



Shape deformation and oscillation of particle-laden bubbles after pinch-off from a nozzle

H. Wang^{*}, P.R. Brito-Parada^{*}

Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, UK

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ABSTRACT

The rise of bubbles in liquid is a common phenomenon in chemical engineering applications. Bubble dynamics, however, are not fully understood, particularly at the early stages after bubbles are released from submerged nozzles, or when particles coat the bubble surface. In this work, a detailed investigation of microparticle-laden bubbles rising in water after being released from a nozzle was carried out to determine the influence of bubble surface coverage on the interface dynamics after pinch-off. The use of high-speed photography, at up to 25170 frames per second, allowed two regimes to be systematically investigated for the first time, i.e. an initial bubble shape deformation and shape oscillations. Surface pressure analysis shows that microparticles reduce the apparent surface tension of the interface by generating surface pressure during the initial bubble deformation. In contrast, during shape oscillations, little effect was observed on the period of the dominant harmonic, indicating that surface tension does not change during the oscillations. Harmonic analysis also showed that microparticles at bubble surfaces significantly increase the damping rate of the dominant harmonic, with a dependency on the bubble surface coverage. By quantifying the effect of particles on bubble dynamics, this work contributes to a better understanding of gas–liquid–solid reactors in which particle attachment plays a key role.

1. Introduction

Bubbles have a wide range of applications in chemical engineering processes such as mixing [1–3] and separation [4–7] by mass and energy transfer through the interfacial area [8]. The rise of bubbles in liquid is a common phenomenon among these processes. Bubbles detached from a submerged nozzle in liquid have a deformed shape and then relax towards a more spherical shape as a result of capillary force, experiencing shape oscillations as they rise [9,10]. Bubble interface dynamics during bubble rising are, however, not fully understood, especially when particles coat the bubble surface, as is the case for some slurry bubble columns or gas–liquid–solid reactors [11]. Considering the importance of the oscillation of bubbles in determining mass transfer rates in bubble column bioreactors [12] and in contributing to predictive models that link the oscillation dynamics to particle attachment and detachment in froth flotation [13], a fundamental understanding of the effect of particles on bubble dynamics is therefore essential for design optimisation and process intensification in such cases.

The shape oscillation of bubbles is caused by the periodic exchange between surface and kinetic energy [14]. The dynamics of the air–liquid

interface, expressed as a sum of oscillation modes, can be obtained theoretically from linearised Navier–Stokes equations [15]. In the absence of gravity, the oscillation frequency and the damping rate of each mode have been shown to be in agreement with predictions from potential flow theory [16]. The oscillation frequency scales with $\sqrt{\gamma/\rho R^3}$ and the damping rate scales with $\mu/\rho R^2$, where γ is the surface tension of the air–liquid interface, ρ is the density of water, μ is the dynamic viscosity of water and R is the bubble radius. Surface tension originates from intermolecular forces and represents the surface energy per unit area of the air–liquid interface. A decrease in the surface tension of the liquid will result in greater wettability and a smaller contact angle [17–20]. When the effect of gravity is considered, the oscillation frequency decreases with bubble aspect ratio (defined as the ratio of the lengths of the semimajor axis to semiminor axis of an ellipse fitted to the bubble image) during bubble rising [10,16]. By applying linear stability theory, Meiron [16] found that the decrease in frequency is caused by the deformation of bubbles during bubble rising. For small deformations, e.g. aspect ratios smaller than 1.12, the oscillation frequency during bubble rising still agrees well with potential flow theory [14]. Similarly, numerical results by Lalanne [10] found that the rising motion of bubbles does not have a significant influence on the damping rate of the

^{*} Correspondence to: Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK.

E-mail addresses: hao.wang16@imperial.ac.uk (H. Wang), p.brito-parada@imperial.ac.uk (P.R. Brito-Parada).

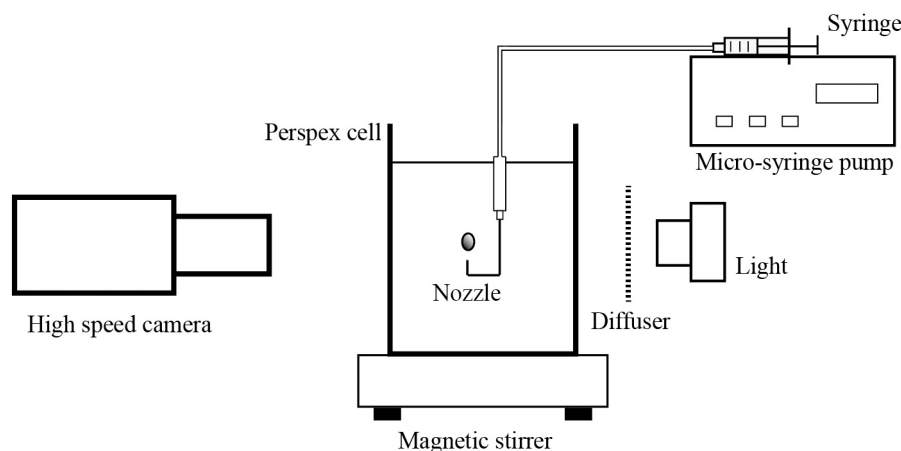


Fig. 1. Schematic showing the experimental setup for the bubble generation, particle-laden bubble preparation and high-speed video recording.

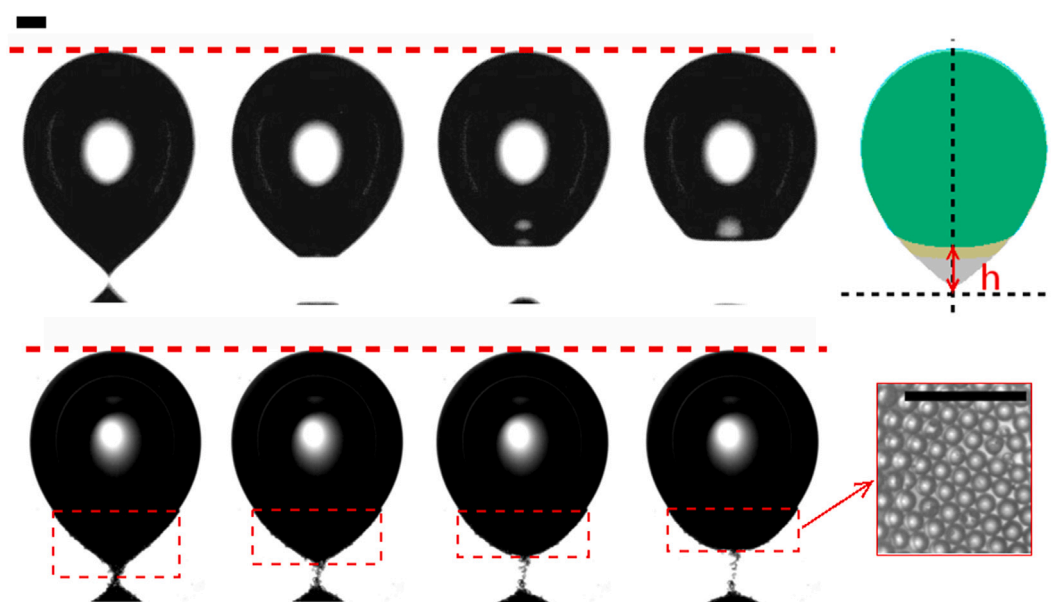


Fig. 2. Top panel: Image sequences showing the deformation of the lower half of the uncoated bubble. The time from the first image to the fourth image is 1.5 ms. The red dotted line is a guide for the eyes showing the top of the bubble does not move during this time period. A schematic of the deformation is also provided, where h is defined as the vertical distance from the pinch-off point to the lowest point of the bubble surface. Bottom panel: Image sequences showing the deformation of the lower half of the particle-laden bubble of low surface coverage during a 1.5 ms period. Dashed rectangles show the region where particles are present as the bubble deformation takes place. An image of the particle packing at the bubble surface is also shown. The scale bars represent 0.5 mm.

shape oscillation at small deformations. Experimental results for rising oil drops also confirm that the drops exhibit a constant damping rate at small deformations, although the damping rates were found to be much higher than theoretical predictions [14].

Oscillation dynamics can be altered by changing the interface properties either by having surface-active impurities or particles coating the interface. Surface-active impurities have been found to play an important role in the oscillation dynamics of oil drops [14], while surface contamination at air–liquid or liquid–liquid interfaces is known to reduce the rising speed of bubbles or drops by generating Marangoni stress at the interfaces [21,22]. This Marangoni effect was found to significantly increase the damping rate of the shape oscillations of heptane drops rising in water while keeping the oscillation frequency unchanged [14].

