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Effect of Particle Adsorption Rates on the Disproportionation Process in Pickering Stabilised Bubbles

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Abstract

The degree of shrinkage of particle stabilised bubbles of various sizes, in a polydisperse bubble dispersion, has been investigated in the light of the finite adsorption times for the particles and the disproportionation kinetics of the bubbles. For the case where the system contains an abundance of particles we find a threshold radius, above which bubbles are stabilised without any significant reduction in their size. Bubbles with an initial radius below this threshold on the other hand, undergo a large degree of shrinkage prior to stabilisation. As the ratio of the available particles to the bubbles is reduced, it is shown that the final bubble size, for the larger bubbles in the distribution, becomes increasingly governed by the number of particles, rather than their adsorption time per se. For systems with "adsorption controlled" shrinkage ratio, the final bubble distribution is found to be wider than the initial one, while for a "particle number controlled" case it is actually narrower. Starting from an unimodal bubble size distribution, we predict that at intermediate times, prior to the full stabilisation of all bubbles, the distribution breaks up into a bimodal one. However, the effect is transient and an unimodal final bubble size distribution is recovered once again, when all the bubbles are stabilised by the particles.

1 Introduction

One of the major challenges in incorporation of fine stable bubbles into foam systems involves the problem of overcoming the inherent instability of the gas bubbles against disproportionation. This becomes a particularly important issue for bubbles of size 100 μm or smaller.[1-3] Like its related counterpart Ostwald ripening in oil emulsions, the disproportionation process is driven by the movement of molecules from regions of high chemical potential to those with a lower value. For a closed foam system, this means the migration of gas from small bubbles to larger ones, causing a gradual coarsening of the foam. For an open system, the same phenomenon results in the loss of gas to the surrounding air and eventual dissolution and disappearance of the gas bubbles. While Ostwald ripening in emulsions is a relatively slow process, occurring over time scales of days, weeks or even months, disproportionation in foams progresses at a considerably faster rate. This is due to a combination of several factors: 1) the generally higher interfacial tension between gas and water as compared to that of oil and water 2) higher solubility of gases in water, and most significantly 3) the much higher molar volume of gases compared to oils. For example the molar volumes of typical food fatty acids, such as oleic or palmitic acids is around 0.3 dm^3/mol, as compared to 25 dm^3/mol for gases at room pressure and temperature.

It is often possible to modify the bulk oil phase in a way that greatly reduces or even arrests Ostwald ripening. A particularly well known method involves the introduction of a small amount of highly insoluble species into the oil phase.[4] As small oil droplets decrease in size, the concentration of the impurity increases within them. The osmotic pressure differences, thus generated between the interior of different sized oils, suffices to make the chemical potential of the oil phase identical in all emulsion droplets.[5, 6] Therefore, the migration of oil molecules from small to larger droplets is completely halted. The same approach is much harder to achieve in gases, not least of all because it is difficult to find gases with small molecules that have very low solubility in water. One example of such low solubility gases are C_nF_m based perfluorocarbon gases,[7] often used as ultrasound contrast agents.[8] However, additional restrictions due to cost and safety issues make the osmotic pressure approach even less feasible in food foams and food related bubble systems. Therefore, techniques for stabilising gas bubbles against dissolution have almost exclusively concentrated on the modifying interfacial properties on the surface of bubbles.

It is well known that in order to stop disproportionation it is necessary to adsorb a surface active species onto the surface of the bubbles capable of forming an interfacial elastic film.[9, 10] This requirement rules out many small surfactant molecules, as well as some widely used proteins such as caseins in food systems which also act like low molecular weight surfactants. Other protein, e.g. β-lactoglobulin, can unfold and cross link on the surface of bubbles[11, 12]and hence produce an elastic film. But it has been shown that even in such cases, often the elastic interfacial film tends to wrinkle as bubbles shrink. The dissolution of bubbles continues and eventually only small protein aggregates remain in the place of what were once gas bubbles.[1] A more effective strategy in recent years has been to consider the stabilisation of bubbles by small nanoparticles, i.e. “Pickering type bubbles”.[13-15] These nanoparticles possess contact angles in a range of values that makes them preferentially reside at hydrophobic-hydrophilic interfaces. The adsorption energies associated with displacing the particles from the surface can easily be of the order of tens of thousands of k_BT, even for relatively small particles with a size of a few tens of nanometer.[16-18] Here T denotes the temperature of the system and k_B the Boltzmann constant. At sufficient surface coverage of the bubbles, the particles form a 2-D network, either through direct contact (hard sphere) or else more specific bonds such as aggregation or even sintering. In either case the films formed can sustain a large amount of interfacial stress without displacement from the surface, due to the magnitude of the particle adsorption energies involve. By taking up the stress, the networks of particles on the surface of bubbles compensate for the Laplace pressure differences and prevent the shrinkage of the bubbles. Since demonstrating the feasibility of the method[13, 19], there has been much interest in the study of particle stabilised bubbles,[3, 14, 20-25] though preparation of Pickering bubbles still remains a more difficult proposition compared to Pickering emulsions.[26]

In achieving the desired bubble stability a number of points have to be considered. In all cases it is necessary to achieve the correct balance of surface activity versus the tendency for bulk aggregation. More hydrophobic particles may be more surface active, but they also flocculate more strongly in the bulk. This in itself may actually help to trap bubbles in a stable network of particles. However, the formation of aggregates also has detrimental effects on stabilisation of smaller bubbles that are not directly incorporated in the particle network. Firstly, finite clusters act as “effective” particles with sizes that are considerably larger compared to those of the primary nanoparticles. Secondly particles that are incorporated in the spanning networks become immobile and can no longer take part in the process of diffusion and adsorption onto the surface of bubbles. This greatly reduces the availability of free nanoparticles in the bulk dispersion. We shall discuss below both the influence of the radius of the nanoparticles and their number density on Pickering stabilisation of bubbles in greater detail. However, in relation to the latter of the two points it is of interest to mention the experiments carried out by Hunter et al.,[27] comparing the two-dimensional behaviour of (silica) particle monolayers with bulk foam stability. It was found that even with the best performing particles, less than 10 % of a given dispersion became incorporated into a stable foam on shaking. On the other hand, Binks and Murakami[28] have shown how the increasing particle hydrophobicity can cause a phase inversion from air-in-water to water-in-air powders, the so called "dry water". These powders may yet find some useful applications in foods and other similar areas. A theoretical study of phase inversion in Pickering stabilized systems, investigating the influence of particle contact angle, particle concentration and the phase volume ratio has recently been reported by Jansen and Harting, based on the use of lattice Boltzmann approach.[29]

