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UNDERSTANDING PARTICLE–BUBBLE ATTACHMENT: EXPERIMENTS TO IMPROVE FLOTATION MODELLING

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ABSTRACT

CSIRO has developed a model of flotation using computational fluid dynamics (CFD) software that incorporates fluid motion in realistic vessel geometries. The model also predicts particle capture by bubbles in the system using equations based on the induction time concept.

This work looks to experimental studies at the microscale to provide an improved basis for the attachment predictions in the overall model of flotation.

A model cell has been set up to study the behaviour of 150 micron glass particles in the vicinity of a captive 1.3 mm air bubble. The interaction is recorded on high-speed video, permitting direct estimation of relevant parameters such as the approach velocity, and the duration of particle sliding over the bubble surface. A new experimental configuration has allowed the particle path toward, around, and away from the bubble to be totally unimpeded.

Particle trajectories show a significant deviation at surprisingly large separations, due to the hydrodynamics. However, surface properties are more important in determining eventual attachment. Sliding durations have been measured, and these can be related back to a threshold duration to achieve attachment, known as the "induction time". Events where a sliding particle 'jumps in' toward the bubble may indicate the precise moment of attachment, providing a more accurate estimate of induction time.

Flotation modellers must consider processes ranging from bulk hydrodynamics to molecular chemistry. However, the micromechanics that forms a bridge between those two processes turns out to be critical. Direct observation of particle–bubble interaction through high-speed videography provides insight into flotation modelling, to allow prediction of attachment based on a realistic combination of hydrodynamic and chemical factors.

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BODY OF PAPER

Introduction

The process of flotation operates by the combination of solid particles with gas bubbles in a liquid medium, with the particle–bubble aggregates rising to the top of the liquid, where they can be removed. Flotation is an important separation technique in a range of industries, including water treatment and mineral processing. The bulk hydrodynamics of the process are very important, and there is typically an optimal amount of liquid agitation that will improve the kinetics, balancing the increasing number of collisions (and hence attachments) with the increasing probability of detachment. At the other extreme it is the surface properties, which operate over nanoscale distances, that control the affinity of the particles and bubbles for each other, thereby limiting the probability of attachment, and the resistance to detachment.

Three distinguishing features of the flotation process as employed in mineral processing are that it is the solid phase that contains the material that will make up the final product, the flotation works selectively on different particle types, and there are fewer restrictions on chemical addition to aid the operation. The material fed to the flotation cell will contain a range of minerals, some of which are of greater value. If those valuable minerals have a greater affinity for the bubbles than the other minerals, then the desired material can be floated to the top while the gangue settles to the bottom of the cell. Conversely, if the gangue minerals have a greater affinity for the bubbles than the valuable components do, then the floated material will comprise the waste, while the concentrated ore is recovered in the sediment. The latter process is called 'reverse flotation'. Some particles will naturally adhere more readily to bubbles than others. However, in current operation it is usual to add chemicals that will modify that affinity.

Over a period of more than ten years CSIRO researchers have developed detailed software models to predict flotation performance in realistic industrial cell geometries. These models encompass computational fluid dynamics (CFD) simulations to capture the complicated hydrodynamics in the bulk, which also governs the frequency of particle–bubble encounters; a number of model equations to describe the probability of attachment and detachment; and a population balance algorithm to keep track of free and attached particles [Koh & Schwarz, 2006]. The applications of these models are in evaluating new equipment designs, or comparing different operating conditions or configurations. Furthermore, detailed spatial data can be extracted relating to local hydrodynamics, attachment–detachment kinetics and particle concentrations, which can improve understanding and inform decision making for optimisation.

The maturity of CFD as a technique, combined with direct experimental estimation of the hydrodynamics within a cell by particle image velocimetry (PIV) [William Yang, unpublished], provides assurance that this component of the overall model is reliable.

The population balance approach is conceptually simple, and likewise quite robust, albeit with the inherent limitations imposed by discretisation of the system.

The model of attachment–detachment kinetics follows primarily from the classical Smoluchowski equation. However the rate coefficients for each process are computed from correlations that depend upon several parameters, chief among them the contact angle of the particle surface, which characterises its hydrophobicity. This contact angle refers to the angle, θ, made between the liquid–gas interface and the liquid–solid interface at the three-phase contact line (TPCL), as illustrated in **Figure 1**. A large

value of θ indicates a hydrophobic surface, corresponding to particles that can readily attach to bubbles.

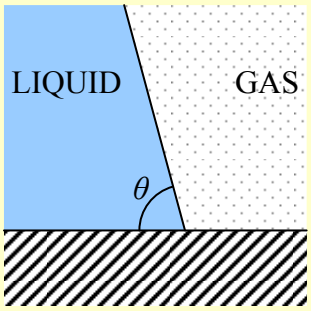

Figure 1: Illustration of contact angle.