Similarly to surface-active impurities, the presence of nanoparticles at the interfaces has also been shown to change the oscillation dynamics of bubbles [23,24]. In particular, Poulichet et al. [25] observed that the oscillation mode of nanoparticle-coated bubbles does not depend on the bubble size, as is the case for uncoated bubbles. Wang et al.

[9,26] found that microparticles attached at the surface of bubbles reduce their rising speed by decreasing the interface mobility and by contributing to drag effects. A decrease in bubble deformations was also observed for microparticle-laden bubbles by the authors [9,26], corresponding to the damping effect on the oscillation amplitude. This strong damping effect on the oscillation amplitude was found to be dependent on the percentage of the bubble surface coated by particles, or bubble surface coverage, with a larger bubble surface coverage leading to a greater damping effect [9]. Similarly, microparticles have been found to have a damping effect on shape oscillations after the coalescence of particle-laden bubbles [27,28]. In addition to the damping effect, nanoparticles at the oscillating bubble surface may change the apparent surface tension of the interface by generating surface pressure through particle interactions [29]. More recently, Wang and Brito-Parada [30,31] found that microparticles at deforming interfaces also generate surface pressure that reduces the apparent surface tension of the interface.

In previous work from our group, the behaviour of a microparticle-laden bubble in water after detaching from a submerged nozzle was

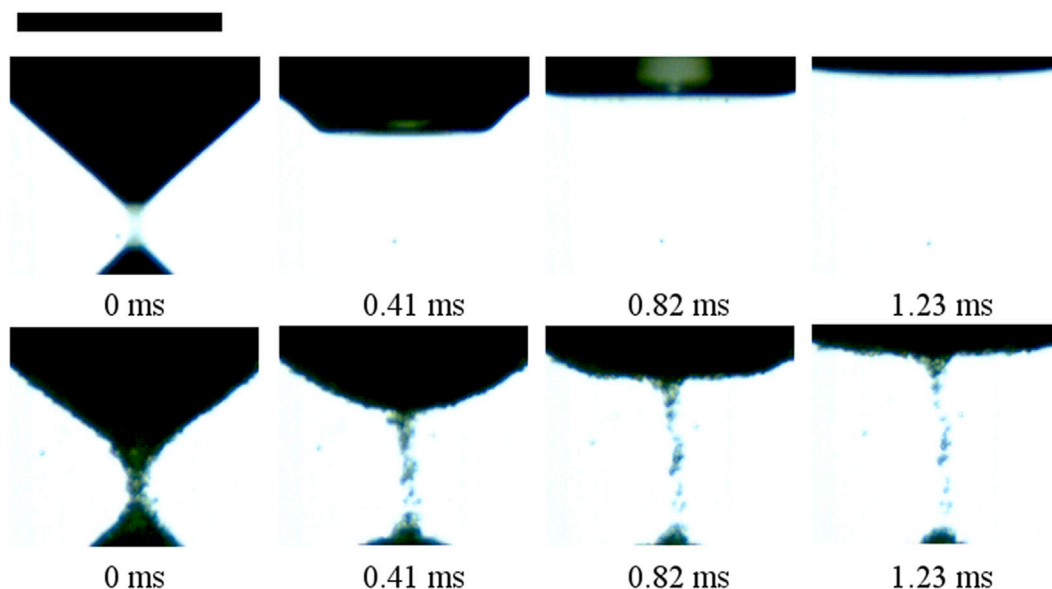


Fig. 3. Image sequences showing a close-up view near the pinch-off region for the uncoated bubble (top) and the particle-laden bubble of low surface coverage (bottom). The first image on both panels starts from the pinch-off. The time from the first image to the fourth image on each panel is 1.23 ms. The scale bar represents 1 mm.

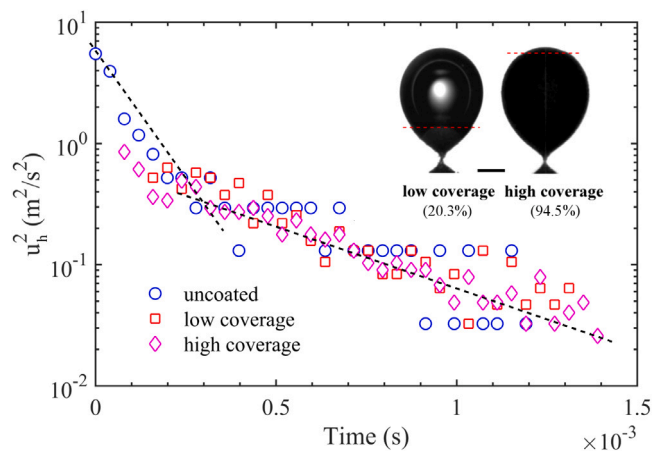


Fig. 4. Change in u_h^2 with time for uncoated bubbles and particle-laden bubbles with two different surface coverages. Black dashed lines are a guide to the eye for the trend in the change in u_h^2 with time. The inset shows images of the particle-laden bubbles with low surface coverage and high surface coverage, 20.3% and 94.5%, respectively. Red dashed lines in the inset show the boundary between the coated and uncoated surfaces. Details on the calculation of the surface coverage can be found in [9]. The scale bar in the inset represents 1 mm.

investigated using a high-speed camera, recording at 1000 frames per second (fps) [9,26]. The particle-laden bubble was observed to oscillate during the rising. The changes in aspect ratio and velocity caused by the particles at the bubble surface were studied and a strong damping effect of the particles on the shape oscillation, as well as minor changes in the oscillation period, were observed.

In the present work, the aim is to investigate systematically the air-liquid interface dynamics during the rising of an individual particle-laden bubble, with a focus on understanding of effect of solids attached to the interface on the bubble's oscillation damping rate and frequency. The effect of microparticles on the interface dynamics of bubbles after being released from submerged nozzles is studied in greater detail using a high-speed camera with a temporal resolution of up to 25170 fps. Two regimes are observed, an initial interface deformation (during approximately the first 1.5 ms) after pinch-off, followed by shape oscillations. The objective is twofold, firstly, quantifying the effect of

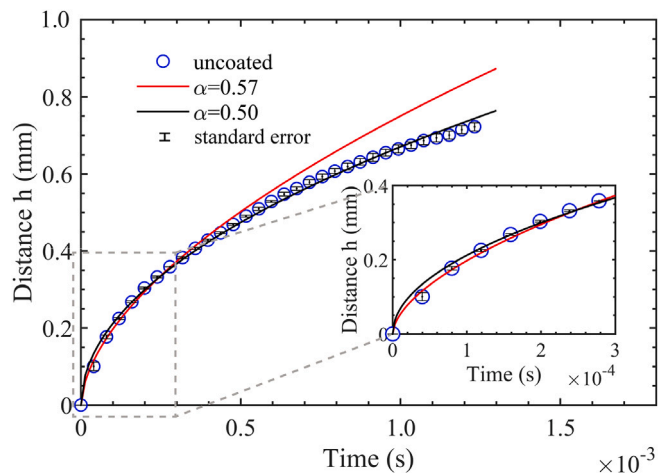


Fig. 5. The change in distance h with time for uncoated bubbles. Error bars represent standard error, calculated from the data of three repeats of the experiment. The black line is the fitting of the power law $h \sim \sqrt{t}$ and the red line is $h \sim t^{0.57}$. The inset shows the change in distance h with time for uncoated bubbles during first 0.3 ms after pinch-off. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

particles on the interface deformation and the apparent surface tension at the very beginning of bubble rising just after the bubble pinch-off; secondly, quantifying the effect of particles on the frequency and the damping rate of the shape oscillations. The effect of particles on the initial interface deformation was studied by tracking the lowest point of the bubble surface, where the apparent surface tension was determined via least square fittings to the power law that describes the initial interface deformation for uncoated bubbles. In addition, the effect of particles on the frequency and the damping rate of bubble shape oscillations was investigated by the decomposition of the shape into spherical harmonics. The oscillations were recorded for about 80 ms, i.e. approximately 4 oscillation periods. The experimental results for the shape oscillations were then compared with predictions from potential flow theory.

The fundamental understanding of the effect of microparticles on the bubble's oscillation damping rate and frequency from this research

can in turn contribute to models that link the oscillation dynamics to particle attachment and detachment. These attachment and detachment phenomena are key in determining the efficiency of the separation process.