Another principle challenge, particularly in relation to Pickering stabilisation of bubbles and emulsions in food systems, is the identification of suitable (i.e., food compatible) particles that can be exploited for this purpose. Solid saturated fat may be an important natural particle stabilizer[30] but health concerns mean that alternatives still need to be sought. Particle-stabilized systems in foods have been reviewed recently by in a number of articles.[3, 14, 31-33] Particles of cellulose and/or cellulose derivatives are promising candidates as Pickering stabilizers of bubbles. Some form of cellulose particle size reduction is normally necessary and as cellulose is not expected to be naturally surface active it has to be made so by the formation of physical complexes between cellulose and ethyl cellulose, as for example has been shown by Murray et al.[23] Ethyl cellulose can itself be used to stabilize a wide range of bubbles sizes, as was demonstrated by Jin et al.[22] In the same study it was found that the ethyl cellulose particles are capable of forming either single or multi-layers on the surface of the bubbles. Ethyl cellulose, waxes, etc., can be precipitated under shear to generate more anisotropic particles to improve foam stabilization efficiency[34]. In particular, more fibre like shaped particles, if sufficiently flexible to adopt to the curvature of the bubbles surface, have a higher desorption energy per unit particle volume and a lower critical particle surface coverage for stabilization. Intriguingly, another recent work has suggested that pure cellulose may itself be a good stabilizer of oil-in-water emulsions.[35] This is of some significance given the large amount of wasted cellulose currently resulting from the agriculture and food production activities.

In many practical systems it is important to realize that the interfacial particle contact angle or 'hydrophobicity' can be affected by a number of factors. Thus ostensibly neutral material such as cellulose may become slightly ionized via harsh acid or alkali processing used to fragment the cellulose in the first place, or via classic adsorption of anions as is illustrated by the wok of Jin et al.[22] Ionization decreases the particle hydrophobicity and the tendency for adsorption onto the air-water or oil-water interfaces. In addition, in most food systems there are low molecular surfactants (e.g., monoglycerides/phospholipids) or high molecular weight amphiphilic macromolecules (e.g., proteins) also present. These can adsorb to the surface of the particles changing their surface activity.[36] Alternatively they may compete with the particles for adsorption onto the surface of bubbles.[37, 38] In some instances there seems to be some synergy between the these surface active molecules and the nanoparticles,[23, 39], whereas the protein hydrophobin seems to behave like a surface active nanoparticle. Much research has recently been devoted to the exceptional stability of bubbles stabilized by hydrophobins. Synergy, or a least compatibility, has also been found between hydrophobin and other surface active proteins.[40, 41] The behaviour of mixed particle + surfactant systems for colloid stabilization and encapsualtion remains a fertile area for further research,[42, 43] but here we return to the situation where the slowest adsorbing entity at the bubble surface is a surface active particle.

In stabilizing small droplets or bubbles, a final major issue is the kinetics of adsorption of nanoparticles to newly created interfaces. Nanoparticles, being much larger than the low molecular weight surfactants or even individual macromolecules, tend to have relatively small diffusion coefficients. This makes the time required for particle coverage to reach the levels necessary to stabilise emulsions sufficiently long for small emulsions droplets to collide and coalesce with each other. This is particularly the case in dense emulsion systems were the rates of droplet collisions are high. As mentioned above, in foam systems disproportionation is also a relatively fast process, to the extent that a substantial degree of shrinkage and dissolution of small bubbles can occur during the period needed for the surface coverage to reach the necessary values.

In section 2, we examine the equations governing the evolution of bubble size distribution function. As we shall see in section 3, in certain cases, and in particular when the system is rich in nanoparticles, or where we have a monodisperse initial bubble size distribution, the equations simplify sufficiently for an analytical solution to be obtained. For the more general case the equations have to be solved numerically. Also in Section 3 we present a suitable numerical scheme for doing so and use this to investigate the evolution of an initial Gaussian distribution of bubble sizes under several different situations (e.g. different ratio of particle size to average bubble size, systems with different concentration of nanoparticles, etc).

2 Mathematical formulation of the problem

2.1 General considerations

Though an interesting problem in its own right, in the current study we shall not discuss the details of the process of formation of the 2D network of particles, on the surface of the bubbles. Nor shall we consider the actual mechanism through which the particles act to stop the disproportionation of bubbles. However, it suffices to say that there exists some critical particle surface coverage, hereafter denoted by λ^*, at which the network develops an interfacial yield stress. Furthermore, that this yield stress increases rapidly with surface coverage from this point onwards and becomes capable of resisting the shrinkage of the bubble. Clearly the value of λ^* will be dependent on the shape, the degree of polydispersity and the nature of interactions between the nanoparticles. There have been a number of theoretical and computer simulation studies in the literature specifically concerned with investigating the formation of such networks and the process through which the interfacial network counteracts the Laplace pressure inside the bubbles.[44-48] Recently there has even been some reports highlighting the formation of non spherical bubbles under the influence of the stresses in the particle network.[25] This is a possibility that can clearly have some bearing on the results of the current work. However, for now the formation of such distorted bubbles will not be included in our model, though one may wish to do so in future.

In this work we focus on dilute bubble systems where the rate of coalescence is not so significant. In such systems disproportionation still occurs and now becomes the main factor in limiting the size of bubbles that can be realistically stabilised by particles. This is particularly the case at moderate viscosities. Addition of thickeners or rheology modifiers has a large impact in slowing down the Brownian movement of the bubbles, thus reducing their collision rates and the flocculation and coalescence that follow as a result. In contrast, such thickeners neither affect the air-gas interfacial tension nor the diffusion of gas molecules to any great extent. That is to say that their influence on the disproportionation kinetics is rather minimal (unless that is, the bubbles are of sub-micron size, where the large shrinkage rates and the resulting stresses may perturb the excess pressure in bubbles at high viscosities). Therefore one may envisage the situation where the dissolution of bubbles becomes the main mechanism of their loss and instability. In our preliminary analysis presented here we will only focus on such cases and for the present will ignore the processes of flocculation or coalescence of bubbles. Extension to cases where such processes are also significant may be possible for coalescing bubbles, though we believe this will be much harder for the case of clustering and flocculation of bubbles. This is due to the distortion of the neighbouring bubbles on the diffusion fluxes of incoming particles and outgoing gas molecules for bubbles in such clusters. A further assumption in our calculation is that our bubble dispersion is open to the air above at all times, a situation that in practice is just as likely as having a closed system. We shall analyse the effects of the competing kinetics of the adsorption of particles on one hand and the disproportionation process on the other in more detail in the next sections. We first give a rough order of magnitude calculation presenting a clearer view of the problem, demonstrating the time scales that are involved in each of the processes that combine to dictate the evolution of the bubble sizes. We then highlight a more detailed mathematical analysis of the problem in order to examine the final size distribution of particle-stabilised bubbles that evolves from a given initial distribution. In addition to disproportion and to the rate of particle adsorption, the presence of a polydisperse distribution of bubbles in a system introduces a third factor in determining the final size of the bubbles. Bubbles of different sizes compete for the adsorption of the available nanoparticles. The flux of particles incident on a small bubble is less than that for a larger bubble. Also, small bubbles shrink at faster rates and have less time to establish the required particle surface coverage. Nevertheless, because the smaller sized bubbles require the adsorption of a fewer number of particles to reach the critical value λ^*, these will tend to be stabilised first. This will have little influence on the shrinkage and subsequent stabilisation of larger bubbles, provided that the bulk concentration of particles is not effected much by their adsorption onto the surface of the bubbles.

