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Bournival, Ghislain; Ata, Seher; Wanless, Erica J. "Behavior of bubble interfaces stabilized by particles of different densities", Published in *Langmuir* Vol. 32, Issue 25, p. 6226-6238. (2016)

Available from: <http://dx.doi.org/10.1021/acs.langmuir.6b00656>

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The behavior of bubble interfaces stabilized by particles of different densities

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Abstract

The stability of bubbles laden with particles of different densities has been investigated. Capillary-held bubbles were produced and coated with particles across the density range $1.2 - 3.6 \text{ g}\cdot\text{cm}^{-3}$. The materials used were poly(methyl methacrylate) (PMMA), glass, and anatase. The interaction of the bubbles, once brought into contact, was monitored using high-speed video recording. Visual inspection indicated that denser particles were more easily displaced during the contact of the bubbles, and therefore that the PMMA particles provided a particle barrier more resistant to coalescence. The coalescence events yielded information on the surface properties of the bubble and the detachment of particles. Attached particles commonly dampen the oscillation of the coalesced bubbles through viscous drag and change in surface properties (e.g. area exclusion principle). The dampening of the oscillation generally leads to a reduced mass of particle detaching from the bubble surface. It was found that the different materials investigated did not offer clear evidence on the effect of particle detachment on the bubble surface properties in the present systems. On the other hand, the detachment of different particle materials seemed to be consistent with one another when comparing the attachment and detachment forces exerted on the particles based on their density, size, and hydrophobicity. It was concluded that particles of lower density are more effective at stabilising interfaces and thus particle density is an important parameter in the selection of materials for the handling of dispersions.

Keywords

Bubble stability, coalescence, particle, density, detachment

1. Introduction

The interaction of solid particles with interfaces, whether liquid-gas or liquid-liquid, is commonplace in many processes. Emulsion droplets and foam bubbles may be stabilised by micron- nano-sized particles, which are smaller than the bubble (or droplet), and where the particles are not perfectly wetted by either phase. In all cases, there are generally three primary processes for the attachment of particles onto an interface ¹ (i) the approach of the interface (e.g. emulsion droplet or air bubble) to the particle thus forming a thin liquid film, (ii) the rupture of the thin liquid film resulting in the formation of a three-phase contact, and (iii) the stabilisation of the particle and bubble aggregate against detachment forces.

The formation of stable particle-bubble/droplet aggregates, although not essential (e.g. Sethumadhavan et al. ²), is regarded as having a stabilising effect on the bubbles/droplets; preventing their coalescence ³⁻⁹. Obviously, the particles must have characteristics suitable for the stabilization of bubbles/droplets

regarding their size, concentration, and hydrophobicity^{10, 11}. The coalescence of drops or bubbles is then necessarily associated with the contact of the bare interfaces, which may be due to a high capillary pressure or the presence of defects in the interfacial particle organisation. These findings generally hold for dynamic experiments¹² as well as quasi-static studies^{13, 14}. It is also noted that the tenacity of the particle-bubble/droplet aggregates is important in preventing the formation of packing defects to further delay bubble (droplet) coalescence.

Colloidal particles have been deployed in a wide range of applications to stabilise emulsions, foams, and liquid marbles^{4, 5, 11, 15-17}. One of the advantages of using colloidal particles stems from the fact that they are thermodynamically irreversibly adsorbed at the interface¹⁸. Thus, they are less susceptible to being removed from the interface compared with larger particles which are influenced to a greater extent by gravitational and inertial forces¹⁹. Although several studies have been dedicated to the effect of the size of particles on foam/emulsion stability^{15, 20-22}, more work is needed to characterise the effect of particle density.

This study reports the effect of particles of various densities on the stability of air bubbles. The particles had densities of 1.2, 2.5, and 3.6 g·cm⁻³ and were similar in size within the range 40 - 50 µm. Although smaller particles are generally preferred to stabilise interfaces, as outlined above, larger particles were used to enable their visual inspection. That is, bubbles were produced on capillary tubes, coated with particles, and their interaction recorded using a high-speed camera. Further, the technique allowed an estimation of the bubble surface oscillation dampening and the detachment of particles upon the coalescence of the bubbles. A force analysis was carried out to compare the behavior of the different particle material system.

2. Experimental Procedure

2.1 Materials

To test the relative effect of particle density, three different materials were used. Low density particles were made of a commercial cross-linked poly(methyl methacrylate), PMMA, Spheromer® CA40 (Microbeads AS, Norway). The particles were manufactured at an average diameter of 40 µm and a density of 1.2 g·cm⁻³. Soda-lime glass beads were purchased from Potters Industries Pty Ltd (Melbourne, Australia). The particles had a density of 2.5 g·cm⁻³ as confirmed by pycnometry. Particles were wet sieved and the size fraction -45 +38 µm was retained. The high density particles were 99.9 % titanium dioxide (anatase) with an average particle size of 40 µm as provided by Atlantic Equipment Engineers (Bergenfield, USA). The density of the particles was measured to be approximately 3.6 g·cm⁻³ by pycnometry, which is smaller than the value of approximately 3.9 g·cm⁻³ reported by others²³. The

water used throughout, except for the initial wet sieving of particles, was dispensed from a Milli-Q[®] Pure system. The water had a resistivity of $18.2 \text{ m}\Omega \cdot \text{m}^{-1}$ and a surface tension of $72.8 \text{ mN} \cdot \text{m}^{-1}$ at 20°C .

A cleaning solution for glassware was made up of sodium hydroxide (NaOH) (Sigma-Aldrich, $\geq 97.0\%$, 120 g), water (120 g), and ethanol (Chem-Supply, $\geq 99.8\%$, 1L). Other laboratory equipment (e.g. stainless steel capillaries, stainless steel baffles, magnetic stirring bar, etc.) was sonicated first in ethanol and then in water. The cleaning of the glass particles used ammonia (Ajax Finechem, 28 %) and hydrogen peroxide (Ajax Finechem, 30%), whereas sodium hydroxide was used to clean the anatase particles. Following the cleaning process, the hydrophobization of the glass particle surfaces was carried out using 1-octanol (Sigma-Aldrich, $\geq 99.0\%$), acetone (Chem-Supply, $\geq 99.8\%$), and ethanol (Chem-Supply, $\geq 99.8\%$). Hexane (Chem-Supply, $\geq 99\%$) was used as a solvent for the measurement of contact angles. Potassium nitrate (KNO_3) (Ajax Finechem, $\geq 99.0\%$) was used as a background electrolyte.

