shrinkage of the larger bubbles is noticeably increased in the presence of the smaller bubbles. Thus, the inclusion of a small portion of the gas in the form of smaller bubbles has a disproportionately detrimental effect on the total amount of gas that is eventually retained, up and above that which would simply be lost from such small bubbles themselves.

The calculations carried out here were done so for nanoparticles with a similar size to those measured for hydrophobin oligomers in aqueous solutions. Similarly, the concentrations of the particles are typical of those used in the stabilisation of foams by hydrophobin, as reported in the literature. Nevertheless, we should stress that the particles here should not entirely be equated with hydrophobin. For example, the adsorption of hydrophobin causes a substantial decrease in the interfacial tension, unlike that exhibited by most types of adsorbing particles. The variation in the value of the surface tension, with a changing level of adsorbed hydrophobin at the surface, has to be reflected in the equations describing the dissolution of the bubbles. Also, in many cases hydrophobin is not the only protein present, but it is used in conjunction with other surface active molecules [37, 38]. For some of these, e.g. β-casein, all that this entails is a simple change in the value of the surface tension in the calculations (viz. Eq. (1)). For others though, e.g. β-lactoglobulin, capable of forming cross-linked networks on the interface, the effect of the resulting visco-elastic film on the shrinkage kinetics of the bubbles needs to be reflected in the theory. This can be achieved by the use of more complicated equations to describe the dissolution of the bubbles covered by such layers, along the lines proposed in the literature [16, 17, 51], within our model. One final additional point to make is that the results presented in the current work have involved systems which are essentially open to the air above. It is a rather interesting to speculate how this situation may alter if the system was closed, i.e. the total amount of gas was conserved. For in such a case, as well as the concentration of the nanoparticles, the amount of dissolved gas in the bulk solution also varies with time. One may equally pose the same question in another way by asking, how does the classical theory of Ostwald ripening becomes modified in the light of the slow kinetics of the adsorption and the limited number of available stabilising nanoparticles in a system? An analysis of this more complex problem is deferred to future work.

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