2. Methodology

2.1. Materials

Micron-sized silica glass beads were obtained from Sigmund Lindner GmbH and were used as received. The particles had a roundness of more than 0.9 and specific weight of 2.5 g/cm³. The volume mean diameter of the particles, d , determined using a Malvern Mastersizer 3000, was 27.5 μm . These glass beads are naturally hydrophilic and Analytical grade tetradecyltrimethylammonium bromide (TTAB), obtained from Sigma-Aldrich, was prepared at a concentration of 10⁻³ mM. The surface tension of the TTAB solution at 20 °C, determined using a SITA Scienceline t60 maximum bubble pressure tensiometer, was 72.1 mN/m. TTAB is a cationic surfactant composed of amphiphilic molecules and is able to adsorb on the negatively charged silica surfaces to enhance the particle attachment to the air–liquid interface.

2.2. Experimental setup

The experimental rig is shown in Fig. 1. A bubble was generated by pumping air into the TTAB solution in a transparent perspex cell (50 mm × 50 mm × 125 mm) via a submerged nozzle (nominal outer diameter 1.27 mm). The injected volume of air was controlled by a micro-syringe pump (World Precision Instrument). In order to prepare the particle-laden bubble, the TTAB solution with particles was stirred to suspend the particles using a magnetic stirrer to promote their attachment to the bubble surface. The bubble behaviour was recorded using a Chronos 1.4 high-speed camera (Kron Technologies Inc.) coupled with a Canon macro lens (magnification up to 5X) after the particles had completely settled. An LED light with 1200 mW output power and a light diffuser (Thorlabs Inc.) were used to provide the required illumination.

2.3. Experimental procedure

Experiments with uncoated bubbles were carried out using deionised (DI) water (resistivity larger than 15 M Ω cm). For the experiments with particle-laden bubbles, two grams of particles were first mixed with 250 mL of the 10⁻³ mM TTAB solution using a magnetic stirrer. The TTAB solution ($\rho_c = 998 \text{ kg m}^{-3}$, $\mu_c = 1.0 \text{ mPa s}^{-1}$) was prepared using DI water. A bubble was generated by pumping air into the TTAB solution using the micro-syringe pump once the particles had completely settled. The size of the bubble was adjusted by changing the air injection via the micro-syringe pump at a constant air flow rate of 0.72 mL h⁻¹, the same flow rate as in the experiment of Wang et al. [9]. The diameter of the bubble just after the pinch-off is 3.24 mm, with negligible dependency on the particles coated at the bubble surface. It took approximately 2 min for the bubble to grow to this diameter. Note that the bubble diameter was calculated from the volume of the bubble. When the bubble grew to a certain size (normally 3 mm in diameter), the TTAB solution with particles was stirred again to suspend the particles and achieve particle attachment to the bubble surface. The fraction of the bubble surface coated by the particles were adjusted by changing the stirring time. The speed of the magnetic stirrer was set at 350 rpm. The particles in the solution were allowed to settle for 10 min after stopping the stirring. The time between consecutive experiments, i.e. between new bubbles being generated, was approximately 20 min; thus, only one bubble was present in the Perspex cell for each set of experiments.

The initial shape deformation and oscillation of the bubbles were recorded using the Chronos 1.4 high-speed camera coupled with the Canon macro lens once the particles had completely settled. Three

frames rates (25 170 fps, 10 800 fps and 3800 fps), corresponding to spatial resolutions of 139.37 pixel/mm, 49.02 pixel/mm and 36.02 pixel/mm respectively, were used to investigate the interface dynamics during about 1.5 ms time period after bubble pinch-off and the shape oscillation during bubble rising.

After the pinch-off event, a first regime in which the lower half of the bubble starts to deform was recorded at 25 170 fps for approximately 1.5 ms. The deformation of the lower half of the bubble during this time period was quantified by the vertical distance, h , between the pinch-off point and the lowest point of the bubble, as shown in the schematic in Fig. 2. The upper half of the bubble did not deform during this regime. A second regime was identified in which the oscillation of the bubbles was recorded at 3800 fps for approximately 80 ms. The temporal resolution is sufficient to capture the shape oscillation since the oscillation period is approximately 20 ms for the bubble size considered in our experiments. The bubble shape was obtained by extracting the edges of the bubble using a Matlab image analysis routine and then calibrated using the diameter of the nozzle. This, in turn, allowed the bubble aspect ratio, volume and surface coverage to be obtained. It is relevant to note that within the 80 ms analysed following bubble pinch-off, the rising trajectory of the bubble remained aligned to the vertical axis. Assuming the bubble is symmetrical about the rising direction, the aspect ratio was calculated as the ratio between the largest length of the bubble in the horizontal direction and that in the vertical direction. The volume of the bubble was computed from the integral of the bubble edges over the vertical direction, from which the bubble radius was obtained. The two surface coverages explored in the current work are 20.3% and 94.5%, referred to in this paper as low surface coverage and high surface coverage, respectively. The stirring time was 20 s for the low surface coverage cases and 3 min for the high surface coverage cases. The image analysis routine was also used to determine the centre of the bubble, from which the bubble velocity was calculated.

3. Results and discussion

3.1. Shape deformation at the early stage of bubble rising

At the instant of the bubble pinch-off, as illustrated in the first image of the top panel in Fig. 2, the radius of curvature of the pinch-off point is the largest, as a result of the formation of a singularity [32] in the pinch-off process. This radius of curvature decreases to achieve a balance between the liquid pressure and gas pressure near the interface according to the Young–Laplace law [33]. Fig. 2 shows that at the very beginning of the bubble rising process for both uncoated and particle-laden bubbles, the bubble becomes more spherical with time; as the lower half of the bubble deforms, however, the top of the bubble remains static during the first 1.5 ms. The deformation of the interface near the pinch-off region can be observed more clearly in the image sequences in Fig. 3. It can also be observed from Fig. 3 that in the case of particle-laden bubbles, particles detach from the interface during the pinch-off process, possibly as a result of the decrease in the interface area in the neck region. Since the viscosity is dominant at length scales smaller than $\eta^2/(\gamma\rho)$, which corresponds to a few nanometers for air bubbles in water [32], the flow is thus considered to be inertia dominated. The dynamic pressure of the liquid at the pinch-off region ρu^2 , where u is the liquid speed, is balanced by the Laplace pressure $\gamma\kappa$, which leads to the model in Eq. (1) that relates the change in distance h with time. The model is a form of the classical Taylor and Culick relation to describe the tip velocity of capillary-driven retracting liquid sheets [34,35].

$$\partial_t h = C \sqrt{\frac{\gamma}{\rho} \kappa}, \quad (1)$$

where the pressure difference across the interface is $\gamma\kappa$ and κ is the radius of curvature of the interface. κ changes with time and C is a fitting parameter. Rearranging Eq. (1) leads to:

$$u_h^2 = C^2 \frac{\gamma}{\rho} \kappa, \quad (2)$$

where u_h is the change in h with time. Fig. 4 shows a semilog plot of the change in u_h^2 with time. u_h^2 decreases faster before approximately $t = 0.3$ ms, after which it decreases at a slower rate, as shown by the black dashed lines. Since u_h^2 is proportional to κ according to Eq. (2), the change in κ with time also has a transition at approximately $t = 0.3$ ms. It is relevant to note that the transition time $t = 0.3$ ms is an estimate from Fig. 4.

It is important to note that the shape deformation after bubble pinch-off, the deformation during the pinch-off process [32] and that during a coalescence process [36,37] all involve the deformation of the air-liquid interface that can be described by Eq. (1). The governing equations of the liquid flow near the interfaces in these three processes are the same. In addition, both the evolution of the neck radius during pinch-off and that of the neck radius during coalescence can be described by a power law relationship with time. The exponent in the power law that describes the change in the bubble neck radius with time during pinch-off is $\alpha = 0.57$ [31,32] while the exponent that describes the neck evolution in bubble coalescence is $\alpha = 0.5$ [30,36]. It is therefore interesting to assess whether the evolution of the distance h after pinch-off follows a power law relationship $h \sim t^\alpha$, using the aforementioned values for α . Fig. 5 shows the experimental results for the change in distance h with time for uncoated bubbles as well as the fittings to power law models $h \sim t^{0.57}$ (shown as a red line) and $h \sim t^{0.5}$ (shown as a black line). In general, the exponent $\alpha = 0.5$ results in a better overall fit to the data during the whole time period. It is noted, however, that the fit to $\alpha = 0.57$ agrees slightly better to the data for the first 0.3 ms, as highlighted in the inset in Fig. 5. This indicates that the initial change in κ during the shape deformation after bubble pinch-off behaves more like that of the radius of curvature of the neck during pinch-off than that during bubble coalescence.