2.2 Cleaning and preparation of particles

The PMMA particles contained residual steric stabilizer. The particles were dialysed to remove this adsorbed surfactant using a cellulose dialysis membrane (molecular weight cut-off $14,000 \text{ g} \cdot \text{mol}^{-1}$). The water was exchanged twice daily for a fortnight until the surface tension of the supernatant was constant at $72.8 \text{ mN} \cdot \text{m}^{-1}$ over the period of the measurement (i.e. 10 min) as recorded on a PAT-1 tensiometer (Sinterface Technologies, Germany). The concentration of particles in the dispersion was determined by thermogravimetric analysis (TGA) (PerkinElmer Diamond TG/DTA thermal analyser). The solution was placed in aluminium pans and the analysis was performed at a temperature ranging from 20 to 560°C with a ramp rate of $10^\circ \text{C} \cdot \text{min}^{-1}$ and a constant flow of nitrogen gas of $30 \text{ mL} \cdot \text{min}^{-1}$. Polymer weight percent compositions were calculated from the mass loss up to 150°C . The concentration of the final dispersion was calculated to be 5.0 wt%.

Glass particles were cleaned according to the methodology of Hunter²⁴. An aqueous solution of 16.5 v/v% ammonia was heated to 80°C . The particles were added to the solution with 14.3 v/v% of hydrogen peroxide and stirred for 5 min. The cleaning solution was removed by multiple suspension/decantation stages until the pH returned to that of Milli-Q[®] water. The particles were dried in an oven at 60°C and stored in a desiccator.

The esterification procedure consisted of refluxing 50 g of particles (placed in an oven at 60°C overnight) in 130 g of 1-octanol in a 500 mL conical flask for 6 hours with a CaCl_2 drying tube on the condenser to limit moisture uptake. Upon cooling, the alcohol was decanted. The particles were re-suspended four times in acetone and twice in ethanol. They were then dried in a clean oven at 40°C and stored in a desiccator.

Rutile particles can be cleaned in a solution of sodium hydroxide within a Soxhlet apparatus ²⁵. Likewise, the anatase particles were heated in water to 85 ± 3 °C. Solid NaOH was added to the suspension to obtain a concentration of 10^{-2} M. Particles remained in the hot solution for 15 min and were then left to cool to room temperature. The solution was removed by centrifuging the suspension (Beckman Coulter, Allegra X-30 Centrifuge) in 50 mL test tubes at 9,000 rpm for 360 min. The supernatant was removed and the particles were re-suspended and centrifuged a number of times until the pH of the water returned to that of Milli-Q[®] water. Fine particles were removed by decantation. The particles were dried in an oven at 40 °C and stored in a desiccator.

2.3 Particle characterisation

2.3.1 Sizing

The shape and size of the particles were characterised using scanning electron microscopy (SEM). Images of PMMA particles were obtained from a Philips XL-30 microscope whereas a Hitachi S-3400N microscope was employed for the glass and anatase particles. In each case, the samples were sputter-coated with gold.

The size distribution of dispersions of the particles was determined by laser diffraction. The size distributions of the PMMA and anatase particles were evaluated using a Mastersizer 2000 while a Mastersizer E (Malvern Instrument Ltd.) was used for the glass particles.

2.3.2 Measurement of contact angle

The contact angle of particles can be measured by the capillary rise of a liquid through a packed bed of particles as developed by Washburn ²⁶. The mass of liquid penetrating the packed bed of particles (w) with time (t) is correlated to the liquid density (ρ), surface tension (γ), viscosity (η). It takes the form $w^2 = (ct\rho^2\gamma \cos \theta)/2\eta$ where c is a constant based on the properties of the packed bed of particles, which was determined here using hexane which has a contact angle (θ) of 0° ²⁷. The contact angle of both the anatase and the glass particles were measured using this method.

2.4 Binary coalescence of bubbles coated with particles

2.4.1 Experimental setup and cleanliness

The interaction of bubble pairs was observed by means of high-speed video using an experimental setup based on the work of Ata ²⁸. A schematic of the setup may be found in Bournival et al. ²⁹ where the sample beaker is placed in a cubic cell filled with water to avoid image distortion. All experiments were performed at 20 °C with aqueous 10^{-2} M KNO₃ as a background electrolyte. The concentration of

electrolyte was chosen to promote bubble coalescence^{14, 30} as opposed to preventing (or delaying) coalescence as occurs at lower concentrations^{31, 32}.

Two independent microsyringe and pump systems were used to produce bubbles of approximately 2 mm in diameter at the tips of stainless steel capillaries (0.69 mm I.D. $\times$ 1.04 mm O.D.). The relative position of the capillaries may be adjusted from the translation stages on which the capillaries were mounted. The bubbles were brought together, until their surfaces are just in contact, using a programmable linear actuator (T-LA28A, Zaber Technologies Inc.). Experiments with PMMA particles were recorded with a Phantom 5 (Vision Research Inc.) while experiments conducted with glass and anatase particles were recorded with a Fastcam APX RS (Photron) high-speed camera. In all cases, a capture rate of at least 50 frames per second (fps) was used to determine the coalescence time and at least 1000 fps for the analysis of the oscillation of the bubble projected area.

The cleanliness of the setup was checked at the beginning of each experiment. Bubbles aged 120 s in water coalesced within 3.3 ms i.e. the time resolution of the experiment when recording at 300 fps. The coalescence time for the solution (including the background electrolyte) was also tested. Finally, particles were added, and bare bubbles (i.e. all particles settled) were coalesced to test for cleanliness to ensure that the continuous phase of the dispersion (PMMA) or the dry particles (glass and anatase) did not contaminate the bubble surface. Moreover, for the anatase particles for which the wettability is known to be controlled by the adsorption of atmospheric contaminants³³, the coalescence time being within 1 or 2 frame intervals indicates that the surface contaminants were not solubilised in the aqueous solution. Thus, the coalescence time measurements are considered to be a more sensitive test than surface tension to detect such contamination³⁰.

2.4.2 Coating and coalescence of bubbles

The PMMA particles were added as a dispersion such that the solids concentration was 0.5 wt%. For glass and anatase particles, 1.0000 g (± 0.0005 g) of particles was added to the beaker and then the coalescence of air bubbles blown at the capillary tips was examined. Bubbles covered with particles were produced by magnetically stirring the dispersion for varying times depending on the desired bubble surface coverage. The particles were then left to settle. The ageing time for all experiments was generally in the range of 1 – 15 min and is calculated from the time the bubbles (or first bubble) were produced to the time they were brought into contact.

