# Long-Lived Antibubbles: Stable Antibubbles through Pickering Stabilization

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ABSTRACT: Antibubbles, which are liquid droplets surrounded by a thin shell of gas in a liquid phase, have several promising applications, among which is encapsulation. A major hurdle toward these applications has hitherto been the inherent instability of antibubbles, leading to lifetimes of at most minutes. Here we show the production of antibubbles with a lifetime of at least tens of hours, with their stability stemming from the adsorption of colloidal particles at gas–water interfaces. Antibubbles were produced by coating aqueous droplets with hydrophobic colloidal particles, gelling the droplets, and then dropping them into an aqueous colloidal suspension. This resulted in the formation of antibubbles with a long lifetime, also after the melting of the gel.
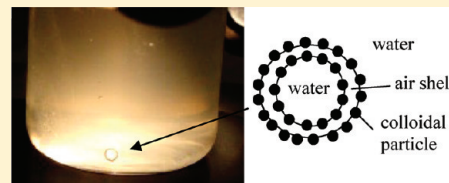
INTRODUCTION

It has been said that anyone washing his hands under the tap with soap probably creates numerous antibubbles.[1] These antibubbles, however, tend to remain unnoticed because most of them will vanish within seconds. This short lifetime has been considered to be an inherent property of antibubbles because they cannot be stabilized by surfactants.[2,3] For antibubbles in water to be stable, the gas film between the inner and outer aqueous phases needs to be stabilized by the presence of repulsive forces between the opposing interfaces. However, because of the low dielectric permittivity and the low solvent quality of the gas film, surfactants adsorbed at both interfaces hardly generate electrostatic or hydrophobic repulsive forces. Therefore, stability is determined by the drainage speed of the gas film, which is on the order of minutes under quiescent conditions, and thus the lifetime of antibubbles is short. Antibubbles were first described in 1932.[4] They have intrigued many and promise several applications.[5–8] Despite this, antibubbles have long been mainly a curiosity and have not found any practical application, probably as a result of their short lifetime.[9] Recently, interest in antibubbles has increased.[2,3,9,10]

In the past few years, a lot of attention has been given to the stabilization of interfaces through the adsorption of colloidal particles, so-called Pickering stabilization.[11] Unlike ordinary surfactants, colloidal particles can adsorb to interfaces irreversibly and can therewith "jam" the interface, making it very stable.[11] It has been shown that several unstable systems could be made remarkably stable using Pickering stabilization. Examples include foams, bicontinuous phase-separated systems, phase-separated aqueous polymer solutions, and water droplets in air.[12–15]

In this study, our aim was to apply Pickering stabilization in order to create stable antibubbles. Several ways have been described to create antibubbles.[1,8] The most common way is to inject a liquid jet gently into a bath of liquid, with both liquids containing surfactant.[9] The liquid jet entrains some of the surrounding air and therewith becomes surrounded by an air column in the receiving liquid bath. This air column eventually pinches off together with the liquid jet to form a droplet enclosed in an air bubble.[9] It is not straightforward to apply Pickering stabilization in the production of antibubbles. To stabilize droplets, colloidal particles need to be wetted predominantly by the continuous phase containing the droplets.[11] Therefore, to stabilize aqueous antibubbles, strongly hydrophobic particles need to adsorb at the inner air–water interface of the antibubble. However, it is difficult to disperse such hydrophobic particles in the inner water phase. Moreover, the antibubble formation process will be too fast for the colloidal particles to adsorb to the newly formed interfaces during the formation process. Additionally, after the formation of antibubbles, the formed air shell may be too thin to accommodate the particles. We solved the problem of how to apply Pickering stabilization to stabilize the aqueous core of antibubbles by coating aqueous droplets with colloidal particles to form so-called "liquid marbles".[16] Liquid marbles were gelled and then dropped into an aqueous suspension of colloidal particles.