For particle-laden bubbles, the dynamics of the change in distance h with time differs from that of uncoated bubbles, as can be seen in Fig. 6. Since the dynamics of h is controlled by surface tension according to Eq. (1), we postulate that this difference is mainly due to the fact that the presence of particles at the air-liquid interface generates a two-dimensional surface pressure by particle interactions during the interface deformation, which acts in the opposite direction to the surface tension. The generation of surface pressure by particle interactions in this case is similar to what was discussed in our previous work during the pinch-off [31] and coalescence [30] of particle-laden bubbles, where the particle interactions at fast deforming air-liquid interfaces lead to surface pressure, which in turn changes the air-liquid interface deformation dynamics. The particle Bond number, quantifying the importance of gravitational forces compared to surface tension forces, was calculated by $Bo = \Delta\rho d^2 g / \gamma_0$, where $\Delta\rho$ is the density difference between the particles and water (1500 kg/m³), g is the gravitational acceleration and γ_0 is the surface tension evaluated for the uncoated bubbles [30,38]. The effect of the particles due to gravity was discounted since the particle Bond number was found to be 1.6×10^{-4} for the particles investigated in this study. The bubble radius and the bubble surface area decrease slightly at the very beginning of the bubble rising. The contribution to the decreased bubble surface area is only from the lower half of the bubble, where the curvature of the interface changes with time. Particles move upwards (see the dotted rectangles in the bottom panel in Fig. 2 as a result of the loss of surface area. The movement of the particles at the deforming air-liquid interface causes particle interactions, which lead to the generation of surface pressure [39].

The surface pressure reduces the apparent surface tension γ of the air-liquid interface according to $\gamma = \gamma_0 - \Pi$, where Π is the surface pressure [40]. To estimate the surface pressure generated by

the particles, the scaling law that describes the neck growth dynamics during bubble coalescence $h \sim (\gamma/\rho)^{1/4} \sqrt{t}$ [41] was used to fit the data for uncoated bubbles in Fig. 6, from which a prefactor of 0.23 was obtained. Similar to Wang and Brito-Parada [30,31], the same prefactor for uncoated bubbles can be used for particle-laden bubbles so that their apparent surface tension is determined from the best fit to the data points in Fig. 6 using the least square fitting method. On the basis of the fittings in Fig. 6a, the apparent surface tension of low surface coverage and high surface coverage particle-laden bubbles was determined to be 32.0 mN/m and 18.5 mN/m, as shown by the dotted lines in Fig. 7, corresponding to the surface pressure of 40.1 mN/m and 53.6 mN/m, respectively. Fig. 6b shows that better fittings were achieved if a quadratic function for the apparent surface tension with time was adopted. The apparent surface tension determined from the fittings in Fig. 6b was shown in squares and diamonds in Fig. 7. Compared to the constant apparent surface tension of uncoated bubbles as shown in blue line in Fig. 7, the apparent surface tension of particle-laden bubbles displays an increasing trend, with low surface coverage bubbles having a higher apparent surface tension. The higher apparent surface tension when the bubble surface coverage is low is caused by the lower surface pressure as a result of the smaller mass of particles at the bubble surface.

3.2. Shape oscillations during bubble rising

3.2.1. Harmonic analysis

Bubbles experience inertial shape oscillations after detaching from the nozzle. Fig. 8 shows the change in the aspect ratio and the bubble ascending Reynolds number [14] with time after pinch-off for an uncoated bubble. Data points for repeats, from which good repeatability was observed, are not shown here for simplicity. The ascending Reynolds number is calculated as $Re_{asc} = 2\rho v R / \mu$, where R is the radius of the bubble. The aspect ratio changes periodically, indicating the bubbles are oscillating. The Re_{asc} of the bubble is inversely related to the aspect ratio, with the local maxima of the ascending Reynolds number roughly corresponding to the local minima of the aspect ratio, and vice versa. The effect of surface coverage on the ascending Reynolds number can be seen in Fig. 9. Similar to Fig. 8, data points for repeats were not shown here for simplicity. A low surface coverage of particles has a negligible effect on Re_{asc} , whereas a high surface coverage of particles dramatically reduces its value. The effect of particles on the reduction of the bubble velocity was explained in detail in our group's previous work [9,26]. The presence of particles at the bubble surface reduces the velocity of the bubbles, and thus Re_{asc} ; this is due to the increase in drag force caused by a reduced mobility of the interface and the extra weight exerted by the particles.

Fig. 10 shows image sequences of the bubble oscillations after bubble pinch-off for both the uncoated and particle-laden cases. At the instant of bubble pinch-off the initial shapes of the uncoated bubble and particle-laden bubble are similar and their aspect ratio is smallest as a result of the deformation caused by buoyancy. The bubble shape then relaxes towards a more spherical shape driven by the capillary force. The first and third images on both top and bottom panels correspond to local minima of the aspect ratio, while the second and fourth images correspond to local maxima of the aspect ratio. It is noted that the bubbles do not oscillate around a fixed shape as gravity effects are significant. From Fig. 10 it can also be observed that the presence of particles delays the oscillation and results in less deformation of the bubble.

To investigate the effect of particles on shape oscillations, it is important to first recall the fundamentals of bubble interface dynamics in the absence of particles during inertial shape oscillations. During the shape oscillations, the hydrodynamic forces deform the bubble, whereas the capillary force acts to restore the spherical shape of the bubble. The evolution of the air-liquid interface can be described by a sum of several modes, with each mode characterised by a spherical

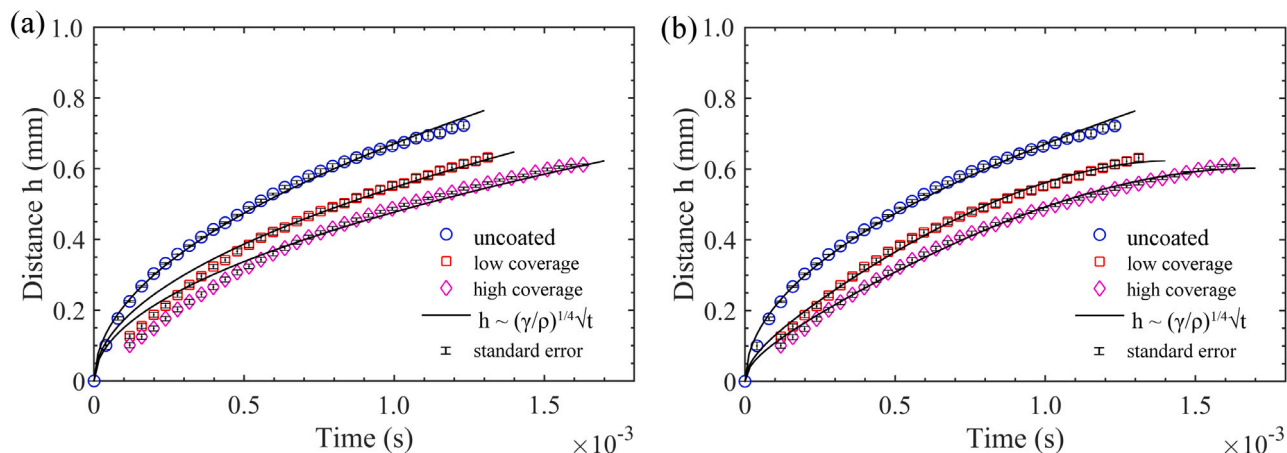


Fig. 6. Change in distance h with time for uncoated bubbles and particle-laden bubbles. Black lines are the least square fittings to the data points using the power law $h \sim (\gamma/\rho)^{1/4} \sqrt{t}$, where γ for the particle-laden bubbles cases is kept constant in (a) but changes with time in (b). Error bars represent standard error, calculated from the data of three repeats of the experiment. It is relevant to note that data points of particle-laden bubbles for $t < 0.1$ ms are not presented as a result of the difficulty in tracking the air–liquid interface due to the presence of particles.

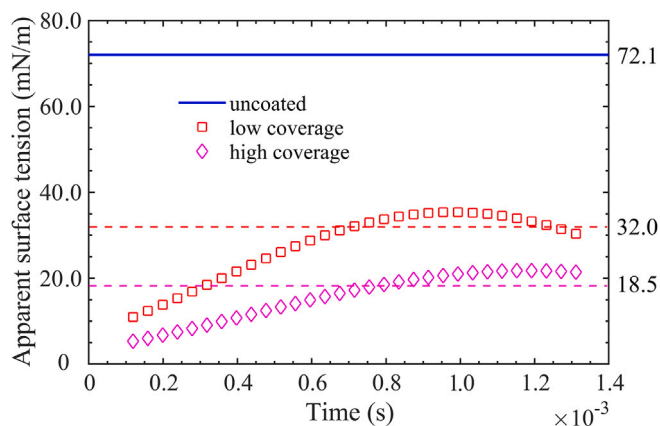


Fig. 7. The apparent surface tension γ for particle-laden bubbles (squares and diamonds) during the shape deformation, determined from the fittings in Fig. 6b. Dotted lines show the average apparent surface tension for particle-laden bubbles, determined from the fittings in Fig. 6a. Blue line shows the surface tension of the uncoated bubbles.