The coverage of the bubbles by particles was calculated using a surface integral on the lower and upper halves of the bubbles^{30, 34}. ImageJ (National Institutes of Health) was used to perform the required measurements (e.g. diameter, heights, etc.). Each bubble was assessed individually, and averages were taken. The interfacial coverage of the bubbles was in most cases below the equator of the bubbles, and

thus no particles were present in the thin aqueous film separating the interfaces upon contact. In addition, some experiments were performed with one bubble covered above its equator while the second bubble was bare, a geometry which resulted in a single layer of particles separating the contacting bubble surfaces. A schematic of the different configurations is presented in Figure 1.

Figure 1. Bubble surface coverage used in most experiments. The shaded area represents the area covered by particles. (A) Low, (B) medium, and (C) high surface coverage with respect to the contact zone, as well as (D) experiments with a single layer of particles separating the bubbles.

The analysis of coalescence dynamic and particle detachment has been described elsewhere³⁰. A summary is presented in the Supporting Information.

3. Particle properties

3.1 Scanning electron microscopy

SEM images of the PMMA, glass, and anatase particles are presented in **Error! Reference source not found..** The PMMA and glass particles were spherical in shape while the anatase particles were angular. The projected area diameter of the particles was $39\ \mu\text{m}$ with standard deviation (σ) of $1\ \mu\text{m}$ calculated from 43 measurements (n) for the PMMA; $39\ \mu\text{m}$ with $\sigma = 4\ \mu\text{m}$ and $n = 171$ for glass; and $51\ \mu\text{m}$ with $\sigma = 8\ \mu\text{m}$ taken from 190 measurements for the anatase. The anatase particles appeared porous, which accounts for the lower than expected measured density (Section 2.1). Figure 2 C and E show the broad range of particles size for glass and anatase, which was mostly likely not captured in the measurements of the projected diameter due to the small size of the samples.

Figure 2. SEM images of (A) PMMA, (B, C) glass, and (D, E) anatase particles.

The volume frequency distributions obtained by laser diffraction are shown in Figure 3. The PMMA particles had a 50 % passing size diameter (D_{50}) of 38.0 μm and a volume-surface equivalent particle diameter (d_{32}) of 36.9 μm . The D_{50} and d_{32} were 41.2 and 39.7 μm for the glass particles and 52.8 and 51.3 μm for the anatase particles, respectively. All samples are relatively monodisperse. Comparing the D_{50} of the samples determined on a volume basis and that of the number distribution (D_v/D_n) gives a polydispersity index of 1.2 for the PMMA and anatase particles, while a polydispersity index of 1.3 was found for the glass particles. Figure 3 also include the average diameters of the particles determined from the SEM images. The projected diameters are consistent with the laser diffraction results.

Figure 3. Volume frequency distributions of PMMA particles (blue), glass particles (red), and anatase (green). Lines mark the projected diameter derived from measurements of SEM micrographs.

3.2 Wettability of particles

The measurement of titania contact angle on particles is complex. For instance, Nowak and co-workers³⁵ used various techniques to determine the hydrophobicity of porous catalytic titania (crystal polymorph unspecified) and found the contact angle to be largely influenced by the method employed. The cleaning of rutile particles in a hot NaOH solution produced a contact angle of $76.6 \pm 1.4^\circ$ using the Washburn method with a phosphate buffered saline solution²⁷. Due to the high surface energy of titania, the contact angle of anatase particles is also expected to be relatively high, albeit below 90° . The quantification of the hydrophobicity of the anatase particles was carried out through the measurement of the contact angle using the Washburn method.

The value obtained is an advancing contact angle and was found to be 64.5° with a standard deviation (σ) of 7.6° , which is in agreement with the control sample of MacDonald et al.²⁷. The cleaning of the surface may lead to a contact angle of 0° ^{33, 36, 37}. Kanta et al.³³ showed that following the cleaning of (amorphous) titania the contact angle starts to increase in a matter of minutes when exposed to the atmosphere due to atmospheric contaminants.

The contact angle of the glass particles was increased by covalently grafting molecules to the surface. Such an esterification procedure has been shown to produce a resistant coating of a uniform layer with a degree of hydrophobicity given by the length of the alkyl chain^{24, 38-41}. The alcohol used to esterify the glass particles was 1-octanol. The advancing and receding contact angles of a water droplet measured on an equivalent silicon wafer were found to be 73.5° and 67.5° , respectively in the water phase⁴² whereas other authors⁴¹ determined an equilibrium contact angle of 75° in the water phase as

measured by the captive bubble technique. Through the Washburn method, the contact angle of the glass particles was calculated to be 79.4° ($\sigma = 2.8^\circ$). This value is higher than the value found by Hunter et al.⁴² but in relative agreement with an equilibrium contact angle of 75° .

The PMMA particles were observed to be relatively hydrophobic, although the contact angle was not measured here. However, Zograf and Johnson⁴³ measured the contact angle of a smooth PMMA surface using the sessile drop technique. They found advancing and receding contact angles of 76° and 52° , respectively, as determined in the water phase.

It should be noted that in foam stabilisation the contact angle of the particles is generally kept below 90° since particles with high contact angles act as froth breakers (i.e. anti-foaming agent). Thus, although the contact angle of the particles was found to be below 90° , such particles are considered 'hydrophobic', which is also the terminology adopted here. Finally, **Error! Reference source not found.** summarises the properties of the particles used in this study as well as particles from other studies for which results were re-analysed to complement this study.

Table 1. Summary of the particle physical characteristics and their preparation for the coalescence experiments. The table also includes particles from other studies for which results were used in the current analysis.