2.2 Comparison of time scales

It is constructive to compare the order of time scales that are involved in adsorption of particles to the surface of bubbles with those characterising the dissolution times. The coverage on the surface of a bubble has to reach a value λ^* before a suitably strong 2D network of nanoparticle, capable of resisting the shrinkage of the bubble, is formed. For a bubble of radius R the rate of particle numbers arriving on its surface is $4\pi n_0 R D_p$, where n_0 is the number concentration of the particles and D_p their diffusion coefficient. For the time being if one ignores the shrinkage of the bubble, then the surface coverage of the bubble increases at a rate of $\pi n_0 R D_p r^2$. The dimensionless quantity $r = R_p/R$ is the ratio of the radius of the nanoparticles, R_p, to that of the bubble. Using this result, the estimated time for the bubble to achieve the required coverage by the particles is given by $t_c=\lambda^*(\pi n_0 R D_p r^2)^{-1}$. For simplicity we have assumed that the contact angle for particles at the air-water interface is 90^0, making the area occupied by a particle on the surface of the bubble $\pi(R_p)^2$. As for the kinetics of the disproportionation process, there have been several models proposed in the literature over a number of years.[1, 49, 50] One such model was developed by us to investigate the dissolution of bubbles trapped immediately underneath air-water interfaces. The predictions of the model were found to provide an accurate description of the experimentally observed shrinkage kinetics of such bubbles in a variety of solutions, involving different proteins.[1, 2] The same theory also gives the lifetime of a bubble of radius R residing away from the interface as $t_d= \tau R^3$. The constant τ depends on the surface tension, γ, ambient temperature and pressure, T and P_0, the Henry's constant for the gas solubility, S, and the diffusion coefficient of the gas molecules in water, D_g. It is given by

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

The universal gas constant, 8.31 J K^{-1} is denoted by R_g in the above equation. The same result can also be obtained from the model of Epstein and Plesset,[50] if one ignores the short lived initial transients and assumes a quasi-stationary solution for the diffusion flux of the gas away from the bubbles throughout the dissolution process. Using typical values for the quantities appearing in eqn (1), T = 298 K, P_0 = 100 kPa, γ = 0.07 Nm^{-1}, $D_g = 2 \times 10^{-9}\ m^2 s^{-1}$ and $S=7 \times 10^{-6}$ mol $N^{-1}\ m^{-1}$, the value of τ is calculated as $6.872 \times 10^{15} sm^{-3}$. For a bubble of size 100 μm (i.e. R = 50 μm), the estimated lifetime is 14.3 min, whereas for R = 5 μm it is only t_d = 0.86 s. More significantly, the ratio of the time required to achieve the necessary surface coverage by the particles to the lifetime of the bubble is

$$\nu = \frac{t_c}{t_d} = \frac{\lambda^*}{\pi D_p n_0 R^2 R_p^2 \tau} = \frac{48\pi N_A \lambda^* \eta \gamma S D_g r^2}{P_0 \phi} \quad , \qquad (2)$$

where N_A is Avogadro's number and the diffusion coefficient of the particles is expressed in terms of the viscosity of the solution, η, using the Stokes-Einstein equation $D_p=(k_BT)/(6\pi\eta R_P)$. Similarly, we have substituted for the number density of the particles in favour of their volume fraction, ϕ, where $n_0 = 3\phi\,(4\pi R_P{}^3)^{-1}$. When the dimensionless number $\nu < 1$, the bubbles have sufficient time to gather the required number of particles, thus stabilising without much shrinkage. On the other hand, large values of ν indicate a considerable degree of dissolution and loss of gas before the disproportionation process is halted. In these latter systems the shrinkage of bubbles may even be so severe so as to rule out the possibility of achieving stable Pickering bubbles altogether. A case in mind is one in which the radii of the bubbles decrease to sizes not large enough compared to that of the particles. In a typical formulation[19, 51] with a particle volume fraction of $\phi = 0.04$ % (~ 0.1 % w/w) and $R_p = 50$ nm, the value of $\nu = 1.1$ for bubbles of radius 50 μm, and 111 when R =5 μm, if one assumes a nominal value of $\lambda^* = 0.5$ for the critical surface coverage. In calculating these values we have taken the viscosity of the solution as that of water. In many food colloid products, including ice cream during the aeration process, whipped cream, mousses and aerated chocolate mixes, the viscosity of the mixture is much higher than 0.001 Pa s, perhaps by two to three orders of magnitude. This is so as to prevent the rapid rise of the bubbles to the surface during the manufacturing process. Therefore, if anything, the values of ν given here will tend to be on the rather low side. The simple calculation presented above clearly highlights the issue we wish to address in the current work.

Before leaving this section, it is worthwhile to briefly consider the processing conditions and the type of particle surface chemistries for which the calculations in this work are intended. We have assumed here that the transport of particles to the surface of the bubbles is a diffusion-limited process. This needn't always be the case. There are many particles with more hydrophilic surfaces (i.e. low contact angles) where the adsorption to the gas-water interface is dominated by the presence of an energy barrier, occurring in the particle-bubble interaction potential. In contrast, for the more hydrophobic particles, such as the ones with contact angles approaching 90^o or above, direct measurements of forces using AFM, reveals only a net attractive interaction upon approach of the particle towards a bubble.[52-54] Indeed, one may also infer the lack of an energy barrier from the relatively low values of measured ζ–potential for such hydrophobically modified surfaces. Values of -10 mV to -20 mV are not uncommon.[55] A large enough energy barrier in the particle-bubble interaction potential, sufficient to dominate the attachment of the particles to the interfaces, is thus not predicted in such cases. This is particularly true in the presence of a moderate to high amount of background electrolyte in the system.