A key concept in the estimation of the probability of particle–bubble attachment is the induction time, t_{ind}, which was first articulated by Sven-Nilsson [1934]. Fundamentally the induction period accounts for thinning and drainage of the film of liquid interposed between the particle and the bubble, until rupture of the film occurs. In flotation the induction time can be interpreted as a threshold sliding duration (provided bubbles do not undergo significant deformation) [Nguyen & Schulze, 2004: 257f.]. When a particle encounters the bubble, it will first deviate slightly from its initial trajectory, due to the action of fluid forces, and then it will slide for a brief period of time over the bubble's surface, t_{slide}. If $t_{slide} < t_{ind}$, then attachment is not expected; if $t_{slide} > t_{ind}$, then attachment is expected to occur. (Some researchers take a pragmatic view that the cut-off may not be as sharp in a real system as the model suggests [Sven-Nilsson, 1934; *cf.* Wang, *et al.*, 2003], perhaps allowing for a degree of chaotic motion [Nguyen & Schulze, 2004: 190f.].)

The literature does contain a large number of publications relating to flotation and the particle–bubble attachment process. Aside from the theoretical treatments, experimental work focussed on interactions between a single bubble and one or more particles has included:

- particle dropping techniques, commencing with Bogdanov & Filanovsky in 1940 [Nguyen & Schulze, 2004: 240], in which particles falling onto a stationary bubble are recorded by high-speed or stroboscopic photography [Schulze & Gottschalk, 1981] and videography [Nguyen & Evans, 2004] [*cf.* Nguyen & Schulze, 2004: 239ff.; Wang, *et al.*, 2003];
- Hallimond tube experiments, popularised by Hallimond [1944] based on a device first described in 1904, in which — in its modern incarnation [Kitchener, 1984: 29] — a bubble rises through a dilute suspension and the attachment outcome is observed;
- particle pick-up (or "bubble pick-up") experiments, introduced by Cooke & Digre [1949], in which the bubble is driven into the particles and the attachment outcome is observed;
- atomic force microscopy, beginning in 1994 [Butt, 1994; Ducker, *et al.*, 1994], in which a particle is driven into a bubble and the force is observed [Johnson, *et al.*, 2006] — almost all concentrating on small separations, typically less than 2 μm.

The present research is part of a larger project aimed at establishing the effect upon the attachment probability of diverse parameters relevant to flotation in real mineral systems. In order to achieve this a systematic study is under way to relate particle, bubble and liquid properties to their behaviours around the moment of attachment, with extra interest in the relevant induction times.

Experimental method

The procedure adopted in the present work is to drop treated glass spheres a short distance (*circa* 22 mm) onto a stationary bubble through a quiescent liquid medium.

The 'ballotini' particles reported herein are composed of soda–lime glass whose surfaces have been fully methylated using chloro(trimethyl)silane in a procedure that has been described elsewhere [Koh, *et al.*, 2009], with $\theta \sim 90°$. The particles had first been dry-screened to a nominal size range of 125 to 150 μm; the estimated median size of the particles observed and reported herein was 150 μm. The bubble was atmospheric air, blown from a blunt-tipped 25 gauge stainless steel capillary attached to a syringe. The needle was bent so that the tip of the capillary was horizontal. The liquid medium was deionised reverse-osmosis water (Millipore *Milli-RX* 75), with no additives, and the entire system was contained in a glass-walled tank with 15 cm sides.

The interactions were recorded on a Photron *Ultima FASTCAM* APX RS 250KC high-speed video camera operating at 1000 frames per second. Images were magnified by a Navitar *Zoom 6000* lens assembly achieving 6.75× magnification (nominal) with a depth of field of 180 μm. Illumination was provided by a 2000 W tungsten lamp filtered through a translucent sheet.

The entire system, except the lamp, was located on an air table (Technical Manufacturing Corporation *MICRO g* model 63-532) to avoid external vibrations.

Video images were subsequently processed using the MATLAB software application. This involved primarily conversion to greyscale, subtraction of the 'background', thresholding, and morphological operations to remove noise and artefacts. Cases in which the particle silhouettes overlapped were not included in the analysis.

Results

Evaluation of experimental configuration

The experimental configuration described has been found to be suitable for the task of observing attachment and estimating induction time. An example of the type of image attainable is presented in **Figure 2**.

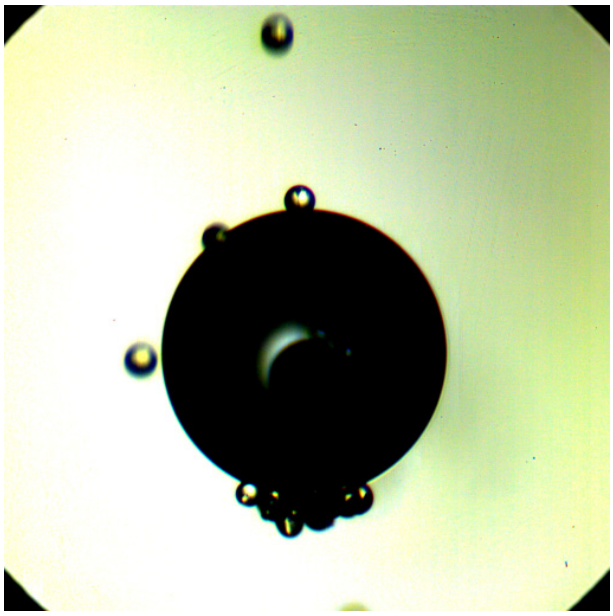

Figure 2: Example of image quality at 1/500 s exposure time.