Characteristic Material	Density g cm^{-3}	Size μm	Shape	Cleaning	Hydrophobisation	Contact angle in the water phase (σ), $^\circ$
PMMA	1.2	D ₅₀ = 38.0 d ₃₂ = 36.9 D _{projected} = 39	Spherical	Dialysis	None	$\theta_{\text{ad}} = 76^{\text{a}}$ $\theta_{\text{rec}} = 52^{\text{a}}$
Glass (finer)	2.5	D ₅₀ = 41.2 d ₃₂ = 39.7 D _{projected} = 39	Spherical	Alkaline solution (H ₂ O ₂ , NH ₃)	Esterification in 1-octanol	$\theta_{\text{ad}} = 73.5^{\text{a}}$ $\theta_{\text{rec}} = 67.5^{\text{a}}$ $\theta_{\text{eq}} = 75 (2)^{\text{b}}$ $\theta_{\text{ad}} = 79.4 (2.8)^{\text{c}}$
Anatase	3.6	D ₅₀ = 52.8 d ₃₂ = 51.1 D _{projected} = 51	Angular	Alkaline solution (NaOH)	None	$\theta_{\text{ad}} = 64.5 (7.6)^{\text{c}}$
Glass (coarser) ³⁰	2.5	D ₉₀ = 92.5 D ₅₀ = 66.0 d ₃₂ = 64.0	Spherical	Alkaline solution (H ₂ O ₂ , NH ₃)	Esterification in 1-butanol	$\theta_{\text{ad}} = 58.0^{\text{a}}$ $\theta_{\text{rec}} = 39.5^{\text{a}}$ $\theta_{\text{eq}} = 43 (6)^{\text{b}}$
Alumina ⁴⁴	3.6	D ₅₀ = 24.2 polydisperse	Spherical	None	None	$\theta_{\text{ad}} = 52.4 (8.8)^{\text{c}}$
Galena ^{45, d}	7.6	D ₉₀ = 52.0 D ₅₀ = 33.4 d ₃₂ = 35.4	Angular	Na ₂ B ₄ O ₇ buffer solution with ethylenediamine tetraacetic acid (EDTA)	None	$\theta_{\text{eq}} = 37 (3)^{\text{b}}$ (at pH 8 on freshly cleaved surface in deoxygenated water)

^a Sessile drop

^b Captive bubble

^c Washburn

^d 0.25 ppm OrePrep F-549 additive

4. Analysis

The interpretation of the results required certain calculations to be performed. Firstly, the interaction of the particles at the interface is believed to influence the elasticity of the interface through variation in the surface pressure as demonstrated for Langmuir trough experiments^{42, 46}. The other calculations are related to the acceleration of the bubble surface, which is needed to estimate the detachment force.

4.1 Interaction of particles at the air-water interface

The interaction force between two partially submerged particles may be calculated following the precedent of Tarimala and Dai⁴⁷ and Ata²⁸. The calculations of the interacting force were estimated for two identical, spherical particles located at the air-water interface. The van der Waals component of the force (F_{vdW}) was assumed to follow⁴⁸:

$$F_{vdW} = -\frac{A_{eff}r_p}{12h^2}f(p) \quad (1)$$

in which A_{eff} is an effective Hamaker constant, h is the separation distance, and $f(p)$ is a function, which corrects the van der Waals force for retardation effects. The effective Hamaker constant was calculated by applying a correction based on the linear fractional immersion height (f) of the particles⁴⁹. The effective Hamaker constant follows:

$$A_{eff} = A_{12} + f^2(3 - 2f)(A_{13} - A_{12}) \quad (2)$$

where A_{12} and A_{13} are the Hamaker constants in the gas and water phase, respectively and were determined using the macroscopic theory⁵⁰. The function $f(p)$ takes the form:

$$\begin{aligned} f(p) &= (1 + 3.54p)/(1 + 1.77p); \quad p < 1 \\ f(p) &= 0.98/p - 0.434/p^2 + 0.067/p^3; \quad p > 1 \end{aligned} \quad (3)$$

where $p = 2\pi h/\lambda$ and λ is the retardation length scale. The electrostatic force (F_{el}) was calculated using:

$$F_{el} = \frac{6\varepsilon_{air}q_{water}^2}{4\pi\varepsilon_0\varepsilon_{water}^2\kappa^2h^4} \quad (4)$$

where ε_0 , ε_{air} , and ε_{water} are the permittivity of vacuum, and the relative permittivity of air and water respectively. κ is the Debye-Hückel parameter and q_{water} is the charge of the immersed section of the particle. The charge on the immersed section of the particle is:

$$q_{water} = 2\pi r_p \kappa^{-1} \sigma \tau_{water} \sin \theta \quad (5)$$

in which σ is the surface charge density, τ_{water} is the degree of dissociation of the particle surface group (e.g. silanol) in water, and θ is the contact angle. The surface charge density was approximated considering two spherical particles of low potential and follows:

$$\sigma = \frac{\epsilon_0 \epsilon_{water} (1 + \kappa r_p) \psi_0}{r_p} \quad (6)$$

where ψ_0 is the surface potential. The capillary force (F_l) was determined using the equation of Chan et al.⁵¹, which, for the interaction of two identical particles, follows:

$$F_l = -2\pi\gamma r_p B^{5/2} S^2 K_1(\lambda_c l) \quad (7)$$

where B is a Bond number ($B = (\rho_l - \rho_g)ga^2/\gamma$; g is the gravitational acceleration, ρ_g is the density of the gas phase), S is a sphere constant ($S = 2D/3 - 1/3 - \cos \theta/2 + \cos^3 \theta/6$, where $D = (\rho_p - \rho_g)/(\rho_l - \rho_g)$ is the density ratio). The expression K_l is a modified Bessel function, which was approximated by $1/\lambda_c l$, in which $\lambda_c = \sqrt{(\rho_l - \rho_g)g/\gamma}$ is an inverse capillary number and l is the separation distance of the particles from the centres of mass (i.e. $l = 2r_p + h$).

Figure 4 shows the total interaction force between two particles of PMMA, glass, and anatase. The exact degree of dissociation of the surface groups by water was unknown but maximum values of 0.53 for glass⁵², 0.67 for rutile⁵³, which was assumed as an upper limit for anatase, and 1 for PMMA were considered (dash lines). The minimum value was assumed to be 0.1 (full lines). It can be seen that the PMMA particles are expected to be attracted to one another regardless of the degree of dissociation of the surface group. On the other hand, the glass and anatase particles may be attractive or repulsive depending on the values of τ_{water} . In water the degree of surface group dissociation was expected to be low in comparison to those obtained in acidic solution containing similar ions to the particles (e.g. polysilicic acid for silica). Thus all three types of particles are believed to be unstable to some extent at the air-water interface with the PMMA particles being the least stable. As such, some coagulates may be observed.

Figure 4. Interaction force between two particles of PMMA (blue), glass (red), and anatase (green). The full lines represent a degree of dissociation of 0.1 while the dashed lines used 1 for PMMA, 0.53 for glass, and 0.67 for anatase.

It is worthy to add at this stage that the calculations are for two similar particles at the air-water interface under equilibrium conditions. That is, no interpretation on the capture rate between a particle at the interface and a second particle in the liquid phase may be obtained. Although the particles may tend to agglomerate over extended time periods, there is no strong indication of multilayer formation at the bubble surface. However, as will be discussed later, some agglomeration was observed in specific cases.