The issue of whether in a particular process the transport of particles to the bubble surface is convective or diffusive is best addressed by considering the dimensionless number, the Peclet number. This is the ratio of the time scale for convection relative to that for diffusion. For hard sphere dispersions, it is given[56] by $\mathrm{Pe} = (6\pi\eta\dot{\gamma}R^3)/k_BT$, where $\dot{\gamma}$ is the typical flow rates involved in the process. For particles of radius 50 nm, at room temperature, this gives $\mathrm{Pe} \sim \dot{\gamma}/1800$. In other words, the flow rates have to be in excess of 1800 s^{-1} before one can begin to attribute the transport of particles to the surfaces as being dominated by convection. While shear rates of this magnitude are not at all unusual in mixing, whisking or during rigorous shaking, there are also many processes for generating dilute dispersions of bubbles that do not involve such large flow rates. Examples of these are ultrasound generation of microbubbles through cavitation, pressure drop techniques involving nucleation and growth of gas bubbles throughout the body of the liquid and even gentle bubbling of the gas into the fluid. It is strictly for these types of processes that the current calculations are expected to apply. It may well be possible to extend the current analysis, within the same general scheme presented in the next section, to study the convective-limited cases. However, we shall not discuss such an extension here and instead defer this to future work.

2.3 More detailed analysis

In the previous section, the effect of shrinkage on the value of the particle surface coverage, λ, was ignored. Also no account of the depletion of particles from bulk, due to their adsorption over time, was taken. In this section we will include these factors in our calculations. The process is schematically visualised in fig. 1. As before we assume that the bubble dispersion is sufficiently dilute. This serves two purposes. Firstly it means that disproportionation rather than coalescence is the primary instability mechanism. Secondly, it insures that the diffusing flux of particles onto the surface of a bubble, and that of gas molecules out and away from it, are not influenced by presence of neighbouring bubbles.

As a bubble shrinks λ increases, even if no further particles are added to the surface of the bubble. The rate of increase is given by $-(2\lambda/R)(dR/dt)$. Combining this with the rate of change of λ due to the arrival of new particles on to the surface of the bubble, we have[51]

$$\frac{d\lambda}{dt} = \frac{-2\lambda}{R(t)}\frac{dR}{dt} + \frac{\pi D_p n(t) R_p^2}{R(t)} \quad , \qquad (3)$$

where now both the bulk concentration of nanoparticles, n(t), and the radius of the bubble, R(t), also vary themselves with time. For low values of λ, the presence of a few particles on the surface of a bubble will not have much of an effect on the rate of shrinkage of the bubble. Consequently the kinetic of dissolution of the bubble will be similar to that of an uncovered bubble. As mentioned before, we model this along the same line as that given by the theory of Epstein and Plesset[50] in absence of short lived initial transients[57], or alternatively through the identical result obtained from our own model for dissolution of bubbles trapped under an air-water interface, in the limit where they are sufficiently far from the surface.[1, 2] Under such conditions we have

$$R(t) = R(0)\left(1 - \frac{t}{\tau R(0)^3}\right)^{1/3} \quad , \qquad (4)$$

with parameter τ given by eqn (1). Substituting the above equation into eqn (3) leads to

$$\frac{d\lambda}{dt} = \frac{2\lambda}{3\tau R(t)^3} + \frac{\pi D_p n(t) R_p^2}{R(t)} \quad . \qquad (5)$$

As the value of λ approaches λ^* the particles start to form stress supporting networks and their presence begins to slow down the disproportionation. The exact manner in which this happens will depend on the nature of the particles and the interparticle forces between them, amongst other things. For particles only interacting through a hard sphere type potential, one expects a relatively sudden and almost abrupt halt to the dissolution process at λ^*, corresponding to the point of close packing of the particles on the surface of the bubbles. For cases involving formation of open ramified clusters on the surface, a more gentle transition and arrest of disproportionation is more likely. In this latter cases, the value of λ^* will also be less well defined, as it will depend on the Laplace pressure inside and therefore size of the bubble. For sake of simplicity and to keep the discussion more general, we will assume that the bubbles continue to shrink unhindered according to eqn (4), until their particle surface coverage reaches a well defined critical value λ^*. At this stage they simply stop to shrink further.

In dilute systems, the presence of neighbouring bubbles does not directly affect the time it takes for a particular bubble to become stabilised by the particles. However, there is an indirect effect which manifest itself through the presence of the n(t) term in equation (5). The size distribution and the number of other bubbles in the system determine the rate at which the particles are removed from bulk. This in turn influences the stabilisation time and therefore the eventual size of any given bubble. For diffusion limited adsorption of particles, the rate of adsorption is given by

$$\frac{dn}{dt} = -4\pi D_p n(r) \int N_b \rho(R,t) R dr = -4\pi D_p n(r) N_b < R(t) > \quad , \qquad (6)$$

where N_b is the total number density of the bubbles in the system, $N_b\rho(R,t)dR$ the number density of bubbles in the radius size range R to R+dR and <R(t)> the average radius of bubbles at time t. Strictly speaking the integral in eqn (6) should only extend to bubbles that have not reached the maximum possible surface packing of particles, λ_{max}, where λ_{max} may or may not be identical to λ^* , though almost certainly it will not be smaller. In fact, in some cases multi-layers of particles can accumulate around bubbles and the value of λ_{max} can be well above one.[51] It is suggested that such layers can eventually connect and overlap to form a three dimensional network of particles, filled with bubbles.[51] The same can also occurs in Pickering emulsions.[58] In this analysis we consider such systems where the value of λ_{max} is large and bubbles continue to gather particles even after they have stopped shrinking. The extension to particle types where this is not the case, while involving some added complexity, is not too difficult to include in the numerical calculations. Equation (6) can be used to yield the following result for n(t)

$$n(t) = n_0 \exp\left(-4\pi D_p N_b \int_0^t < R(t) > dt \right) \quad , \qquad (7)$$

where the initial number concentration of particles is $n(0) = n_0$. Equations 5 and 7 can now be solved in conjunction with eqn (3) for bubble sizes where $\lambda < \lambda^*$, or dR/dt = 0 where $\lambda > \lambda^*$, to determine the temporal changes in the size distribution of the bubbles. Eventually, when the particle surface coverage of all bubbles is above the critical value, the final stabilised bubble size distribution is obtained.

In the next section we shall first consider some limiting cases where an analytical solution to the problem becomes possible. We then examine the numerical solutions to the above set of equations more generally and discuss their implications.

3 Results and Discussion

3.1 Final bubble sizes for systems with large excess of particles

In systems where the number of particles is far more than that required to stabilise the bubbles, the adsorption of particles onto the surface of bubbles has little effect on the number density of the nanoparticles. To clarify what we mean by excessive number of particles, let us define the dimensionless parameter

$$\beta = \frac{n_0 R_p^2}{4N_b < R(0) >^2 \lambda^*} \quad . \qquad (8)$$

Roughly speaking β is a measure of the ratio of the surface area that can potentially be covered and stabilised by the nanoparticles to the initial air-water interface. For a system with a large excess of particles, $\beta >> 1$. It is much more convenient to express eqns (4),(5) and (7) in terms of the dimensionless parameters $r = R_p/<R(0)>$, β, and ν as defined in eqn (2). Also from now on, unless stated otherwise, we shall take the unit of length as the initial average radius of the bubbles, <R(0)>, and the unit of time as $\tau<R(0)>^3$. In these new units equation 7 now reads

$$\frac{n(t)}{n_0} = \exp\left(-\frac{1}{\nu\beta} \int_0^t < R(t) > dt \right) \quad , \qquad (9)$$

where <R(0)> = 1 by definition, while eqns (4) and (5) become

$$R(t) = \left(R(0)^3 - t \right)^{1/3} \qquad (10)$$

and

$$\frac{d\lambda}{dt} = \frac{2\lambda}{3R(t)^3} + \frac{\lambda^*}{vR(t)}\frac{n(t)}{n_0} \quad , \quad (11)$$

respectively, for a bubble of original radius R(0).