EXPERIMENTAL SECTION

An aqueous solution containing 30% maltodextrin 33DE (Roquette) and 2.5% gelatin (Dr. Oetker) was made (1.1 g/mL density) at 45 °C. In some cases, 0.1% methylene blue was added as a colorant. Small drops of this solution with a size of 2.5 mm were made using a syringe. Droplets were rolled through a layer of hydrophobized H18 fumed silica particles (Wacker-Chemie) to coat them. Hydrophobized fumed silica particles are known to produce strong liquid marbles.[17] Silica particles consist of nanosized primary particles agglomerated into particles with a typical size of 10 μm. Particles were hydrophobic with a residual silanol group content of 25% of that of hydrophilic fumed silica. Silica-coated droplets
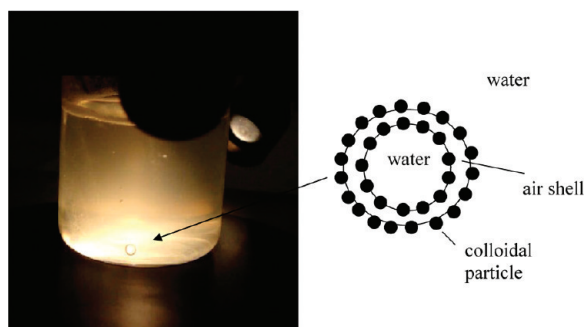
Figure 1. Photograph and schematic picture of an antibubble in a dispersion of silica particles. (The schematic picture is not drawn to scale.)

are held at 5 °C for 1 h to gel them. Mild shaking was applied to keep the droplets spherical. Thus-produced gelled liquid marbles are dropped from a height of 4 cm into a 40 mL glass beaker filled with liquid. When a gelled liquid marble enters the liquid, it becomes entrapped in a bubble (i.e., an antibubble is formed). The beaker was filled with a freshly made 1:1 mixture of a suspension of 1% H30 fumed silica particles (Wacker-Chemie) and an aqueous solution of 1% NaCl and 10% sucrose (with a mixture density of 1.02 g/mL). Particles were dispersed using sonication. H30 particles are less hydrophobic than H18 particles with a residual silanol content of 50%. NaCl was used to promote the adsorption of the H30 particles at the air−water interface.[18] Sucrose was present to decrease the osmotic pressure difference between the core of the antibubble and the surrounding solution. Stability testing was done by placing the beaker containing antibubbles in a water bath at 45 °C to melt the cores of the antibubbles. Stability testing began at least 10 min after the creation of the antibubbles to provide enough time for the H30 particles to adsorb at the antibubble surface.

■ RESULTS AND DISCUSSION

We produced Pickering-stabilized antibubbles by coating aqueous droplets with hydrophobic colloidal particles to form liquid marbles, gelling the liquid marbles by cooling and then dropping them into an aqueous colloidal suspension. When a gelled liquid marble is dropped into a water bath, it drags with it a thin layer of air in which it becomes entrapped (i.e., an antibubble is formed, Figure 1). After the formation of the antibubble, the gelled core can be liquefied to a viscosity close to that of pure water by melting. This does not destroy the antibubble. Although liquid marbles floating on the surface of water has recently been studied,[19] to our knowledge the production of antibubbles from (gelled) liquid marbles has not yet been shown. We use liquid marbles with a density higher than that of water produced by dissolving 30% maltodextrin in the aqueous phase. When no maltodextrin was used, the buoyancy was so strong that the formed antibubble immediately "jumped" back out of the water bath. Antibubbles produced with maltodextrin in their cores sink to the bottom of the water bath. In contrast to what is generally observed,[3] our antibubbles are not disrupted when they touch the bottom of the bath, indicating their robustness. When liquid marbles were not gelled, the marbles lost their particle shell when they impacted the water bath and no antibubbles were formed. We hypothesize that gelling prevents the marbles from being elongated when they dive into the water bath. Elongation causes the adsorbed particles not to be closely packed; therefore, the particle layer becomes much less effective in opposing the drainage of the air film. Under the conditions used in our
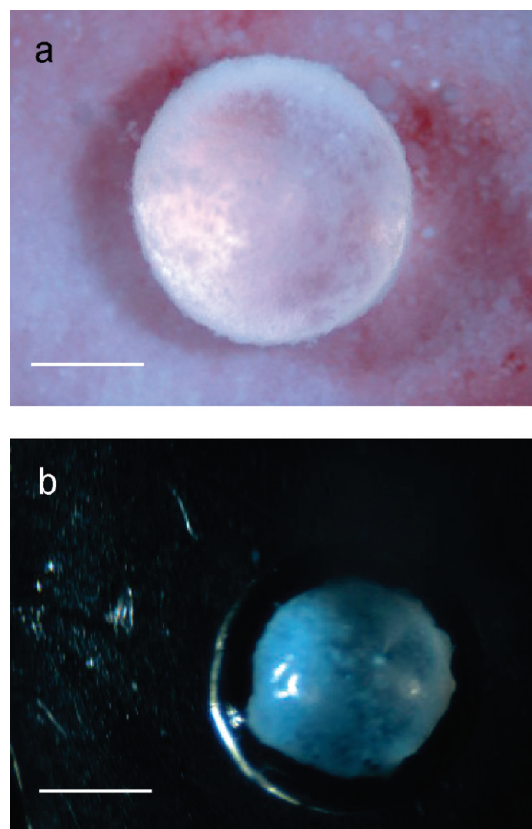