4.2 Acceleration of the bubble surface

In the absence of surface active solutes, the dampening of the bubble oscillation is influenced by the presence of particles. However, the dampening seems not to be the driving force to expel the particles in the present system. An attempt has been made to investigate the acceleration encountered by the particles during the contraction of the interface. The horizontal distance (d) between the ends of the bubble at the height of bulging was measured as a function of time. An example measurement is given in Figure 5A. The half distance ($d/2$) representing the displacement of one interface was plotted as a function of time (see Figure 5B – left vertical axis) and fitted with Equation 8, which is an adaptation of the equation for the coalescence dynamic (Equation S1) where $d/2$ is the displacement of one interface and $(d/2)_0$ is the initial amplitude.

$$\frac{d}{2} = \left(\frac{d}{2}\right)_0 \times e^{-\delta t} \times \sin(\omega_0 t + \psi) + B \quad (8)$$

In Figure 5B (right vertical axis) the acceleration of the interface was calculated from the second derivative of Equation 8 where the maximum values can be determined using the third derivative. The detachment of particles occurs upon the rapid contraction of the interface during the first cycle of the oscillation³⁰. A maximum is found at approximately 3.7 ms in Figure 5B. It is hypothesised that particles which remain attached to the interface may affect the acceleration of that interface. Conversely, a high detachment of particles may not impede the motion of the interface yielding an acceleration close to that of a coalescing bare bubble. The calculated acceleration values were used in the estimation of the detachment force as presented in Section 4.3.

Figure 5. (A) Distance between the bubble ends at the plane of bulging during post-coalescence oscillation. (B) The displacement of one interface is plotted as a function of time ($\diamond$) with the fitted curve (dashed line) (left vertical axis). The full line shows the calculated acceleration based on the fitted parameters (right vertical axis).

4.3 Comparison of forces between a particle and bubble couplet

An attempt to quantify the tenacity of the particle-bubble aggregate, and compare them on the basis of a dimensionless number, as introduced by Schulze^{54, 55}, was made in order to get a better insight into

the cause of the detachment of particles during the coalescence of two bubbles. The system was simplified to a single particle at a bubble surface as illustrated in Figure 6 where some key variables are also defined, which include α the half angle formed by the non-wetted portion of the particle and β is the supplementary angle.

Figure 6. Schematic of a spherical particle attached to an air bubble. Drawn after ^{1, 56, 57}.

Among the forces acting on the particles ⁵⁴⁻⁵⁷ is the gravitational force (F_g), which follows:

$$F_g = \frac{4}{3} \pi r_p^3 \rho_p g \quad (9)$$

where ρ_p is the density of the solid particle and g the gravitational acceleration. The portion of the particle submersed in the liquid phase is subject to a buoyancy force (F_b) given by:

$$F_b = \frac{\pi}{3} r_p^3 \rho_l g (1 - \cos \beta)^2 (2 + \cos \beta) \quad (10)$$

in which ρ_l is the density of the liquid phase. The pressure inside the bubble is larger than in the surrounding liquid due to the curvature of the bubble as defined by the Young-Laplace equation ⁵⁸. This additional force, a capillary pressure force (F_p), thus exerted on the particle may be approximated by ^{56, 59}:

$$F_p = \pi r_p^2 \left(\frac{2\gamma}{r_b} - 2r_b \rho_l g \right) \sin^2 \beta \quad (11)$$

where r_b is the radius of the bubble and γ is the surface tension. The inertial force is composed of the mass of the particle and the added mass multiplied by the acceleration of the particle (b_m) ⁵⁷. In this particular context, the acceleration was taken as the maximum acceleration as found by the horizontal displacement of the interface as shown in Figure 11. The inertial force (F_i) takes the form:

$$F_i = \frac{\pi r_p^3}{6} b_m (8\rho_p + \rho_l (2 + 3 \cos \alpha - \cos^3 \alpha)) \quad (12)$$

Finally, unlike the other forces the capillary force (F_c), which arises from the tension of the interface on the three-phase line of contact, keeps the particle at the interface.

$$F_c = 2\pi\gamma r_p \sin(\alpha) \sin(\theta - \alpha) \quad (13)$$

The formation of a meniscus due to the deformation of the bubble surface causes the three-phase line of contact to lie below the plane formed by the undeformed interface. This phenomenon gives rise to a hydrostatic force (F_h), which is dependent upon the depth of the meniscus depression (H).

$$F_h = \pi r_p^2 \rho_l g L H \sin \alpha \quad (14)$$

where L is the capillary length and is defined as:

$$L = \sqrt{\frac{\gamma}{\rho_l g}} \quad (15)$$

The depression of the meniscus may be approximated from the relationship proposed by Nguyen and Schulze⁵⁸:

$$H = 2L \sin\left(\frac{\theta - \alpha}{2}\right) \left(1 + \frac{L}{r_p \sin \alpha}\right)^{-1/2} \quad (16)$$

The modified Bond number (Bo_m), which is an expansion of the Bond (or Eötvös) number, is simply defined as the ratio of the detachment forces over the attachment forces, or mathematically,

$$Bo_m = \frac{(F_g - F_b) + F_p + F_i}{F_c + F_h} \quad (17)$$

Theoretically, a Bo_m of 1 indicates that the attachment and detachment forces are equivalent. A $Bo_m < 1$ means that the attachment forces dominate the force balance while a $Bo_m > 1$ signifies that the detachment of particles is expected.

5. Results and Discussion

5.1 Stability of bubbles covered by particles

The stability of bubbles covered with different particulate materials was assessed by measuring the coalescence time. Results, which are reported in Table 2, were divided into two groups composed of measurements where particles are not in the contact zone (configurations A, B, and C in Figure 1) and with one layer of particles separating the bubbles (configuration D in Figure 1). In the absence of particles in the contact zone coalescence always occurred. These coalescence times are relatively short compared to those obtained when one layer of particles was present. For the latter configuration, the coalescence times increased with decreases in the density of the particulate materials. As coalescence

time is a measure of bubble stability, it is not surprising that the probability of the coalescence event followed a similar trend.

Table 2. The range of coalescence times and coalescence probability (brackets) of bubble pairs covered with particles.