For a system with a moderate value of ν, but a large excess of particles such that $\nu\beta >> 1$, we can approximate eqn (9) by $n(t)/n_0 \approx 1$ over the time period needed for the bubbles to become stable. This implies that bubbles of different size in such a system shrink, gather particles and eventually stabilise independent of each other. Therefore eqn (11) for the variation of the particle surface coverage of each bubble can now be solved for each bubble irrespective of others. Substituting this result together with eqn (10) in eqn (11) and solving the resulting differential equation for λ with the boundary condition $\lambda(0) = 0$, we have

$$\lambda(t) = \frac{3\lambda^*}{4v}\left(\frac{R(0)^4 - R(t)^4}{R(t)^2}\right) \quad , \quad (12)$$

valid for $\lambda < \lambda^*$. In fig. 2 we have plotted the variation of the surface coverage with time (in seconds) on a semi-logarithmic scale for three bubbles with initial sizes, 5, 15 and 50 μm. We have taken the volume fraction of the nanoparticles to be 0.04 %, $\lambda^* = 0.5$ and assumed the number of bubbles to be small enough for $\beta >> 1$. As mentioned before, in such a system the variation of λ with time or the degree of shrinkage for each bubble size does not depend on the presence of other bubbles. The results will be the same irrespective of the degree of polydispersity of the bubble size distribution or the actual value of <R(0)>. Comparison of graphs in fig. 2 demonstrates the large contrast in the time it takes the bubbles of varying sizes to become stable. While it takes a much shorter period for smaller bubbles to stabilize (i.e. reach a coverage of λ^*), this is comparable to the life time of the bubbles. Smaller bubbles only ever manage to gather a small number of particles. The steep increase in the particle surface coverage, seen in the graph of fig. 2 for the 5 μm bubble, comes about as a result of a rapid decrease in the surface area of the bubble, when it has shrank to only a small fraction of its original size. For moderately sized bubbles, the arrival of new particles on the surface and the decrease in the surface area, both play equally important roles in the increase of the surface coverage. This is evident from the more gradual change in λ with time, seen from the corresponding graph for the 50 μm bubble (fig. 2). Obviously, for even larger bubbles, the dominant mechanism contributing to the increase in λ shifts towards the gathering of the particles by the bubble.

The final size of a bubble, where the particle surface coverage reaches the critical value needed to prevent further shrinkage, is obtained by setting the right hand side of the eqn (12) to λ^* and solving the corresponding quadratic equation in $R(t)^2$. For a bubble with initial radius of R(0), we find the final stabilised radius, R_f to be

$$R_f = R^* \left[\sqrt{1 + \left(\frac{R(0)}{R^*} \right)^4} - 1 \right]^{1/2} \quad . \qquad (13)$$

where we have defined a characteristic radius (in units of <R(0)>) such that

$$R^* = \sqrt{\frac{2\nu}{3}} \quad . \qquad (14)$$

It is seen that when $R(0) >> R^*$ then $R_f \approx R(0)$ and bubble shows little sign of shrinkage prior to becoming stabilised. On the other hand, if $R(0) << R^*$ we have $R_f \,/\, R(0) \approx R(0)/(\sqrt{2}R^*) << 1$ and a substantial decrease in the size of the bubble is expected.

In many applications it is the amount of gas retained in the system that is of primary interest. In fig. 3 we have plotted the ratio $(R_f/R(0))^3$ against R(0), for the same system as that in fig. 2. For initial bubbles of size $R(0) = \sqrt{2}R^*$ (~ 60 μm in the case considered here) the fraction of retained gas is only around 50 % of its original amount. For $R(0) = R^*$, this drops to 25 % and decreases very rapidly as the initial size of the bubbles is made even smaller. From a practical point of view we conclude that for any given system, small bubbles with $R(0) < R^*$ cannot realistically be stabilised using nanoparticles. The existence of a limiting lower size for stabilisation of bubbles using nanoparticles was also predicted and experimentally verified in our previous work.[51, 59]

3.2 Monodisperse bubble size distribution

When the initial size distribution of bubbles is highly monodisperse, one can approximate $\rho(R,0) \approx \delta(R - R_0)$, where $R(0) = R_0$ is now the initial size of all the bubbles. Thus, in our normalised unit of length <R(0)>, the initial radius of any bubble is 1. Furthermore, for a dilute bubble system, where the local environment of all bubbles remains more or less identical, the bubbles continue to maintain the same radius as they shrink. In such cases the average radius in eqn (9) can be replaced with the radius for just one of the bubbles. Substituting for the term $n(t)/n_0$ in eqn (11) using this result, we have

$$\frac{d\lambda}{dt} - \frac{2\lambda}{3(1-t)} = \frac{\lambda^*}{v(1-t)^{1/3}} \exp\left(-\frac{1}{\nu\beta} \int_0^t (1-t)^{1/3}\, dt \right) \quad , \qquad (15)$$

where the time dependence of the bubble radius R(t) is made explicit using eqn (10), with R(0) = 1. Multiplying both sides of the above equation by $(1-t)^{2/3}$ and integrating with respect to t, one arrives at the required result

$$\lambda(t) = \frac{\beta\lambda^*}{R(t)^2}\left[1 - \exp\left(-\frac{3}{4\nu\beta}(1-R(t)^4) \right) \right] \quad . \qquad (16)$$

For large values of β, the exponential term can be expanded leading to the same equation, eqn (12) for $\lambda(t)$, with a bubble of average size R(0) = 1, as might be expected. However, note that eqn (12) also applies to bubbles in a polydispersed bubble distribution, as long as $\beta >> 1$, whereas eqn (16) is strictly valid for a monodispersed distribution of bubble sizes, but for any value of β. Once again the final stabilised bubble radius can be obtained by setting $\lambda(t)=\lambda^*$ and solving the resulting equation for $R(t) = R_f$:

$$R_f^2 = \beta\left[1 - \exp\left(-\frac{3}{4\nu\beta}(1-R_f^4) \right) \right] \quad . \qquad (17)$$

It is clear that for bubbles of any initial size the final radius $R_f < \sqrt{\beta}$. In particular, for bubbles where R^* (as defined by eqn (14)) is small or ~ 1 and $\sqrt{\beta} << 1$, the exponential term in eqn (17) is negligible and therefore $R_f \approx \sqrt{\beta}$ (i.e. $(R_p^2 n_0/(4N_b\lambda^*))^{1/2}$ in SI units). The fact that the final size of the bubbles is now independent of their initial size is not all that surprising in such circumstances. In systems starved of sufficient number of nanoparticles, it is not the bubble shrinkage kinetics that is the main factor in determining R_f. Rather, it is the maximum surface area of gas-water interface that can potentially be stabilised by the particles that decides the final bubble size. The total amount of surface (per unit volume) that can be stabilised by particles is $(\pi R_p^2 n_0/\lambda^*)$. This has to be the final surface area of bubbles $(4\pi R_f^2 N_b)$, when all the particles are adsorbed. Equating these two terms gives the predicted result $R_f = \sqrt{\beta}$.