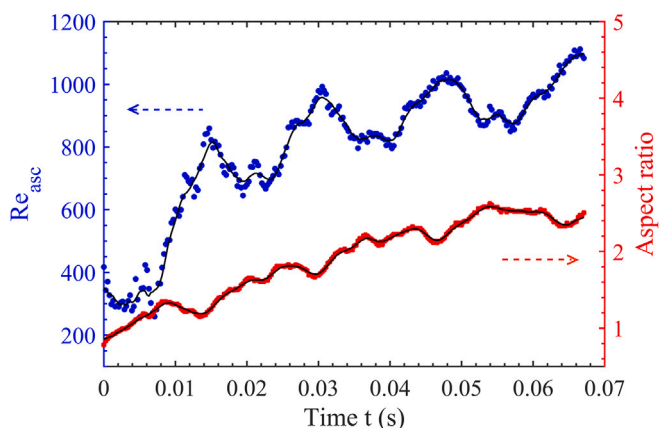


Fig. 8. Ascending Reynolds number Re_{asc} and aspect ratio for an uncoated bubble. The solid lines are the moving average of the data points with a window size of 10.

harmonic $Y_{m,n}$, where n and m are the polar and azimuthal wavenumbers, respectively [42,43]. The shape of the bubble can be expressed using spherical coordinates $r(\theta)$, as illustrated in Fig. 10. The spherical

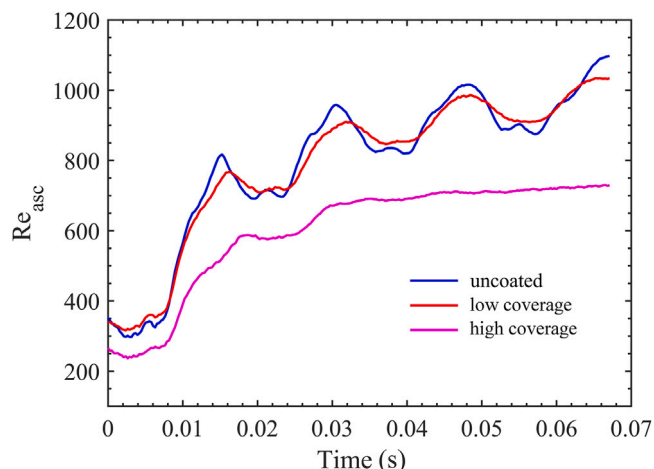


Fig. 9. Ascending Reynolds number, Re_{asc} , for an uncoated bubble, a particle-laden bubble with low surface coverage and a particle-laden bubble with high surface coverage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coordinates $r(\theta)$ were first fitted by a polynomial of order 10 in MATLAB. Assuming the bubble is axisymmetric ($m = 0$), the shape of the bubble, expressed in the polynomial of order 10, can be decomposed into spherical harmonics as shown in Eq. (3),

$$r(\theta, t) = R(1 + \sum_{n=2}^{10} A_n(t)Y_{0,n}(\theta)), \quad (3)$$

where $r(\theta, t)$ is the coordinate of the bubble contour, which changes with time and the angle θ respective to the vertical axis; $A_n(t)$ is the amplitude of the harmonic n . The decomposition into the spherical harmonics starts from $n = 2$ and stops at $n = 10$, which is enough for an accurate description of the bubble shape [10]. The volume of the bubble was assumed to be constant and, as a result, the amplitude A_0 can be ignored, whereas A_1 was set to zero since the bubble centre is the origin of coordinates.

Legendre polynomials, the solutions to the Legendre differential equation, are a system of complete and orthogonal polynomials. The first five Legendre polynomials are: $P_0(x) = 1$, $P_1(x) = x$, $P_2(x) = \frac{1}{2}(3x^2 - 1)$, $P_3(x) = \frac{1}{2}(5x^3 - 3x)$, $P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$ [44]. By reducing the spherical harmonics $Y_{0,n}$ to Legendre polynomials $P_n(\cos(\theta))$, the shape

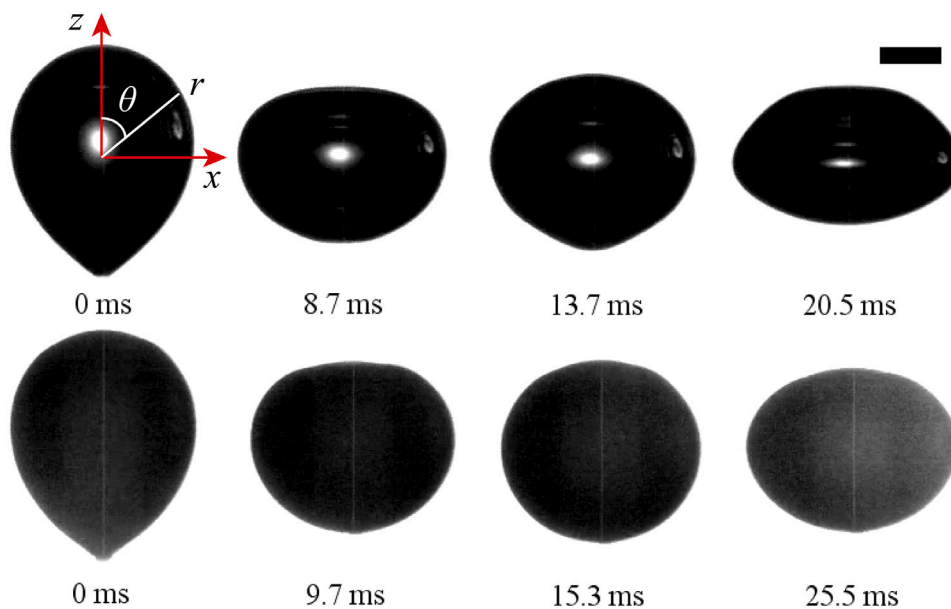


Fig. 10. Image sequences showing the oscillations of the uncoated bubble (top panel) and the high surface coverage bubble (bottom panel) after bubble pinch-off. The first and third images on both top and bottom panels correspond to the local minima of the aspect ratio, while the second and fourth images correspond to the local maxima of the aspect ratio. Scale bar represents 1 mm.

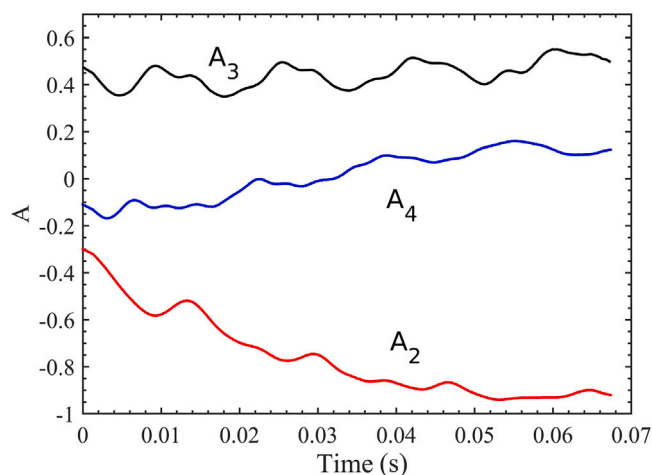


Fig. 11. Amplitudes A_2 , A_3 and A_4 for uncoated bubbles, determined by decomposing the bubble shape into spherical harmonics according to Eq. (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the bubble can thus be described by the following equation,

$$r(\theta, t) = R(1 + \sum_{n=2}^{10} A_n(t) P_n(\cos(\theta))), \quad (4)$$

from which $A_n(t)$ was obtained. This procedure involved using Legendre polynomials function `legendreP` in MATLAB. Fig. 11 shows the change in amplitude with time for the first three harmonics, $n = 2, 3, 4$, for uncoated bubbles. The harmonic 2 is the dominant harmonic since the absolute value of its amplitude A_2 is higher than that of the harmonic 3 and 4 as shown in Fig. 11. The amplitude A_2 takes negative values since the bubble is flattened (aspect ratio being larger than one). Harmonic 3, which accounts for fore-aft asymmetry [10], is moderate and the corresponding amplitude A_3 takes positive values. The absolute value of amplitude A_4 is smaller compared to A_2 and A_3 . A_4 initially takes negative values, before taking positive values, meaning the shape