Material	No particles in the contact zone	One layer of particles in the contact zone
PMMA	0.1 – 0.6 s (100%)	0.7 - 336 s (78%)
Glass	0 – 0.018 s (100%)	0.5 – 90 s (83%)
Anatase	0 – 0.02 s (100%)	0.02 – 2 s (100%)

Studies ^{6, 10, 12} have shown that for bubbles and emulsions, the formation of defects such as the lowering of the particle packing density (i.e. expansion of the interfacial area) or the displacement of particles is the most likely explanation of the instability of the bubble pairs separated with a particle layer. The capillary pressure needed to contact the bubble surfaces is not expected to be overcome when the particle layer is intact under the current experimental conditions. The displacement of particles may lead to a decrease in the packing density of the particles, which may cause the coalescence of the bubbles through: (i) the exposure of areas of bare bubble surfaces, or (ii) the exceeding of the maximum capillary pressure. The latter is reduced due to the increase in the spacing between particles ^{60, 61}.

The PMMA particles appeared to form a more resistant coating which prevented coalescence more often, and offered a prolonged stability against coalescence. On the other hand, the anatase particles were a poor bubble stabilizer. The effect of the density of the particles may not be obvious, but other results (e.g. Figure 9) showed that the denser particles were more easily removed from the interface. This observation was also confirmed through the comparison of the forces acting on the particles, which indicates that anatase particles are more prone to detachment (as discussed later – see Figure 12). Thus, it can be inferred that packing defects may be more readily created with anatase (and glass) particles than with PMMA particles. The presence of packing defects was deduced through visual inspection as depicted in Figure 7. Figure 7B also illustrates how a lateral force induced by the second bubble may push particles off the interface, which will then lower the packing density around the contact point. In the case of the glass particles, the force between the particles in the water phase was such that they remained agglomerated. This removal of particles creates the packing defect required to promote bubble coalescence as depicted in Figure 7.

Figure 7. (A) Visual evidence of the anatase particle coating movement (yellow line) and the detachment of particles during the contact and the re-organisation of the particles (circled in red). The outer diameter of the capillary tube is 1.04 mm and is used as an effective scale bar. (B) Schematic of the lateral force caused by the contact of the second bubble. The lateral force may cause particles to detach. In (C) there is evidence of particles agglomeration upon the rupture of the thin liquid film. The lateral force exerted by the second bubble causes the removal of particles from the interface, which agglomerates to the surrounding particles as shown in (D).

The formation of a defect sufficient for the destabilisation of the contacting bubbles may take some time, as shown by Bournival et al.¹⁰, and explains the large coalescence time reported in Table 2 when a layer of particles is present between the two bubble surfaces. In terms of mechanisms which may generate packing defects, the lateral displacement of the particles combined with the removal of particles from the interface is a plausible hypothesis as evidenced in Figure 7. This lateral displacement of the whole coating may be accompanied by a localised displacement of particles near the contact point (see Supporting Video – displacement of glass [finer glass, $\theta_{ad} = 79.4^\circ$]). The force analysis presented in Section 4.1 may partly explain the greater stability of the bubbles covered with PMMA particles as a larger force is required to move particles away from each other and create packing defects. PMMA particles are believed to be difficult to displace from the interface (see Figure 12). In addition, Figure 4 revealed that the particles are strongly attracted to each other at the interface, which may lead to the formation of a coherent network of particles resistant to the formation and propagation of defects. That is to say, the phenomena observed for glass and anatase (illustrated in Figure 7) were not observed for

the experimental system containing PMMA particles. It should also be noted that due to the configuration of the experimental systems, gravitational forces and a radial force⁶², which arises from the packing of particles, may still overcome the total (repulsive) force shown in Figure 4. It may be speculated that the displacement/sliding of particles is easier for glass and anatase, e.g. Supporting Video. In addition, the fact that glass and anatase are denser may lead to the increased likelihood of particles detaching from the bubble surface, e.g. Figure 7.

5.2 Effect of bubble loading on the bubble surface properties and particle detachment

The analysis of the interfacial properties of the bubble during coalescence may be performed by modelling the projected area as a function of time^{10, 29, 30}. Figure 8 compares the dampening of the bubbles during coalescence as a function of the coverage of the bubble by particles. The increased loading of the bubble caused an increase in the dampening of the bubble oscillation in the case of PMMA and, less significantly, for the glass particle system. It has been noted that geometrically, the particle coverage of the bubbles need to be relatively high in order to possibly affect the bulging of the bubble periphery, which occurs approximately at the same height as the point of rupture of the thin liquid film¹⁰. Thus, the dampening of the oscillation may be a function of the initial coverage of the bubbles¹⁴, especially when the particles remain on the surface. The damping coefficient appears to remain relatively constant for the anatase system regardless of the initial fractional coverage of the bubble by particles, which may be caused by the high degree of detachment of particles.

Figure 8. Effect of the initial fractional coverage of the bubbles by particles on the dampening of the coalescence oscillation. The closed markers represent the coverage of two bubbles (e.g. configurations A – C in Figure 1) whereas the open markers show the coverage of one bubble (configuration D in Figure 1). Results are presented for (♦) PMMA, (■) glass, and (▲) anatase particles.

The effect of the initial coverage of the bubbles on the detachment of particles is shown in Figure 9. Except in the case of a single bubble covered above its equator by glass particles (configuration D in Figure 1), the detachment of particles appeared to be unaffected by the initial bubble loading.

Figure 9. Effect of the initial fractional coverage of the bubbles by particles on the fractional detachment of particles upon bubble coalescence. The closed markers represent the coverage of two bubbles (e.g. configurations A – C in Figure 1) whereas the open markers show the coverage of one bubble (configuration D in Figure 1). Results are presented for (♦) PMMA ($\rho_p = 1.2 \text{ g cm}^{-3}$), (■) glass ($\rho_p = 2.5 \text{ g cm}^{-3}$), and (▲) anatase ($\rho_p = 3.6 \text{ g cm}^{-3}$) particles.

The damping coefficient may be used to predict the ability of the bubble surface to retain particles as previously reported for the detachment of glass particles in cetyltrimethylammonium bromide (CTAB),¹³ or frother solutions³⁰, and for galena particles in frother solutions⁴⁵. In these studies the effect of the dampening of the oscillation related to the detachment of particles (i.e. comparing the same experimental system). However, the establishment of a relationship between the damping coefficient and the degree of particle detachment has not previously been attempted for different particulate systems. For the sake of generality, data from previous studies has been added to those measured in the current study. The characteristics of these additional particles are reported in **Error! Reference source not found.**, which comprise alumina, galena, and glass particles. The glass particles were coarser and less hydrophobic than those used in this study while of similar density. Figure 10 shows that the lower damping coefficients are generally associated with a higher fractional detachment of particles with the exception of the finer (39.7 μm) glass particles. The transition, in Figure 10, may occur at a damping coefficient of approximately $0.06 - 0.08 \text{ ms}^{-1}$, which is interestingly close to the value found for the reduction in detachment of glass particle by adsorbed frothing agents³⁰. Thus, there may be an oscillation dampening, characteristic to two coalescing bubbles, in which particles are more likely to detach regardless of their properties. However, the relationship between particle detachment and

oscillation dampening is not straightforward when considering the effect of the different particle materials on the latter which is distinct for the different particles (Figure 8).