In fig. 4 we have shown the numerical solutions to eqn (17), displaying the values of R_f for bubbles of initial radii 50, 75, 100 and 120 μm in four different monodispersed bubble systems. The radius of the particles is once again taken to be 50 nm, but their volume fraction is now set to a much lower value of 0.004 %. The results are plotted as a function of parameter β. For a constant concentration of particles, and in a monodispersed bubble system, β is inversely proportional to the specific surface area of gas-water interface. The lowest value of β for each graph corresponds to the highest volume fraction of bubbles (~ 40 %), beyond which the bubbles can no longer be considered sufficiently isolated. The dotted line in fig. 4 is the predicted ratio of the final to the initial radius, assuming that all the particles adsorb to the surface instantaneously. Bubbles then shrink and λ increases until the critical particle surface coverage is obtained. In such a situation the final size ratio is dominated by the number of particles present and the initial gas-water surface area, as discussed above. Consequently, for bubbles of any size, the final size ratio approaches $\sqrt{\beta}$ independent of the initial size. This is clearly seen to be the case for the more concentrated bubble systems with low values of β. Various graphs in fig. 4, representing different initial bubble radii, all approach the same limiting result indicated by the dotted line. Similar situations also occur in coalescence-controlled particle stabilised emulsions[60] and during the arrest of phase separation of immiscible fluids by particles in the so called "Bijels" systems.[61] In these cases also, it is the stabilised interfacial area dictated by the number of available particles, which ultimately determines the final structural length scales once the system is fully evolved. Behaviour of the final size ratio at low β is to be contrasted with that at higher values. At low bubble concentrations (i.e., large β) the final size ratio becomes independent of β, governed now by the adsorption rate of the particles as given by eqn (13). The graphs in fig. 4 are seen to plateau out at higher values of β, once this limit is reached, reflecting this point.

The effect of the number of particles on the fraction of retained gas is displayed in the graphs of fig. 5. The two graphs are for systems with 0.04 % (solid line) and 0.004 % (dashed line) particle volume fractions. Unlike the graph of fig. 3 which was obtained in the very dilute bubble limit, the initial volume fraction of bubbles in both cases shown is somewhat higher at 25 %. The results are presented as a function of the initial bubble radius. The difference between the two graphs is relatively small for very large bubbles, R(0) > 0.8 mm, but very significant as the initial bubble size is reduced. At R(0) = 50 μm and $\phi = 0.04$ % the fraction of retained gas is already lower at 0.25 instead of 0.35 found in fig. 2. When the nanoparticle volume fraction is reduced to 0.004 %, only 1 % of the initial gas is retained following the shrinkage of the bubbles. The corresponding values are 0.92 at $\phi = 0.04$ % and 0.55 at $\phi = 0.004$ % when the initial bubble size is 200 μm, instead of 0.98 predicted from eqn (13). For a fixed volume fraction of gas, the small bubbles not only have less time to gather the required number of particles, but the total air-water surface area to stabilise is also higher. Both these factors contribute to a rapid drop in the final size of bubbles and therefore the fraction of remaining gas in the system.

3.3 Evolution of bubble size distribution: The general case

For a bubble system with neither a monodisperse initial size distribution and nor a large excess of stabilising nanoparticles, the set of equations governing the evolution and the final distribution of bubble sizes, i.e. equations (9)-(11), was solved numerically. The scheme implemented for this purpose is as follows. We divide the polydispersed distribution into narrow size intervals, ΔR. To start with the number of bubbles in each interval is specified by the initial size distribution $\rho(R,0)$, with all bubbles having $\lambda(0)=0$ and $n(0)/n_0$ set to 1. The upper and lower limits for each interval i, R_i and R_{i+1}, are updated over a short time period Δt according to equation (10):

$$R_i(t+\Delta t) = \left[R_i^3(t) - \Delta t\right]^{1/3} \quad . \qquad (18)$$

At the same time the value of ρ for each interval is scaled by $[R_{i+1}(t+\Delta t)-R_i(t+\Delta t)]/[(R_{i+1}(t)-R_i(t)]$ to account for the change in the size of the interval. Similarly, the value of the particle surface coverage at time $t+\Delta t$, for all the bubbles in each size range, is calculated using a finite difference form of eqn (11):

$$\lambda(t+\Delta t)=\lambda(t)+\left[\frac{2\lambda_i(t)}{3\bar{R}_i(t)^3}+\frac{\lambda^*}{v\bar{R}_i(t)}\frac{n(t)}{n_0}\right]\Delta t \quad . \qquad (19)$$

The radius $\bar{R}_i$ in the above equation is taken as the average value $(R_{i+1} + R_i)/2$ for any given size interval. As bubbles shrink, intervals move downwards towards lower size values. However, bubbles in the lower end of each size range contract slightly faster than those at the upper end. As a result the intervals also begin to broaden out. When the width of any size range exceeds one and half times its original size, we split the interval into two new size ranges each half as wide. The bubbles in the original interval are divided equally between these two, with the number distribution function ρ remaining the same as that for the original size interval at this stage. However, from this point onwards the upper and the lower size limits, as well as $\lambda(t+\Delta t)$ values, are calculated separately for the two newly created size ranges. As soon as the value of the particle surface coverage for the bubbles in a particular size interval reaches the critical value λ^*, these bubbles stop shrinking. The upper and the lower radii for this interval now remain the same throughout the rest of the calculation and are no longer updated. Such bubbles nevertheless can still gather particles, as discussed below. When a bubble stops shrinking the only remaining contribution to any further increases in the particle surface coverage arises solely from the arrival of new particles. Consequently, for these bubbles, eqn (19) has to be modified to

$$\lambda(t+\Delta t)=\lambda(t)+\left[\frac{\lambda^*}{v\bar{R}_i(t)}\frac{n(t)}{n_0}\right]\Delta t \quad . \qquad (20)$$

At each step in the calculation we also renew the concentration of the remaining particles in the bulk solution, with the integral in eqn (9) at any time t given by $\sum_i \rho(R_i,t)\bar{R}_i\Delta R_i$. We check to make sure that the initial width of the size intervals and the time step used are both adequately small by halving these and repeating the whole procedure again. A suitable value is taken as one for which this halving of the time step or the size intervals produces no appreciable difference in the final bubble size distribution obtained by the method. Also, at regular intervals throughout the calculation, we obtain the area under the size distribution function, $\rho(R,t)$, to ensure that this too always remains very close to its initial value (relative error < 10^{-5}).

