Soft Matter



PAPER

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Cite this: Soft Matter, 2017, 13, 3879

Received 15th January 2017, Accepted 21st April 2017

DOI: 10.1039/c7sm00097a

rsc.li/soft-matter-journal

1 Introduction

Armoured bubbles, i.e. bubbles coated with a dense layer of partially wetting particles, exhibit fascinating properties such as increased stability toward dissolution^{1,2} or the ability to sustain non-spherical shapes.³ These bubbles can be massively produced by bulk emulsification techniques⁴⁻⁶ or by bubble injection in a suspension of particles,⁷ but with a limited control over the bubble properties. Recently microfluidic techniques have been considered to produce some calibrated armoured bubbles of tailored shapes, sizes and composition.⁸ Some of these techniques simply rely on the natural inclination of particles to be adsorbed at air/liquid interfaces,^{9,10} while others exploit fancy chemical- or temperature-mediated processes^{11,12} or the deep modification of liquid/air interface dynamics in particle covered capillary tubes.^{13,14} In parallel, much effort has been devoted to the characterization of armoured bubble properties, and in particular their stability toward dissolution,^{1,2} their lifetime when exposed to a surfactant¹⁵ or their mechanical strength when subjected to ambient overpressure.¹⁶ Surprisingly, less effort has been devoted to the study of the response of armoured bubbles to mechanical vibrations,17,18 while bubbles are known to be outstanding resonators,19-23 with high quality factors and remarkably low resonance frequencies.²⁰ Recently, Poulichet et al.17,18 investigated the acoustically driven oscillation of particle-coated spherical bubbles. They showed that these oscillations can lead to the tailored expulsion of the particles from the surface at sufficient acoustic power. To the best of our knowledge, the response of their nonspherical counterpart to

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7sm00097a

Nonspherical armoured bubble vibration[†]

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In this paper, we study the dynamics of cylindrical armoured bubbles excited by mechanical vibrations. A step by step transition from cylindrical to spherical shape is reported as the intensity of the vibration is increased, leading to a reduction of the bubble surface and a dissemination of the excess particles. We demonstrate through energy balance that nonspherical armoured bubbles constitute a metastable state. The vibration instills the activation energy necessary for the bubble to return to its least energetic stable state: a spherical armoured bubble. At this point, particle desorption can only be achieved through higher amplitude of excitation required to overcome capillary retention forces. Nonspherical armoured bubbles open perspectives for tailored localized particle dissemination with limited excitation power.

mechanical vibrations has not been reported so far in the literature.

In this paper, we characterize the dynamics of cylindrical armoured bubbles excited with vertical vibrations produced using a vibration exciter. We show that the vibration leads to a step by step transition of the bubble shape from cylindrical to spherical as the amplitude of the vibration is increased. This shape evolution leads to a decrease of the surface of the armoured bubble and thus a release of excess particles in the liquid. This evolution is shown to be highly dependent on the excitation frequency: lower excitation amplitude is required near the Minnaert bubble resonance to trigger this transition. We demonstrate through energy balance that nonspherical armoured bubbles constitute a metastable state. The bubble vibration enables the release of the mechanical constraint between the particles which maintains the bubble shape and thus lets it evolve toward the least energetic stable state: a spherical armoured bubble. This transition does not require the overcoming of capillary retention forces and thus enables particle dissemination with reduced excitation power. Once the armoured bubble is spherical, massive particle desorption is only observed when the kinetic energy instilled from the surface vibration overcomes the capillary retention forces. The required power in this case is thus larger than that for a nonspherical bubble and is expected to increase as the particle dimensions are decreased as demonstrated through dimensional analysis.

2 Materials and methods

Cylindrical armoured bubbles of tailored radius $R_c = 0.49 \pm 0.01$ mm and length $L_c = 8.5 \pm 0.5$ mm are produced using the method introduced in ref. 13: first, glass capillary tubes of radius $R_t = 501 \ \mu$ m are cleaned by successive sonication in acetone and alcohol. Then the tubes are treated with piranha

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solution (sulfuric acid + hydrogen peroxide) to clean organic residues off the glass. They are then kept in DI Water in a sealed recipient before use. Prior to the particle dispersion, they are dried for 1 hour in an oven at 120 °C. Second, Rilsan (Polyamide 11) particles of mean radius $R_p = 15 \pm 1 \mu m$ are scattered into the tube by gently blowing them with an air jet. Third, a DI water liquid finger is pushed at constant flow rate ($Q = 0.2 \text{ ml h}^{-1}$) with a syringe pump inside the tube leading to the formation of a long cylindrical armoured bubble through the process described in ref. 13.