Figure 10. Fractional detachment of particles as a function of the damping coefficient of the oscillation of the projected area of the coalescing bubble. Experiments were performed with (♦) PMMA, (■) glass (finer, $\theta_{ad} = 73.5^\circ$), and (▲) anatase particles. Also included are results from other studies using (□) glass (coarser, $\theta_{ad} = 58.0^\circ$), (×) alumina, and (○) galena.

The comparison of the two experiments with glass particles in Figure 10 may shed light on the many factors influencing the damping coefficient. Between the two sets, the hydrophobicity and the size of the particles were different, while the density remained constant. The results show that the damping coefficients are nearly identical for the two glass samples, which however yielded convincingly different detachment values. The larger and less hydrophobic particles detached in greater numbers than the smaller more hydrophobic particles as expected but the detachment cannot here be attributed to the mass of particles remaining on the surface. Smaller particles are known to produce a larger damping coefficient of the bubble oscillation^{10, 13} most probably through increases in the elasticity of the surface⁶³⁻⁶⁵. In addition, the dampening of the oscillation of the bubble may be found to increase with increases in the degree of hydrophobicity of the particles¹⁰. Thus, the damping coefficient found for the smaller (39.7 μm) and more hydrophobic (73.5 $^\circ$) particles was found to be unexpectedly low.

During the oscillation of the bubble surface, the particles on the surface may affect the oscillation through the formation of a connected particle network⁶⁶, viscous energy dissipation (i.e. drag)²⁸, and a change in the properties of the composite surface made up of particle and bubble surfaces⁶⁷. It is difficult to measure these properties when the mass of particles is changed during the dynamic oscillation. However, it has been noted that most of the particles detach during the first contraction of the bubble. Thus was hypothesized that a relationship may exist between the detachment of particles and the maximum acceleration, which, for the bubble interface, occurs in the first cycle when the bubble

is fully contracted (Figure 5B). Figure 11 shows the maximum acceleration of the interface as a function of the detachment of particles, as outlined in Section 4.2. The figure compares the average maximum acceleration of the bubble interface from the different systems with a system without particles (dash line).

The fact that the particle-bubble surface composite changed due to the detachment of particles does not appear to systematically influence the acceleration of the bubble surface. Such information may be too sensitive to be detectable through a change in the displacement of the interface as depicted in Figure 5A. It should also be noted that the detachment of particles itself may affect the total energy of the system knowing that thermodynamically an energy decrease is calculated for the adsorption of particles at an air-water interface^{68,69}. Conversely, the surface properties of the bubble surface may be explained by the detachment of particles. It has been shown that the dampening of the bubble surface oscillation is influenced by the loading of particles¹⁴. It was speculated that the high detachment of anatase particles observed here may limit the dissipation of energy through viscous resistance. On the other hand, the PMMA particles, which tended to remain at the bubble surface, were subject to the smallest acceleration force. However, no clear correlation emerged between the fractional detachment of the particles and the maximum acceleration of the bubble surface. Nevertheless, the average acceleration found for the different systems was used in the detachment analysis outlined in Section 4.3 and presented in Section 5.3.

Figure 11. Effect of fractional particle detachment on the maximum acceleration of the projected area during the first contraction of the interface upon the coalescing of bubble pairs. Experiments were performed with (♦) PMMA, (■) glass (finer, $\theta_{ad} = 73.5^\circ$), and (▲) anatase particles. Also included are results from previous studies using (□) glass (coarser, $\theta_{ad} = 58.0^\circ$), (×) alumina, and (○) galena and are all compared to the average for bare bubbles coalescing in water (dashed line).

5.3 Detachment analysis in terms of bubble surface properties

Figure 12 shows the effect of the force balance, that is the modified Bond number, on the fractional detachment of particles from the bubble. It can be observed in Table 1 that the value of the contact angle of the particles may be affected by the method employed. The horizontal error bars in Figure 12 show the variation in the modified Bond number for a change of $\pm 5^\circ$ in the advancing contact angle. For the different materials, a transition can be observed with low detachment for, generally speaking, smaller, low density particles and higher detachment for larger, higher density particles. As such, the results are following the expected trend except for the fact that the transition was observed to be two orders of magnitude lower than anticipated and seemed to be unaffected by slight variations in the contact angles of individual particles (i.e. calculations not affected by the contact angles measuring technique). It should be emphasized that the force balance^{1, 55} which lead to the development of the modified Bond number was based on a single spherical particle. The calculated capillary force is approximately two orders of magnitude larger than the other detaching forces, which explain the low values of the modified Bond number. It is believed that the attachment force estimated using Equation 13 were an overestimation from the fact that there is more than one particle, and the particle surface is not homogeneous. Other factors may have influence the magnitude of the modified Bond number as follows.

Particles which are positioned higher on the bubble may exert a radial force on the lower particles^{62, 70}, which may act as an effective detachment force. Moreover, it was found that angular particles had a broader detachment probability distribution than spherical particles. These results were corroborated by Goel and Jameson⁵⁶ who observed a 10 to 15% increase in the detachment of angular particles compared to nearly spherical particles. However, when comparing similar wetted perimeters, sharp edges may accentuate the capillary force⁷¹. The pinning of the interface onto the particle due to surface roughness (or even superficial pores) may give rise to a larger attractive force. Thus, particles like the anatase (see **Error! Reference source not found.**) may appear more hydrophobic. It should be noted that such pinning may be followed by a slip of the three-phase line of contact and destabilisation of the particle-bubble aggregate⁷²⁻⁷⁴. In addition, the orientation of the particles, if irregular, may determine whether the pinning promotes particle detachment. Thus, the low transitional value noted in Figure 12 may be partly imputed to superficial defects. However, in the specific case of the anatase and galena particles, it appears that the trend corresponds to that observed with the spherical glass particles. Thus, any pinning is considered to be negligible compared to other forces.

Figure 12. Fractional detachment of particles expressed as a function of the modified Bond number. Experiments were performed with (♦) PMMA, (■) glass (finer, $\theta_{ad} = 73.5^\circ$), and (▲) anatase particles. Also included are results from other studies using (□) glass (coarser, $\theta_{ad} = 58.0^\circ$), (×) alumina, and (○) galena. The dashed line shows the general trend. The horizontal error bars represent the effect of a change of $\pm 5^\circ$ in three phase contact angle on the modified Bond number.