In many practical systems the maximum particle surface coverage achieved by the bubbles can exceed the value needed to stabilise the bubbles. In such cases the bubbles continue to gather particles up to a value $\lambda_{\max} > \lambda^{*}$. As discussed in the introduction, for some particles[51, 58, 59] the adsorption can lead to the formation of multi-layers. For these systems $\lambda_{\max} > 1$. In principle, it is possible to incorporate any value of $\lambda_{\max}$ into the model presented here by a suitable modification of eqn (9). This involves ensuring that the integral appearing in this equation is only taken over the bubble size range for which the bubbles have not as yet reached the maximum surface coverage. In our preliminary calculations presented here, we assume that $\lambda_{\max}$ is large and therefore bubbles continue to contribute to the depletion of particles from the bulk, well after they have stopped shrinking. This case is chosen here as we feel it provides the most interesting situation. The results for smaller, finite values of the maximum surface coverage will be reported elsewhere in a future publication.

The time evolution of the bubble size distribution, for a system starting with a normal distribution, is displayed in figure 6. The initial average radius by definition is 1 and the standard deviation is set to 0.15 (in units of $\langle R(0)\rangle$, here assumed to be 50 μm). The radius of nanoparticles in the same unit is 0.01, with their concentration taken as 0.04 % by volume. This fixes the parameter $\nu = 1.1$. Similarly, the initial number density of bubbles is taken such that β is 1.0. The starting size distribution of the bubbles is shown by the dotted line for reference. As expected, the distribution shifts towards lower size values with time, until all bubbles reach a surface coverage of λ^{*}. The final stable size distribution is represented by the solid line. It is interesting to note that at intermediate stages prior to stabilisation of all bubbles, the size distribution broadens at first but then starts to become narrower later on. The broadening is understandable as the smaller bubbles shrink at a faster rate than the larger ones. However, as these small bubbles stabilise earlier in the process the large bubbles start to catch up and the width of the distribution decreases once again. The final width of the size distribution function is crucially dependent on the value of the parameter β, as will be shown below. Another interesting feature of the distribution function at the intermediate times is its breakup into two distinct parts, producing a bimodal type size distribution. This is most clearly seen for the dashed-dotted line in fig 6, showing the distribution function at time 0.3 (in units of $\tau \langle R(0)\rangle^{3} \sim 14.3$ min). The two distinct parts of the size distribution correspond to those bubbles that are still shrinking and the ones that have already stabilised. Due to the nature of our model and the way that we assume the disproportionation process is halted by the particles, a sharp discontinuity in the distribution function develops between these two separate parts.

As discussed in section 2.2, in our model, the presence of the particles on the surface of the bubbles has no effect on the shrinkage rate of bubbles, that is of course until the surface coverage reaches the critical threshold λ^*. At this point, a bubble stops shrinking suddenly and abruptly. While this is an idealised model, it nevertheless captures some of the essential features of the particle networks formed on the interfaces. This is particularly the case for systems where the interfacial yield stress of the network, beyond a given threshold, is a rapidly increasing function of the surface coverage. However, even in such systems the shrinkage kinetics of the bubbles is expected to show some degree of slowing down, at some stage before the critical surface coverage is reached. In other words, the particles start to make their presence felt ahead of the full stabilisation of the bubble. Thus, in practice, one may expect the sharp discontinuity in the bubble size distribution function, seen in fig. 6, to be rounded off to some extent. Nevertheless, one should still be able to observe the development of a bimodal distribution at intermediate times, prior to the complete arrest of disproportionation for all the bubbles.

The discontinuity in the distribution function occurs at a radius at which the bubbles of that size have just reached a particle surface coverage of λ^*. This is most clearly illustrated by considering the graphs of fig. 6 in conjunction with those in fig. 7. The curves in figure 7 show the value of λ, for different sized bubbles, at the same stages as those in fig. 6. The horizontal dotted line in the figure indicates the threshold value $\lambda^* = 0.5$, with all bubble sizes for which $\lambda > \lambda^*$ already having been stabilised by the particles. It is clear that the bubble radii at which the graphs of the surface coverage cross the value 0.5 are the same ones as those for which the discontinuities in the distribution function, at the same time t, also occur in fig. 6. The cross over radius shifts to higher values with time, as increasingly bigger bubbles in the dispersion are stabilised by the particles.

We have plotted the fraction of retained gas as a function of time in fig. 8 for the above system together with two others, one having a higher ($\beta = 0.25$) and the other a lower ($\beta = 5.0$) number of bubbles. The initial size distribution and the total concentration of the nanoparticles are kept the same in all three cases studies. Initially there is no difference in the amount of gas lost in these systems, with all three graphs overlapping at short times. This is because a bubble of a given size finds itself in precisely the same initial environment, irrespective of the presence of other bubbles, given that the bulk concentration of the particles is identical in all three systems. Thus, the bubbles in each system shrink and gather particles in exactly the same manner to begin with. However, at longer times, the difference in the number of bubbles begins to manifest itself as the curves start to diverge from each other. The bulk concentration of particles is depleted much more quickly for a system with a larger number of bubbles. This has a pronounced effect on the final size of the bigger bubbles, which tend to stabilise later on in the process, in such cases. Without many particles left in the bulk, these larger bubbles will shrink much further than otherwise suggested by the calculations in section 3.1, where a large abundance of nanoparticles was assumed. Consequently the amount of retained gas is much lower for the case with $\beta = 0.25$, as can be seen in fig. 8.

We also considered several other situations involving values of β larger than 5. The corresponding graphs for these are not shown here, as they are nearly indistinguishable from the one in fig. 8 for the case with $\beta = 5$. Once there is an excess of nanoparticles, each bubble size shrinks to a final size given by eqn (13). Therefore, the final stabilised size distribution and the fraction of the retained gas both become independent of the value of β.