Finally the bubble is extracted from the tube and injected inside a rectangular plexiglas closed chamber of height 20 mm, length 75 mm and width 55 mm filled with DI water, by applying a larger flow rate of Q = 5 ml h⁻¹. The bubbles are cut at the appropriate length by twisting the capillary sideways while keeping it horizontal. This cuts the bubble on the open end of the capillary.

Then the chamber is vibrated vertically with a Bruel & Kjaer 4809 vibration exciter driven by a sinusoidal Voltcraft FG 250D function generator whose signal is amplified with a 2718 Bruel & Kjaer amplifier (Fig. 1). The amplitude of the excitation A is measured with an IEPE Deltatron type 4519-002 Bruel & Kjaer accelerometer. The evolution of the bubble shape is recorded with a Hamamatsu C9300 high resolution camera mounted on an Olympus SZX7 microscope, while the fast bubble oscillations are captured with a Photron SA3 high speed camera. Finally images are treated with ImageJ software and the evolution of the bubble shape is quantified by using the roundness shape descriptor $R_0 = 4S/\pi L_m^2$, with S being the apparent surface area of the bubble (the surface area occupied by the bubble in the 2D picture) and $L_{\rm m}$ being the length of the bubble major axis. This shape descriptor gives a measure of the deviation of the bubble from a circular shape, with $R_0 = 1$ as the bubble becomes perfectly spherical.

3 Experimental results

3.1 Shape evolution

The vertical vibration of the cylindrical armoured bubbles at a given amplitude A (0.1 µm < A < 50 µm) and frequency f_e (0.5 kHz $< f_e < 4$ kHz) leads to an isovolume evolution of its shape through a reduction of its surface and a release of excess particles in the liquid (see Fig. 2–4 and Movie S1, ESI†).



Fig. 1 Scheme of the experimental setup.

When the power is turned on, the bubble shape evolves at first over characteristic times <1 min and then evolves slowly toward an asymptotic shape, which depends on the excitation amplitude *A* and the excitation frequency f_e (see Fig. 5). As the amplitude of excitation is increased gradually, this asymptotic shape is more and more spherical, eventually leading to a spherical armoured bubble ($R_o \rightarrow 1$) (see Fig. 2 and 4). This transition is nevertheless not regular as a function of the excitation amplitude *A*: under a frequency-dependent threshold, the bubble keeps its cylindrical shape (see Fig. 5 and 6). Above this threshold, the bubble shape evolves at first weakly as the amplitude of the excitation is increased and then undergoes a sharp transition toward a spherical shape for a critical amplitude $\approx A_c$, defined



Fig. 2 Evolution of a cylindrical armoured bubble of initial length $L_c = 8.5$ mm and radius $R_c = 0.5$ mm vibrated vertically with a vibration exciter at frequency $f_e = 1$ kHz and at an amplitude *A* indicated at the top of each picture. Each picture is taken after two minutes of excitation.



Fig. 3 Evolution of a cylindrical armoured bubble of initial length $L_c = 8.5$ mm and radius $R_c = 0.5$ mm vibrated vertically with a vibration exciter at frequency $f_e = 2.5$ kHz and at an amplitude *A* indicated at the top of each picture. Each picture is taken after two minutes of excitation. In the final picture, all the particles initially at the surface of the bubble have been disseminated in the liquid.



Fig. 4 Evolution of a cylindrical armoured bubble of initial length $L_c = 8.5$ mm and radius $R_c = 0.5$ mm vibrated vertically with a vibration exciter at frequency $f_e = 3$ kHz and at an amplitude *A* indicated at the top of each picture. Each picture is taken after two minutes of excitation.



Fig. 5 Transient evolution of roundness R_{o} of a cylindrical armoured bubble excited at 1 kHz as a function of time (in min). The squares show the evolution of the bubble roundness when amplitude *A* is increased step by step every 10 min from $A = 9.7 \,\mu$ m to $A = 51.7 \,\mu$ m. The circles show the evolution when the amplitude is directly set up to 51.7 μ m.



Fig. 6 Evolution of the roundness as a function of the excitation amplitude for different excitation frequencies f_{e} . For each frequency, the roundness is measured sequentially after 2 minutes of excitation at each amplitude.

here as the amplitude necessary for the bubble to achieve a roundness of 0.4 (see Fig. 6).