becomes more complex as the bubble rises. In comparison, it was found that for small droplets (diameter being $177 \mu\text{m}$ [45] and $590 \mu\text{m}$ [14]), amplitudes A_2 and A_3 both take positive and negative values in a decaying sinusoidal trend. The difference in the trend of the amplitude for small droplets and large bubbles is caused by the fact that the small droplets oscillate around a fixed shape whereas the relatively larger bubbles explored in this work oscillate around a changing shape. The absolute value of the amplitude becomes very small for harmonics 5 to 10, so A_5 to A_{10} are not presented in this study. It is also shown that the absolute value of the amplitude A_2 displays a trend to increase during bubble rising. As the bubble rises up, the shape of the bubble flattens. The equilibrium shape around which the bubble oscillates thus changes with time, as can be seen in the amplitude change of the dominant harmonic 2 in Fig. 12a and the secondary harmonics 3 and 4 in Fig. 12b and c, respectively. For particle-laden bubbles, a drastic change in the amplitude for all three harmonics was observed compared with that of the uncoated bubbles. The oscillations of the harmonics 2, 3, and 4 for the high surface coverage bubbles almost damped out after the first two periods.

Each harmonic can be described by a sum of a time-average amplitude $\bar{A}_n$ and an oscillating component ΔA_n , where $\bar{A}_n$ is calculated by averaging A_n over a moving window of the oscillation period. The window size depends on the value of the period and ranges from 61 to 68. Note that since the discussion in Section 3.2.2 is on the period and amplitude of the dominant harmonic (harmonic 2), only the results on amplitude A_2 , average amplitude $\bar{A}_2$ and oscillation amplitude ΔA_2 of harmonic 2 are presented. The red line in Fig. 13 shows the total amplitude A_2 of the dominant harmonic; the negative value indicates the aspect ratio of the bubble is always larger than one. The blue line in Fig. 13 shows that the oscillating component ΔA_2 of the dominant harmonic for uncoated bubbles changes around zero and the dotted line illustrates that the absolute value of A_2 is increasing. The increase in the absolute value of $\bar{A}_2$ means the average shape of the bubble is becoming increasingly deformed during bubble rising.

In order to determine the damping rate of the dominant harmonic, Fig. 14 compares the oscillating component ΔA_2 for uncoated bubbles, bubbles of low surface coverage and bubbles of high surface coverage. Clearly, the absolute value of the local maxima and minima of ΔA_2 decreases with time, meaning the bubbles experience damped oscillations.

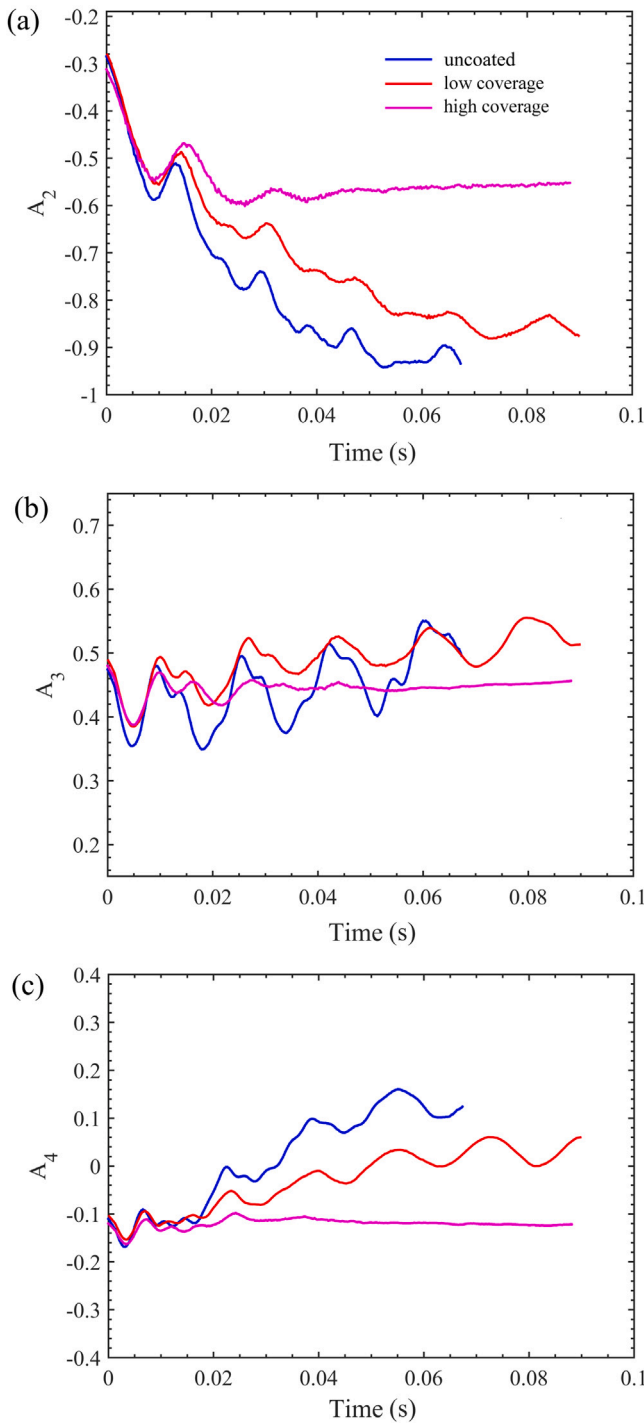


Fig. 12. Amplitude for uncoated bubbles, low surface coverage bubbles and high surface coverage bubbles, determined by decomposing the bubble shape into spherical harmonics. (a) Amplitude A_2 . (b) Amplitude A_3 . (c) Amplitude A_4 . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The damping rate is determined from the slope of the data in the semi-log plot for the absolute value of the local maxima and minima of ΔA_n with time, as illustrated in Fig. 15. Note that the damping rates of both uncoated bubbles and low surface coverage bubbles are almost constant as time progresses, whereas the damping rate of high surface coverage bubbles increases, as shown in the deviation of the data from the fitting.

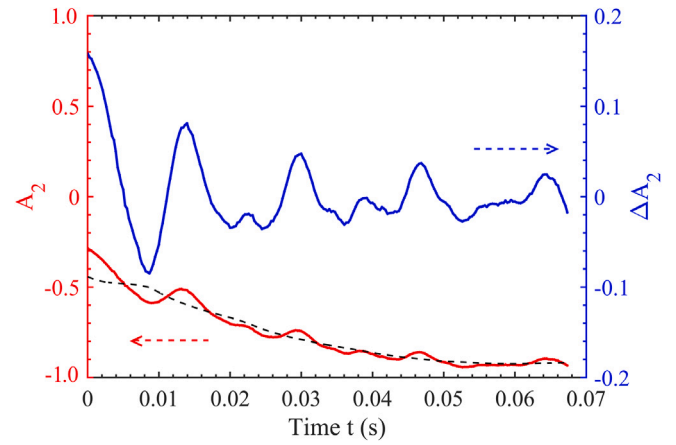


Fig. 13. Total amplitude A_2 of the dominant harmonic (red line), slowly changing average amplitude $\bar{A}_2$ (black dotted line) and oscillation amplitude ΔA_2 (blue line) for uncoated bubbles.