The influence of the ratio of the number of particles to bubbles on the final bubble size distribution is displayed in figure 9. The final size distributions are shown for each of the three systems considered above, together with the initial starting one for comparison. As well as the expected differences in the mean values, the widths of the final distributions are also seen to be quite different. Once again this can be attributed to a transition from an "adsorption controlled" to a "number of particle controlled" shrinkage of the larger bubbles. With a relative abundance of particles, as is the case for the system with $\beta = 5$ (the dash-dotted line in fig. 9), the shrinkage is "adsorption controlled", as discussed in section 3.1. In such cases, the final size ratio is not small for the bigger bubbles, unlike the smaller ones. Thus, we have a final distribution that is slightly broader than the starting one, with a standard deviation of 0.164, as oppose to 0.15 initially. This value drops to 0.145 when $\beta = 1$ (dashed line). But when the system is starved of particles due to a much larger number of bubbles, $\beta = 0.25$, then the shrinkage becomes "particle number controlled". The small bubbles are not affected as much and shrink to approximately the same radii as before. On the other hand, the bigger bubbles stabilising later on, find themselves left without a sufficient number of particles. As a result they shrink to a much larger extent than that expected from an “adsorption controlled” process. This means that the final bubble size distribution becomes much narrower. Indeed the standard deviation for the system with $\beta = 0.25$ (solid line in fig. 9) is only 0.07, about half its initial value. It is seen that the presence of a large number of small bubbles may be quite detrimental if it is the larger bubbles that one really wishes to stabilise. Nevertheless, the same result also means that, by a careful control of the number of nanoparticles in the system, it may be possible to produce a much more monodispersed final bubble size distribution in certain types of applications that require them. The final distribution of bubbles sizes for $\beta = 0.25$ is also shown in the inset in fig. 9 in greater detail. This shows the distortion of the distribution function away from its initial Gaussian symmetrical form.

Some tentative experimental results supporting the predictions of figure 9 can be found in the recent work by Stocco et al.[62] In this study a combination of X-ray tomography and light scattering was used to monitor the evolution of bubble size distribution, stabilised by hydrophobically modified silica particles. Rather than changing the volume fraction of gas bubbles while keeping the particle number fixed, as has been done here, in the study of Stocco et al it was more convenient to alter the concentration of silica nanoparticles. Despite this difference and the fact that the initial bubble size distributions is unlikely to be the same as the normal distribution considered by us, some interesting similarities are nevertheless found. The bubble systems considered by Stocco et al[62] are also relatively concentrated and a closed system. However the authors do report the existence of a few very large bubbles that in some sense play the same role as the infinite sized bubbles (the open air-water interface) in our calculations. Indeed, with time these large bubbles are seen to get bigger; an observation that we believe was correctly attributed to disproportionation. In particular, it is observed that the average size of the smaller bubbles decreases by reducing the concentration of silica particles, in agreement with our predictions. More interesting, it is noticed that the plotted distribution of bubble sizes is as broad, if not more so, for a system with 0.5 wt% silica compared to one with 0.9 wt%. Yet, the narrowest distribution is obtained for 0.3 wt% silica. This is much as we find in the results of fig. 9, where the relative width of distribution increases at first but then decreases as the number of particles in the system is made smaller. Extension of the present work to more concentrated bubble systems and foams, through the inclusion of bubble coalescence, should provide an even more accurate description of the systems studies by Stocco et al,[62] where the effects of coalescence are not negligible.

4 Conclusions and Summary

Pickering stabilisation of bubbles against disproportionation requires the formation of networks of nanoparticles on the surface of the bubbles. These networks need to have a sufficient interfacial yield stress to compensate and counteract the excess Laplace pressure inside the bubbles. We argue that, due to the finite adsorption rate of particles onto the surface of the bubbles, such networks take a certain given period to develop, during which time the bubbles can undergo a large degree of shrinkage. This is particularly the case for the smaller bubbles with faster dissolution rates. A similar problem does not occur in Pickering stabilised oil emulsions because Ostwald ripening is a much slower process than particle adsorption in these systems. Additionally, in bubble dispersions with polydispersed size distributions, bubbles of varying sizes compete with each other for the adsorption of the stabilizing particles, as the bulk concentration of particles is gradually depleted. In the current study, we have investigated the interplay between disproportionation kinetics on the one hand and rate of adsorption and finite number of available particles on the other hand, to determine the extent of shrinkage, the degree of gas loss and changes occurring in the bubble size distribution for an initially polydisperse dispersion of gas bubbles.

When the concentration of particles is much higher than that required to stabilises the initial gas-water interfaces on the surface of bubbles, the shrinkage is adsorption rate limited. Bubbles of different sizes shrink and eventually become stable independent of others in the distribution. For such a case, we have derived an analytical expression for the extent of shrinkage. This shows the existence of a threshold bubble radius. We find that those bubbles, with an initial radius much larger than this value, are stabilised by the nanoparticles without undergoing any appreciable degree of reduction in their size. In contrast, for bubbles starting with a radius below the threshold, the final size ratio decreases very rapidly as the bubbles become smaller. As the number of nanoparticles relative to the total surface area of bubbles requiring coverage is decreased, the behaviour of the system alters. This is particularly the case for the larger bubbles with radii above the threshold value. We have shown that the shrinkage ratio is now determined by the number of particles rather than their adsorption rate, i.e., the final stabilised radius approaches the value one would expect if all the particles were to be placed on the surface of the bubbles from the very onset. The transition from an “adsorption controlled” to a “particle number controlled” final size is demonstrated analytically for monodispersed bubble distributions and by numerical solutions for the more general case. For the “adsorption controlled” system, where there is an excess of particles, the final stable bubble distribution is found to be slightly broader than the starting distribution. However, when the system is starved of particles in the “particle number controlled” cases, the width of the final distribution is considerably smaller than the initial value. These results can be rationalised in terms of the behaviour of different sized bubbles in the two distinct regimes discussed above. In the adsorption controlled situation, the small bubbles suffer a considerable degree of shrinkage, while the larger ones are stabilised with almost no change to their initial radius. Thus, not surprisingly, the bubble size distribution broadens. In the particle number controlled case, the bigger bubbles, which will tend to stabilise much later in the process than the small ones, end up in a situation where very few nanoparticles remain in the bulk solution. Therefore they also shrink to a much greater extent, producing a final distribution that is now narrower than the initial one.

It is interesting to note that, while the small bubbles only contain a small fraction of the initial total gas, due to the surface to volume ratio effect, they can have a disproportionate influence on the total fraction of the gas that is retained in the system, via their removal of particles from the bulk. However, it should be noted that, the current analysis was performed for bubble systems open to the air above. A similar investigation for closed systems would require combining this approach with the classical Lifshitz-Slyozov-Wagner theory[63, 64] of Ostwald ripening. It may be possible to extend the model to more concentrated bubble dispersions, where the collision rates and coalescence of bubbles is equally important as disproportionation, if not the primary mode of bubble instability. These should prove an intriguing but mathematically more challenging problems for future study, whilst it would be interesting to compare in more detail the predictions of the present analysis with current[62] and future experimental observations in real systems.

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