It is also interesting to note that different transition modes are observed depending on how much the excitation amplitude A is increased at each step. For small steps, the bubble undergoes a highly asymmetric evolution with the bubble collapse occurring first at one side of the bubble (see e.g. Fig. 2 and 4 and Movie S1 in the ESI[†]). When high power is applied directly, the evolution is more symmetric (see Fig. 7 and Movie S2, ESI⁺). The transition shapes observed in the present paper are reminiscent of some previous observations by Caggioni et al.²⁴ on a different fluidic system: these authors studied the evolution of an initially cylindrical liquid droplet whose shape is maintained by bulk yield stress and whose transition toward a spherical shape is triggered by an increase in the temperature. While the systems are different, a parallel can be drawn between these two studies: in the two cases, activation energy (in the present case vibrations and heat for the study by Caggioni et al.) is used to overcome retention forces (jamming of particles trapped at the bubble surface in the



Fig. 7 Evolution of a cylindrical armoured bubble of initial length $L_c = 8.5$ mm and radius $R_c = 0.5$ mm vibrated vertically with a vibration exciter at frequency $f_e = 2.5$ kHz and excitation amplitude $A = 1.6 \mu$ m, shot at 250 frames per second with a Photron SA3 high speed camera. Time elapsed between two successive pictures: 280 ms. These snapshots correspond to Movie S2 in the ESI.†

present case and yield stress resulting from the soft wax crystal endoskeleton in the study by Caggioni *et al.*) and reach a final spherical shape corresponding to a minimal surface energy. Similar to the present study, the authors report that a slow increase in the activation energy (temperature in their case) leads to some asymmetric evolution of the drop shape while a faster increase leads to more symmetric evolution.

3.2 Minnaert resonance frequency

Gas bubbles surrounded by a liquid are spring-mass systems whose retention forces (spring) come from a combination of (i) the overpressure and vacuum inside the bubble when the bubble contracts or expands, respectively, and (ii) Laplace pressure (induced by surface tension), and whose mass is the mass of the surrounding liquid. From this simple consideration and dimensional analysis, one can show that the resonance

frequency of a spherical bubble is
$$f_{\rm M} = \frac{1}{2\pi R_{\rm s}} \sqrt{\frac{3}{\chi_{\rm g}\rho_{\rm l}} - \frac{2\sigma}{\rho_{\rm l}R_{\rm s}}}$$
, with

 $R_{\rm s}$ being the radius of the spherical bubble, $\chi_{\rm g}$ being the compressibility of the gas, $\rho_{\rm l}$ being the liquid density and sigma being the surface tension. This resonance frequency is known as the Minnaert frequency.²⁰ For a spherical air bubble surrounded by water, this leads to a resonance frequency (if surface tension is neglected): $f_{\rm M} \approx 3.26 \times R_{\rm s}^{-1}$ with $R_{\rm s} = (3V/4\pi)^{1/3}$ and thus for the bubbles considered in this paper to: $f_{\rm M} \approx 2.8 \pm 0.1$ kHz. In the present experiments, we observe that the critical amplitude $A_{\rm c}$ necessary to trigger the bubble shape transition from a cylindrical to a spherical shape highly depends on the excitation frequency $f_{\rm e}$ and decreases by several orders of magnitude close to the Minnaert resonance frequency (see Fig. 8). This suggests a strong link between the bubble volumetric oscillations and its shape evolution. Close to the resonance the bubble indeed undergoes larger oscillations at equivalent excitation power than away from the resonance.

It is interesting to note that two extremely different behaviors are observed around the Minnaert frequency: at 3 kHz the transition from cylindrical to spherical shape is achieved with the weakest excitation amplitude. The evolution of the bubble shape starts at very low excitation amplitude ($A = 0.1 \ \mu m \ll A_c$) and then goes on progressively when the amplitude is increased, until a spherical armoured bubble is obtained (see Fig. 4 and 6). Paper



Fig. 8 Critical excitation amplitude A_c required for the bubble to reach roundness $R_o = 0.4$ as a function of the excitation frequency f_e . Two experiments have been carried out for each frequency.

At 2.5 kHz, no shape evolution is observed until the critical amplitude A_c is reached. Then, when $A = A_c$ the bubble directly evolves into a particle-free spherical bubble with a release of all surrounding particles in the liquid (see Fig. 3, 6 and Movie S2, ESI†).