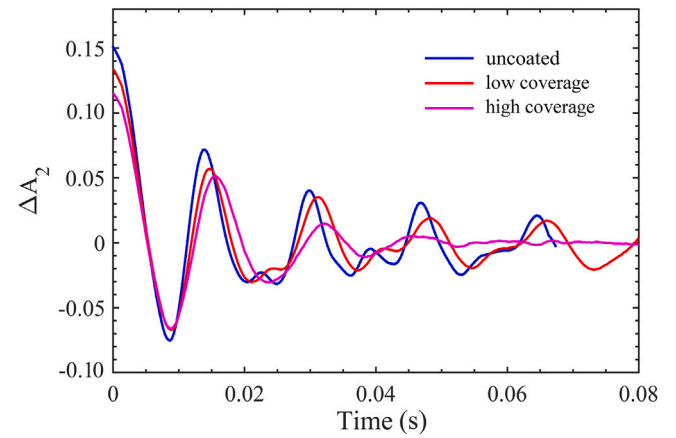


Fig. 14. Oscillation amplitude ΔA_2 for uncoated bubbles, low surface coverage bubbles and high surface coverage bubbles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2.2. Oscillation period and damping rates

Assuming potential flow near the bubble, the oscillation period, T_n^{th} , can be written as [46]

$$T_n^{th} = 2\pi \sqrt{\frac{\rho R^3}{(n-1)(n+1)(n+2)\gamma}}, \quad (5)$$

and the damping rate from the dissipation of the potential flow can be obtained by the following scaling law [43]:

$$\beta_n^{th} = (2n+1)(n+2) \frac{\mu}{\rho R^2}. \quad (6)$$

The prediction of the oscillation period of the dominant harmonic for uncoated bubbles, calculated from potential flow theory is 14.1 ms according to Eq. (5). Fig. 16 shows the experimental data of the period of the dominant harmonic, T_2^{exp} , for consecutive periods for the uncoated and particle-laden cases. The average value, calculated from the first four periods, is 16.2 ms, which is 14.9% higher than the theoretical value. It is important to note that if only the first period of the dominant harmonic obtained from experiments is analysed, the value obtained is 13.5 ms, which is in closer agreement with the theoretical prediction. The second period increases to 16.1 ms and the third one increases slightly further to 17.2 ms. The fourth period reaches to 17.9 ms. The discrepancy between the experimental and theoretical values is caused by the increase in the aspect ratio with time as the bubble rises up, leading to the change in the eigenmodes of the oscillation and the

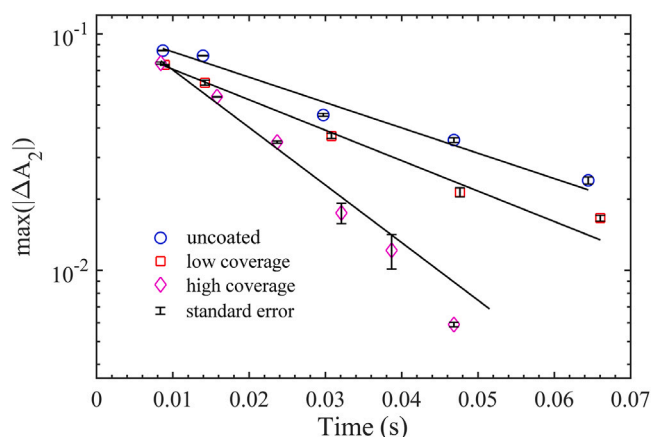


Fig. 15. The absolute value of the local maxima and minima of ΔA_2 , solid lines are the least square fittings to the exponential functions. The damping rate is determined from the slope of the solid lines in the semi-log plot. Error bars represent one standard error, calculated from the data of three repeats of the experiment.

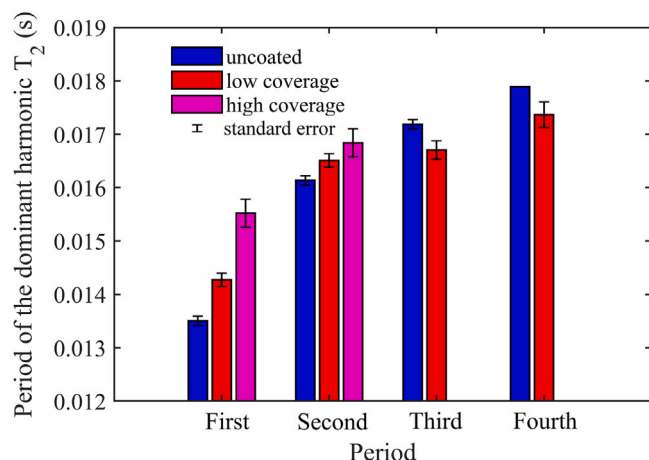


Fig. 16. The first four periods of the dominant harmonic for uncoated bubbles and low surface coverage bubbles. Only the first two periods were presented for high surface coverage bubbles as the oscillation almost completely dampens out after the first two periods. Error bars represent standard error, calculated from the data of three repeats of the experiment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

change in the oscillation period [10,16]. For particle-laden bubbles, the first oscillation period of the dominant harmonic for both low surface coverage and high surface coverage bubbles, 14.3 ms and 15.5 ms, respectively, is higher than that of the uncoated bubbles, namely 13.5 ms. The oscillation period of the dominant harmonic for low and high particle surface coverage is close to that predicted from potential theory: 14.2 ms and 14.5 ms, respectively ($94.8\% \leq T_2^{th}/T_2^{exp} \leq 97.9\%$). The minor difference in the first period of the dominant harmonic for particle-laden bubbles and uncoated bubble means that the effect of particles on the apparent surface tension is negligible.

The damping rate for the dominant harmonic, obtained from the slope of the data in the semi-log plot in Fig. 15, was shown to be affected by the presence of particles at the bubble surface. While the damping rate for uncoated bubbles was found to be 24.7 s^{-1} , as shown in Fig. 15, the value obtained from potential flow theory was 7.5 s^{-1} , according to Eq. (6). The damping rate from the potential flow theory prediction is thus much lower than that obtained from our experimental results. It is postulated that the reason is the energy dissipation associated with the vorticity generated by bubble rising and oscillation is not considered in Eq. (6). In fact, Chebel et al. [14]

also identified that the experimental damping rates for a rising drop are much higher than the theoretical predictions. Similarly, numerical results have also revealed that the damping rates are higher than the theoretical prediction for a rising uncoated bubble [10]. In the case of particle-laden bubbles, the dissipation of the mechanical energy is much faster than that for uncoated bubbles. The damping rate for high surface coverage cases and low surface coverage cases were 56.1 s^{-1} and 29.6 s^{-1} , as shown in Fig. 15, being 2.3 and 1.2 times the damping rate of an uncoated bubble. Since the energy dissipation is controlled by the vortices generated by the oscillatory deformation and rising motion [10], the increase in the damping rate when particles are present at the bubble surface might be caused by the change in vorticity field, which might be associated with the reduced mobility of the interface.

4. Conclusions

The interface dynamics of microparticle-laden bubbles after their pinch-off from a nozzle were systematically investigated in this work. Two regimes were observed, an initial interface deformation after pinch-off, followed by shape oscillations. The effect of microparticles on the apparent surface tension was found to be different in the two regimes. Microparticles decrease the apparent surface tension of the interface during the initial interface deformation after pinch-off, leading to less bubble shape deformation. It is postulated that the decrease in the bubble surface area during the initial interface deformation causes surface pressure induced by the particles, which decreases the apparent surface tension of the interface. On the other hand, as the bubble shape oscillates as it rises up there is a slight increase in bubble surface area and thus no effect of microparticles on the surface pressure, nor a subsequent change in the apparent surface tension.

The frequency and the damping rate of shape oscillation were determined by decomposing the bubble shape into spherical harmonics. Results show that the presence of particles at bubble surfaces decreases the damping rate of the dominant harmonic significantly while having a minor influence on the oscillation frequency. Since oscillation frequency is not affected by the presence of particles, the surface tension of particle-laden bubbles is the same as that of uncoated bubbles during the oscillations.

The damping rate of the dominant harmonic for uncoated bubbles was 24.7 s^{-1} , while it was 29.6 s^{-1} and 56.1 s^{-1} for a bubble with low surface coverage and high surface coverage, respectively. The damping rates determined from experimental results were found to be much higher than those predicted from potential flow theory. This discrepancy is postulated to be caused by the increase in the energy dissipation related to bubble rising. The oscillation frequencies, however, were only affected slightly by the rising motion of bubbles and agreed well with the prediction from potential flow theory.

This work thus contributes to a better understanding of the initial deformation and shape oscillations of particle-laden bubbles, in particular with regards to quantifying the effect of particles on the oscillation damping rate and frequency during bubble rising. This is important given that interface dynamics of particle-laden bubbles play a key role in a wide range of three-phase systems in chemical engineering processes. Future work on this line of research could consider modifying Eq. (6) to take vorticity into account; additional experiments with different bubble size or surface coverage would contribute to a data set to validate the modified equation.