Figure 2. (a) Microscopic picture of a liquid marble. (b) Microscopic picture of an antibubble produced by dropping the liquid marble shown in part a into water. The scale bar denotes 1 mm.

experiments, the air film probably does not drain to such an extent that the adsorbed particles contact the outer air−liquid interface because a comparison of parts a and b of Figure 2 shows that the layer of adsorbed particles remains substantially unchanged during antibubble formation. The two forces acting on the liquid marble when it enters the water bath, the Laplace pressure and the viscous shear tension, which were estimated to amount to 100 and 1 Pa, respectively, thus seem unable to deform the marble, in line with the fact that the yield stress of the gel is estimated to be 10^5 Pa.

Figure 2 shows a liquid marble in air and the antibubble formed after dropping this liquid marble into an aqueous solution. From the fact that antibubbles made from 2.5 mm marbles are nearly buoyant, we estimate the air shell to have a thickness of around 30 μm. Note that, because of the total reflections of the light, the air shell appears to be much thicker. The air-shell thickness is larger than the ∼1 μm thickness normally seen in antibubbles of comparable size.[3] In our experiments, the adsorbed particles have a typical size of 10 μm as claimed by the supplier and confirmed by us using microscopy. These particles will consequently drag along an air layer with a thickness of the same order of magnitude. When antibubbles with a melted core are punctured with a needle to make them burst, the shell is released as a small bubble with a size of around 1 mm, in reasonable correspondence with the estimated air-shell volume. The observed antibubble formation process is in line with recent work by Aristoff and Bush, who observed that when millimeter-sized particles with a rough hydrophobic surface were gently dropped into water, the particles became surrounded by a thin shell of air.[20]
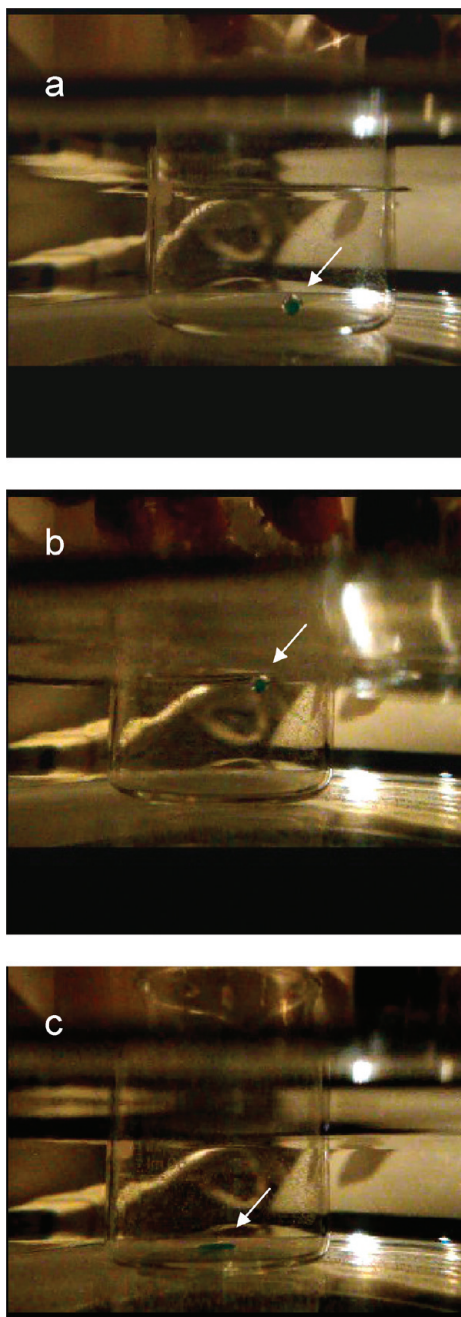
Figure 3. Stills from a movie showing a burst antibubble. Arrows indicate the (bursted) antibubble. The antibubble is contained in a beaker filled with water that is placed in a heated water bath. (a) Picture of an antibubble with a blue core. To facilitate the rupture of the antibubble and to obtain clear pictures, the antibubble was produced in plain water. (b) The beaker is shaken such that the antibubble whirls up. The picture shows the antibubble right before it coalesces with the surface of the water. (c) Burst antibubble, about 2 s after it has coalesced with the surface.