4 Discussion

4.1 Cylindrical bubbles: a metastable state

Nonspherical armoured bubbles constitute a metastable state. This can be shown by computing the interfacial energy required for a quasi-static and isovolume transformation of a spherical armoured bubble into a nonspherical one. Such a transformation necessarily requires an increase in the particle-covered interface of the bubble since the spherical shape minimizes the bubble surface. We can compute the energy ΔE , which is necessary for the migration of a particle from the liquid to an extended airliquid interface (see Fig. 9). In the calculation below we assume that the particles are hydrophilic (with a liquid-air-particle contact angle $0 \le \theta_p \le \pi/2$), spherical and that their radius R_p is much smaller than the radius of curvature of the bubble.

The energy ΔE is simply the difference between the interfacial energy $E_{\rm b}$ of the particle integrated at the air–liquid interface and the interfacial energy $E_{\rm a}$ of the particle lying in the liquid:

$$\Delta E = E_{\rm b} - E_{\rm a} \tag{1}$$

The interfacial energy E_a in configuration (a) is:

$$E_{\rm a} = \gamma_{\rm LP} A_{\rm LP}^{\rm a} = \gamma_{\rm LP} 4\pi R_{\rm p}^{-2} \tag{2}$$

with γ_{LP} being the interfacial energy per unit area of the liquidparticle interface and A_{LP} being the liquid-particle interface in the configuration (a). The interfacial energy E_{b} in the configuration (b) is the sum of the gas-particle (GP), liquid-particle (LP) and gas-liquid (GL) interfacial energies:

$$E_{\rm b} = \gamma_{\rm GP} A^{\rm b}_{\rm GP} + \gamma_{\rm LP} A^{\rm b}_{\rm LP} + \gamma_{\rm GL} A^{\rm b}_{\rm GL} \tag{3}$$



Fig. 9 Sketch illustrating the migration of a particle lying in the liquid to an extended meniscus.

with γ and *A* being the interfacial energies per unit area and the areas of the corresponding interfaces. Since the particles intersect the liquid–air interface with a contact angle $\theta_{\rm P}$ (to minimize interfacial energy), we deduce from simple geometric considerations that:

$$A_{\rm GP}^{\rm b} = 2\pi R_{\rm p}^{2} (1 - \cos \theta_{\rm P}) \tag{4}$$

$$A_{\rm LP}^{\rm b} = 2\pi R_{\rm p}^{2} (1 + \cos \theta_{\rm P}) \tag{5}$$

Then, due to their shape and arrangement, the particles cover only a fraction ϕ of the gas–liquid interface, called the specific surface area. Thus, the gas–liquid interface that is necessary to incorporate a new particle is $\pi R_P^2/\phi$, with $\phi < 1$. If we subtract the surface occupied by the particle itself, we obtain:

$$A_{\rm GL}^{\rm b} = \pi R_{\rm P}^{2} / \phi - \pi R_{\rm P}^{2} \sin^2 \theta_{\rm P}.$$
(6)

If we now combine eqn (1) to (6), we obtain:

$$\Delta E = \gamma_{\rm GL} \pi R_{\rm P}^2 \left[\frac{1}{\phi} - \left(1 - \cos \theta_{\rm P} \right)^2 \right]$$
(7)

Since $0 \le (1 - \cos \theta_{\rm P})^2 \le 1$ (for hydrophilic particles) and $1/\phi > 1$, we have:

 $\Delta E > 0$

This energy is positive indicating that the quasi-static transformation of a spherical bubble into a nonspherical one (through migrations of particles lying in the liquid to an extended interface) costs some energy. In other words a nonspherical bubble is not in a stable state and would return to its least energetic state, *i.e.* a spherical armoured bubble in the absence of other constraints.

Nevertheless, as discussed initially in ref. 3, jamming prevents the particles from leaving the surface of the cylindrical armoured bubble and thus maintains them in a metastable state. In the present experiments, the bubble vibration instills the activation energy required to trigger this transition. Indeed, during the expansion phase of the bubble oscillation, the particles

[‡] *N.B.*: The calculation of the energy required for the migration of a hydrophobic particle from the gas to the air-liquid interface also gives $\Delta E > 0$.

are no more in contact, and are thus freed from their interparticle mechanical constraint. In addition, the kinetic energy instilled to the particles by the vibration of the surface contributes to the release of the particles. This enables the bubble shape reconfiguration into a spherical armoured bubble. The bubble shape transition is therefore directly linked to its amplitude of oscillation. Since bubbles are oscillators with high quality factors, significantly less excitation power is required at the bubble resonance frequency (Minnaert frequency) to reach the same amplitude of surface vibrations, thereby leading to a dramatic reduction (two orders of magnitude) of the critical excitation amplitude A_c required to trigger the bubble shape transition, as can be seen in Fig. 8.