Declaration of competing interest

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

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References

- [1] M. Martín, F.J. Montes, M.A. Galán, Mass transfer from oscillating bubbles in bubble column reactors, *Chem. Eng. J.* 151 (1–3) (2009) 79–88.
- [2] D.D. McClure, N. Aboudha, J.M. Kavanagh, D.F. Fletcher, G.W. Barton, Mixing in bubble column reactors: Experimental study and CFD modeling, *Chem. Eng. J.* 264 (2015) 291–301.
- [3] E. León-Becerril, A. Cockx, A. Liné, Effect of bubble deformation on stability and mixing in bubble columns, *Chem. Eng. Sci.* 57 (16) (2002) 3283–3297.
- [4] Y.J. Chan, M.F. Chong, C.L. Law, D.G. Hassell, A review on anaerobic-aerobic treatment of industrial and municipal wastewater, *Chem. Eng. J.* 155 (1–2) (2009) 1–18.
- [5] J.M. Navaza, D. Gómez-Díaz, M.D. La Rubia, Removal process of CO₂ using MDEA aqueous solutions in a bubble column reactor, *Chem. Eng. J.* 146 (2) (2009) 184–188.
- [6] A.M. Pintor, V.J. Vilar, C.M. Botelho, R.A. Boaventura, Oil and grease removal from wastewaters: Sorption treatment as an alternative to state-of-the-art technologies. A critical review, *Chem. Eng. J.* 297 (2016) 229–255.
- [7] D. Mesa, P.R. Brito-Parada, Scale-up in froth flotation: A state-of-the-art review, *Sep. Purif. Technol.* 210 (2019) 950–962.
- [8] H. Mirsandi, W.J. Smit, G. Kong, M.W. Baltussen, E.A. Peters, J.A. Kuipers, Bubble formation from an orifice in liquid cross-flow, *Chem. Eng. J.* (2019) <http://dx.doi.org/10.1016/j.cej.2019.01.181>.
- [9] P. Wang, J.J. Cilliers, S.J. Neethling, P.R. Brito-Parada, The behavior of rising bubbles covered by particles, *Chem. Eng. J.* 365 (2019) 111–120.
- [10] B. Lalanne, Effect of rising motion on the damped shape oscillations of drops and bubbles, *Phys. Fluids* 25 (2013) 112107.
- [11] S. Orvalho, M. Hashida, M. Zednikova, P. Stanovsky, M.C. Ruzicka, S. Sasaki, A. Tomiyama, Flow regimes in slurry bubble column: Effect of column height and particle concentration, *Chem. Eng. J.* 351 (2018) 799–815.
- [12] F. Montes, M. Galan, R. Cerro, Mass transfer from oscillating bubbles in bioreactors, *Chem. Eng. Sci.* 54 (15–16) (1999) 3127–3136.
- [13] M. Kostoglou, T.D. Karapantsios, O. Oikonomidou, A critical review on turbulent collision frequency/efficiency models in flotation: Unravelling the path from general coagulation to flotation, *Adv. Colloid Interface Sci.* (2020) 102158.
- [14] N.A. Chebel, J. Vejražka, O. Masbernat, Shape oscillations of an oil drop rising in water : effect of surface contamination, *J. Fluid Mech.* 702 (2012) 533–542.
- [15] P.L. Marston, Shape oscillation and static deformation of drops and bubbles driven by modulated radiation stresses—Theory, *J. Acoust. Soc. Am.* 67 (1) (1980) 15–26.
- [16] D.I. Meiron, On the stability of gas bubbles rising in an inviscid fluid, *J. Fluid Mech.* 198 (1989) 101–114.
- [17] X. Gong, S. He, Highly durable superhydrophobic polydimethylsiloxane/silica nanocomposite surfaces with good self-cleaning ability, *ACS Omega* 5 (8) (2020) 4100–4108.
- [18] X. Gong, J. Zhang, S. Jiang, Ionic liquid-induced nanoporous structures of polymer films, *Chem. Commun.* 56 (20) (2020) 3054–3057.
- [19] L. Zhong, X. Gong, Phase separation-induced superhydrophobic polylactic acid films, *Soft Matter* 15 (46) (2019) 9500–9506.
- [20] J. Peng, X. Zhao, W. Wang, X. Gong, Durable self-cleaning surfaces with superhydrophobic and highly oleophobic properties, *Langmuir* 35 (25) (2019) 8404–8412.
- [21] R. Clift, J.R. Grace, M.E. Weber, Bubbles, Drops, and Particles, Academic Press, New York, 1978.
- [22] I.U. Vakarelski, R. Manica, E.Q. Li, E.S. Basheva, D.Y. Chan, S.T. Thoroddsen, Coalescence dynamics of mobile and immobile fluid interfaces, *Langmuir* 34 (5) (2018) 2096–2108.
- [23] B. Dollet, P. Marmottant, V. Garbin, Bubble dynamics in soft and biological matter, *Annu. Rev. Fluid Mech.* 51 (2019) 331–355.
- [24] A. Jamburidze, A. Huerre, D. Baresch, V. Poulichet, M. De Corato, V. Garbin, Nanoparticle-coated microbubbles for combined ultrasound imaging and drug delivery, *Langmuir* 35 (2019) 10087–10096.
- [25] V. Poulichet, A. Huerre, V. Garbin, Shape oscillations of particle-coated bubbles and directional particle expulsion †, *Soft Matter* 13 (2017) 125–133.
- [26] P. Wang, J.J. Cilliers, S.J. Neethling, P.R. Brito-Parada, Effect of particle size on the rising behavior of particle-laden bubbles, *Langmuir* 35 (10) (2019) 3680–3687.
- [27] S. Ata, Coalescence of bubbles covered by particles, *Langmuir* 24 (12) (2008) 6085–6091.
- [28] Y. Saavedra Moreno, G. Bournival, S. Ata, Analysis of bubble coalescence dynamics and postrupture oscillation of capillary-held bubbles in water, *Ind. Eng. Chem. Res.* 56 (50) (2017) 14781–14792.
- [29] A. Huerre, M. De Corato, V. Garbin, Dynamic capillary assembly of colloids at interfaces with 10,000 g accelerations, *Nature Commun.* 9 (1) (2018) 3620.
- [30] H. Wang, P.R. Brito-Parada, Coalescence dynamics of particle-laden bubbles, *Langmuir* 36 (5) (2020) 5394–5399.
- [31] H. Wang, P.R. Brito-Parada, The pinch-off dynamics of bubbles coated by microparticles, *J. Colloid Interface Sci.* 577 (2020) 337–344.
- [32] J.C. Burton, P. Taborek, Bifurcation from bubble to droplet behavior in inviscid pinch-off, *Phys. Rev. Lett.* 101 (21) (2008) 214502.
- [33] S.T. Thoroddsen, T.G. Etoh, K. Takehara, Experiments on bubble pinch-off, *Phys. Fluids* 19 (4) (2007) 042101.
- [34] G.I. Taylor, The dynamics of thin sheets of fluid. III. Disintegration of fluid sheets, *Proc. R. Soc. Lond. Ser. A Math. Phys. Eng. Sci.* 253 (1274) (1959) 313–321.
- [35] F. Culick, Comments on a ruptured soap film, *J. Appl. Phys.* 3 31 (6) (1960) 1128–1129.
- [36] S.T. Thoroddsen, K. Takehara, T.G. Etoh, The coalescence speed of a pendent and a sessile drop, *J. Fluid. Mech.* 527 (2005) 85–114.
- [37] Á. Moreno Soto, T. Maddalena, A. Fraters, D. Van Der Meer, D. Lohse, Coalescence of diffusively growing gas bubbles, *J. Fluid. Mech.* 846 (2018) 143–165.
- [38] G.D. Morris, S.J. Neethling, J.J. Cilliers, A model for the stability of films stabilized by randomly packed spherical particles, *Langmuir* 27 (18) (2011) 11475–11480.
- [39] V. Garbin, Collapse mechanisms and extreme deformation of particle-laden interfaces, *Curr. Opin. Colloid Interface Sci.* 39 (2019) 202–211.
- [40] V. Garbin, I. Jenkins, T. Sinno, J.C. Crocker, K.J. Stebe, Interactions and stress relaxation in monolayers of soft nanoparticles at fluid-fluid interfaces, *Phys. Rev. Lett.* 114 (10) (2015) 108301.
- [41] J.D. Paulsen, J.C. Burton, S.R. Nagel, Viscous to inertial crossover in liquid drop coalescence, *Phys. Rev. Lett.* 114501 (2011) 114501.
- [42] C.A. Miller, L.E. Scriven, The oscillations of a fluid droplet immersed in another fluid, *J. Fluid Mech.* 32 (3) (1968) 417–435.
- [43] A. Prosperetti, Free oscillations of drops and bubbles: The initial-value problem, *J. Fluid Mech.* 100 (2) (1980) 333–347.
- [44] Ş.S. Bayın, Ş.S. Bayın, Mathematical Methods in Science and Engineering, Wiley Online Library, 2006.
- [45] W.J. Hiller, T.A. Kowalewski, Experimental Analysis of Free Oscillating Drops, AFMC, Melbourne, 1989, pp. 7.21–7.24.
- [46] H. Lamb, Hydrodynamics, sixth ed., Cambridge University Press, 1932.