The stability of the antibubbles was tested by placing the beaker containing the antibubble in a water bath of 45 °C, which is sufficient to melt the gelled core of the antibubble. When the outer air—water interface of the antibubble was stabilized by adsorbed colloidal particles, lifetimes exceeding 20 h were found. This is more than 2 orders of magnitude longer than hitherto reported. Dorbolo et al. found that increasing the surface

modulus of antibubbles by a factor of 100 doubles the average lifetime to around 200 s.[10] The use of Pickering stabilization, as described here, will also strongly increase the surface modulus of the antibubble interfaces but will effectively stop the drainage of the air shell when the shell has become so thin that the colloidal particles adsorbed at the inner and outer interfaces of the antibubble touch. This may explain the extremely long antibubble lifetime observed here. Antibubbles, even with a melted core, also resisted gentle stirring. When methylene blue was added to the core as a colorant, no leakage was observed during the lifetime of the antibubble. This shows that the air shell provides an excellent barrier against the leakage of molecules with a low vapor pressure. Interestingly, when antibubbles burst, the colorant is almost immediately distributed over a volume much larger than the volume of the antibubble (Figure 3). This is particularly interesting because coated bubbles are used more and more as controlled release agents that can be triggered to release by an ultrasound field, for example.[21] The antibubble geometry provides a way to load bubbles with large amounts of actives, notably inside the core. The combination of good barrier properties with the possibility of extremely fast, controlled release that can be achieved with stable antibubbles has long been an elusive goal for the controlled delivery of drugs and other actives.[22]

■ CONCLUSIONS

The results presented here show that antibubbles with long-term stability can be produced through stabilization of the interfaces by adsorbed colloidal particles (i.e., by Pickering stabilization). This is remarkable because until now antibubbles always had a short lifetime of up to several minutes. Because antibubbles are unique structures, it is expected that they can find numerous applications in fields such as encapsulation, food technology, flotation, and reaction engineering. Ordinary bubbles (e.g., gas spheres in liquid) are already used in many applications.[23] These are, however, often hindered by the tendency of bubbles to cream, which is an important cause of bubble instability.[23] The buoyancy of antibubbles, however, can be easily controlled.[1] Antibubbles could thus be a substitute with increased potential for ordinary bubbles. We feel that the possibility presented here to stabilize antibubbles removes the main hurdle toward the further study of their properties and toward their application.

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