4.2 Particle expulsion from spherical armoured bubbles

Spherical armoured bubbles on the other hand constitute a stable state. Indeed, a bubble without particles is a minimum surface energy configuration. Then, if a particle lying in the liquid migrates at the already existing liquid–air interface, the energy necessary for this migration ΔE^* is simply:²⁵

$$\Delta E^* = \Delta E - \frac{\pi R_{\rm P}^2}{\phi} \gamma_{\rm GL} = -\gamma_{\rm GL} \pi R_{\rm P}^2 (1 - \cos \theta_{\rm P})^2 < 0 \qquad (8)$$

which is negative, indicating that the minimization of surface energy leads to an adsorption of the particles which come into contact with the air-liquid interface. This principle was used in ref. 9, 10 and 16 to create armoured bubbles.

Thus the desorption of particles lying at the surface of a spherical armoured bubble requires to overcome capillary retention forces as noticed by Poulichet and Garbin.^{17,18} These authors showed experimentally that localized particle desorption occurs for weak oscillations of spherical armoured bubbles but that the massive release of particles in the liquid requires higher amplitudes of vibrations.

We can estimate the kinetic energy that is necessary to overcome the capillary barrier, by simply equating $E_c = \frac{1}{2}m_P v_p^2$ and $|\Delta E^*|$, with $m_p = 4/3\pi\rho_p R_p^3$ being the mass of the particles, ρ_p being their density, $v_p = 2\pi f_e \Delta R_s$ being their velocity at the oscillating interface, and ΔR_s being the radial variation of the bubble.

We performed experiments on individual spherical armoured bubbles of radius $R_{\rm s} = 1.25$ mm covered with Rilsan particles of radius $R_{\rm p} \approx 15 \,\mu$ m, density $\rho_{\rm p} \approx 1050$ kg m⁻³, contact angle $\theta_{\rm p} \approx 70^{\circ}$,¹³ lying in water with surface tension $\gamma_{\rm GL} \approx 70$ mN m⁻¹ (see *e.g.* Movie S3, ESI†). In movie S3 (ESI†), massive particle detachment was observed when the bubble oscillation magnitude reached $\Delta R_s/R_s \approx 10\%$ of the initial radius of the bubble, with an excitation frequency $f_{\rm e} = 1.3$ kHz. This leads to $E_c/|\Delta E^*| \approx 0.4$. For the experiments performed at 2.5 kHz (see *e.g.* Movie S2, ESI†), the ratio $E_c/|\Delta E^*|$ measured when massive desorption of the particles occurs is approximatively equal to 2. These experiments are thus consistent with this criterion.

It is also interesting to note that this simple criterion is in qualitative agreement with the data provided by Poulichet *et al.*¹⁸ Indeed, in their experiments, the latex particle size and density are, respectively, $R_{\rm p} = 250$ nm and $\rho_{\rm p} = 1040$ kg m⁻³,

the air–liquid–particle contact angle is $\theta_{\rm p} \approx 45^{\circ}$,¹⁷ the frequency of excitation is $f_{\rm e} = 40$ kHz, the surface tension is $\gamma_{\rm GL} \approx 70$ mN m⁻¹ and the amplitude of oscillation required for particle dispersion is typically 40 μ m. This leads to a ratio $E_c/|\Delta E|$ required for particle dispersion of ≈ 3 .