More significant is the finding by Nutt⁷⁵ that the centrifugal forces needed to detach a raft of particles was considerably less than the force required to remove a single particle. A single particle, as calculated in section 4.3, is subject to an absolute inertial force⁵⁷. It is hypothesised that the formation of rafts due to attractive inter-particle forces⁷⁶ underestimated the actual mass of the particle while considering the raft as a single entity. Stevenson et al.⁵⁷ also noted the finite response of the three-phase contact line (formed by α in Figure 6). The three-phase contact line is necessary to establish an equilibrium position and retain the particles at the interface⁷⁷. The time lag of the three-phase contact line due to the high frequency oscillation may lead to the premature detachment of the particles since the three-phase contact line is not in an equilibrium position. On a similar note, the contact angle hysteresis has been shown to influence the detachment of a particle⁷⁸ and is not accounted for in force balances e.g.^{55, 56, 58, 79}. Finally, a knowledge of the local forces is required to estimate properly the detachment force¹⁰. In other words, phenomena such as particle motion on the surface of the bubble or the presence of surface waves^{80, 81} are not incorporated in the estimated acceleration of the particles, which was taken as the acceleration of the interface (see Figure 5A). It is speculated that the method presented in section 4.2 may be an underestimation of the actual acceleration acting on the particles.

The trend shown in Figure 12 facilitates comment on the relative magnitude of the forces involved. Among those considered, the hydrostatic force may rightly be ignored for the current particulate systems^{54, 56, 57}. The major detachment force arose from the pressure inside the bubble exerting a force

on the particle (F_p). While investigating different particulate systems, the main parameters affecting this force are the size and the hydrophobicity of the particles. Similarly to the inertial force, the capillary pressure force may be underestimated. The local pressure inside the bubble is unknown during the dynamic oscillation process. For instance, the radius of curvature is changing with time and in the different location on the surface of the bubble (see Figure 5A bubble contour). Thus, the force exerted by the capillary pressure on the particle may also be more elevated.

The other major force contributing to the detachment of the particles was related to the density (and size) of the particles. Whereas the weight of the particles themselves (F_g) was not especially significant, the added mass due to the inertial forces, which like the gravitational force combines the density and size of the particles, was one order of magnitude higher than the latter and comparable to F_p in terms of magnitude (except for the PMMA where F_a was an order of magnitude lower). While other investigations^{56, 59, 75, 82} indirectly studied the effect of the gravitational and inertial forces through a change in the size of the particles, the role of density may here be discussed in terms of the PMMA. It is, in fact, interesting to note that although the modified Bond number of the PMMA rests between that of the alumina and the 39.7 μm glass particles the fractional detachment remained negligible. It is theorized that the inertial force may contribute to the motion of the three-phase contact line, which subsequently caused the destabilisation of the bubble-particle aggregate.

The potential importance of the density of the particles thus highlighted may be important in the selection of materials to stabilise foams, emulsions, and liquid marbles. A considerable number of studies has shown that the stability of such dispersions is affected by the concentration of particles^{7, 42, 60, 83}. Assuming that the attachment/adsorption of particles is independent of the density of the particles, the lower density particles were shown to be more effective at preventing bubble coalescence (Section 5.1). In addition, due to the lower detachment of particles, the coverage of the coalesced bubble is higher in the case of PMMA. As such, it is suggested that the stability of the coalesced bubble may be increased compared to those of other particulate systems. Thus, the selection of relatively low density particles, relative to the continuous phase, may be a key factor in the handling of dispersions requiring high stability against coalescence.

The finding is also significant for industrial processes such as froth flotation. In froth flotation, valuable particles are promoted to attach on air bubbles, which rise to the surface to form a froth. The froth is collected to recover the valuable materials. The bubbles in such a system are transiently stable, and bubble coalescence regularly takes place. To optimise the recovery of particles, the probability of a particle to detach should be low⁸⁴. A few strategies may be put in place to reduce this probability. The attachment force may be increased by increasing the hydrophobicity of the particles, which should be kept below 90 °. Alternatively, the detachment force may be decreased for dense particles through size reduction to reduce the inertial force experienced by the particles, although this would be a less

preferable approach due to the high cost associated with grinding. Due to the added cost of grinding, another option is to reduce the detachment force by designing flotation devices, which are more quiescent⁸⁵, or modify the bubble interfacial properties through the addition of surface active reagents

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6. Conclusions

The stability of bubbles loaded with particles of different densities was tested through the pairwise interaction of bubbles. Coated bubbles were brought into contact, and the stability of the bubbles was evaluated by their coalescence probability and the time needed for coalescence to occur. The surface properties of the bubbles as well as the stability of the bubble-particle aggregate were estimated during the coalescence of the bubble pairs.

The less dense particles tended to form a more resistant coating against coalescence. In fact, denser particles were seen to be dislodged during the contact of the coating with a second bubble, which may have facilitated coalescence.

It is unclear if the density of the particles directly influenced the properties of the bubbles. The fact that more particles remained on the surface of the coalesced bubble may partly explain the high dampening observed with PMMA particles. However, no clear correlation emerged between the maximum acceleration of the bubble surface (i.e. which is a measure of energy) and the detachment of particles. Whilst the presence of particles may give rise to a viscous (drag) resistance and alter the surface properties, the results are inconclusive in terms of how the interfacial energy balance is affected by the removing of particles (i.e. creation of new bubble surface).

The detachment of particles for the different particulate systems was compared via a modified Bond number. This number represents the balance between attachment and detachment forces. Although the magnitude of the modified Bond number was lower than theory predicted, it showed a very good consistency. It was found that the PMMA may not have followed the description of the modified Bond number theory due to its density being similar to the continuous phase. Therefore, the density of the particles appears to be an important parameter in the selection of particles to stabilise dispersed phases. In addition to the increase in the stability of the bubbles, the fact that the particles of lower density remained on the surface implies that a higher coverage is present on the coalesced bubble which may help prevent further coalescence in many bubble systems.

Supporting Information

Details on the numerical modelling of coalescence dynamics may be found. Moreover, a video showing the lateral displacement of a portion of the particle coating may be viewed.

Acknowledgements

The Australian Research Council is acknowledged for financial support through grant DP120102305. The authors also wish to thank Penelope Wilcher and Sin-Ying Tan for the experimental work on the PMMA particles. Kitty Tang is also acknowledged for the measurement of contact angle (galena) and sizing of particles (anatase).

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