4.3 Analysis of the dynamics observed near the Minnaert resonance frequency

The analysis detailed in the two previous subsections provides insightful elements, which help in understanding the two different behaviors observed at 2.5 kHz and 3 kHz, near the Minnaert resonance frequency of the spherical bubble. When the bubble is excited at 2.5 kHz, no shape modification is observed when $A < A_c$ and then brutally, all particles are ejected from the interface when $A = A_c = 1 \mu m$. While at 3 kHz, the shape evolution starts at low amplitude $A = 0.2 \,\mu\text{m} \ll A_c$ and reaches a spherical armoured bubble shape at $A = 1 \mu m$. This suggests that 2.5 kHz is closer to the resonance frequency of the spherical bubble and that 3 kHz is closer to the resonance frequency of the cylindrical armoured bubble. Indeed, at 2.5 kHz, the bubble response is weak (since the excitation differs from the cylindrical armoured bubble resonance frequency) until the vibration is sufficient to induce a shape transformation. As the shape becomes more and more spherical, the bubble amplitude increases up to an amplitude that is sufficient to overcome capillary retention forces, resulting in the release of all interfacial particles in the liquid. At 3 kHz, the bubble starts responding at low amplitude of excitation (since the excitation frequency is close to the cylindrical armoured bubble resonance frequency), but as the bubble shape evolves, the excitation frequency differs from the resonance frequency, requiring more and more power to enable a shape evolution of the bubble. When the spherical shape is reached, the excitation amplitude of $A = 1 \ \mu m$ is not sufficient to overcome the capillary retention forces and thus the bubble retains its armour.

4.4 Nonspherical bubbles: powerful vectors for particle transport and dissemination with reduced activation power

All the experimental and theoretical results provided in this paper indicate that particle dissemination can be achieved with less power with nonspherical than with spherical armoured bubbles. The dimensional analysis below suggests that this tendency should increase as the size of the particles are decreased.

Let us consider a spherical bubble of radius $R_{\rm s}$ covered with particles of radius $R_{\rm p}$ excited at its resonance frequency $f_{\rm M}$ (for maximum efficiency) oscillating at an amplitude of oscillation $\Delta \bar{R}_{\rm s} = \Delta R_{\rm s}/R_{\rm s}$ sufficient to disseminate the particles. The equality $E_{\rm c} = |\Delta E^*|$ leads to:

$$1/2[\rho_{\rm p} \times (4/3\pi R_{\rm P}^{-3})] \times [2\pi R_{\rm s} \Delta \bar{R}_{\rm s} \times 3.26 R_{\rm s}^{-1}]^2 = \gamma_{\rm GL} \pi R_{\rm P}^{-2} (1 - \cos \theta_{\rm P})^2$$

If the density and wetting properties of the particles are kept constant and only the size of the bubble and particles are changed, one obtains:

$$\Delta \bar{R}_{\rm s} \propto {R_{\rm p}}^{-1}$$

The bubble amplitude of oscillation required for particle dissemination does not seem to depend on the bubble size but is nevertheless inversely proportional to the size of the particles. This means that for smaller particles, a larger relative amplitude of oscillation is required to untrap the particles located at the surface of a spherical armoured bubble. While for a cylindrical bubble, the same relative amplitude of oscillations would enable the release of particles since there is no need to overcome capillary retention forces, but only to suppress the contact between the particles. This might be essential for medical applications. Indeed, contrast agents currently used in the body have a typical size of a few microns and active materials of typically a few nanometers are generally required for efficient dissemination in the body. It might thus become difficult to overcome capillary retention forces at this scale.

5 Conclusion and perspectives

In this paper, the response of nonspherical armoured bubbles to mechanical vibrations was studied experimentally and analyzed theoretically. In particular, it was shown that a nonspherical armoured bubble constitutes a metastable state, which evolves toward its minimum energy state, *i.e.* a spherical armoured bubble, as its surface is vibrated. This shape evolution leads to a reduction of the bubble interface and consequently a release of the excess particles. Once the spherical shape is reached, the massive release of particles from the interface requires the fact that the kinetic energy instilled to the particles by the vibration of the bubble surface exceeds the desorption energy. Scaling laws indicate that the release of particles from spherical armoured bubbles becomes extremely challenging as the size of the particles is decreased. Thus nonspherical armoured bubbles appear as a tremendous alternative for controlled particle dissemination at small scales with limited input power. Applications can be envisioned in medicine for in vivo active drug delivery through the use of robust acoustical methods precedently developed for ultrasound contrast agents.

Finally, since elongated cylindrical bubbles are unstable without their armour, the modes of vibrations of these objects have never been studied in the literature. It would be interesting in the future to look more closely at the breathing mode of these singular bubbles and in particular (i) verify that their asymmetric evolution observed when the power is increased progressively is indeed due to a larger amplitude of vibration at the positions where the radius of curvature is larger and (ii) investigate the evolution of the particle arrangement during bubble expansion and dilatation.

Acknowledgements

This work was supported by Agence Nationale de la Recherche (Grant No. ANR-12-BS09-0021- 01).

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