The present system allows direct observation of interaction including sliding and attachment or disengagement. The Hallimond tube allows only efficiencies or probabilities to be calculated, and does not permit direct estimation of induction time.

Even though ultimately capture probabilities are to be predicted in our complete flotation simulation, the simulation needs to be based on more fundamental properties in order to have sufficient flexibility to provide valid predictions in both highly turbulent and laminar regimes of the cell, for example. An advantage of the present set-up over studies using an atomic force microscope (AFM) or bubble 'pick-up' apparatus is that those alternative techniques inherently restrict the movement of the interacting objects that is not a feature of the real physical system. *I.e*. they rely on 'forced' film drainage, while the present system permits 'natural' drainage [Nguyen & Schulze, 2004: 521f.; Wang*, et al.*, 2003].

The limited number of particle dropping experiments reported all seem to have used a vertically oriented capillary to blow the bubble [*e.g*. Nguyen & Evans, 2004; Wang*, et al.*, 2003], which can promote distortion from the ideal circular cross-section in the focal plane, and also interferes with motion of the particle around the underside of the bubble, and possible disengagement. Specification of a sufficiently long length of horizontal capillary (here approximately 30 mm) means that the vertical portion of the needle is far enough from the focal plane so as to not interfere with the capture images.

Trajectories

The trajectories of several particles interacting with a stationary bubble are depicted in **Figure 3**. The trajectories all lie approximately in the focal plane, and show a range of behaviours. Some particles deviate around the bubble without ever coming very close; typically the deviation in the trajectories becomes evident at separations of the same magnitude as the particle diameter, and are therefore attributed to fluid forces, which may include drag forces, lift force and other pressure gradient effects. Other particles slide over the surface of the bubble, and then withdraw. Finally, a number of the particles attach to the bubble after a short period of sliding; they then continue to move under the influence of gravity to the bottom of the bubble. (Note that some of the trajectories are truncated due to either video capture limitations or obscuration of the particle of interest by other particles in the foreground or background.)

The above trajectories, or 'pathlines' are notably different from the 'streamlines' that they resemble. Streamlines are usually derived for a homogeneous fluid that flows in or around an object with a specified geometry. Attempts have indeed been made to use streamlines corresponding to various flow regimes around a bubble to predict particle trajectories and furthermore the fluid forces acting on the particle during the sliding period [Yoon & Luttrell, 1989]. However, such derivations are based on conflicting assumptions, in which the particle is treated partly as an object of finite size, and partly as an infinitely small point that does not interfere with the liquid flow. Of course, a real particle of the sizes presently discussed would cause substantial deviations from the ideal streamlines calculated in the absence of the particle. Such considerations can often be neglected for motion in the bulk, but can be crucial when dealing with flow near boundaries.

Of further interest is the velocity at which the particles move. **Figure 4** displays the foregoing trajectories coloured according to the instantaneous speed. As there is some variation in particle diameter, the results have been replotted in **Figure 5**, with the speed normalised by the Stokes settling velocity, given by $u_{\text{Stokes}} = \Delta\rho\, g\, d^2 / 18\, \eta_{\text{L}}$ [Nguyen & Schulze, 2004: 75], in which the variables have their usual meanings and $\Delta\rho \approx 1450$ kg/m^3. (It is recognised that u_{Stokes} only applies in creeping flow [*e.g*. Nguyen & Schulze, 2004: 74,77], at Reynolds numbers smaller than those encountered presently, which are of order 2; nevertheless, u_{Stokes} provides an adequate estimate of the terminal velocity for the current purposes.)

The particle velocities display a range of behaviours. Those particles that have deviated away from the bubble without coming close enough to slide over its surface generally do not exhibit significant decreases in speed, but rather maintain their speed. Those particles that slid over the bubble surface slowed appreciably when sliding beside the more horizontal sections, but sped up when sliding against the more vertical sections. This behaviour was seen irrespective of whether the particles attached or not. Although previous reports in the literature speculated that the velocity of attached and unattached particles following (approximately) the same trajectory would deviate [Wang, *et al.*, 2003], no obvious change in the velocity due to attachment was observed in the present work. This could be due to the bubble in the present system having a more mobile surface, a characteristic that is known to significantly affect the hydrodynamics [Manor, *et al.*, 2008; Nguyen & Schulze, 2004: 99ff., 138ff., 225ff.]. Addition of surfactant to the system may cause more of a change in particle motion following attachment due to a reduction in bubble surface mobility [Manor, *et al.*, 2008; Nguyen & Schulze, 2004: 101f.; Wang, *et al.*, 2003]. While the water used in the present work could not be absolutely free of trace impurities, the adopted procedure in which bubbles were freshly blown shortly before particle dropping may have provided too short a time for trace surface active impurities present in the bulk to accumulate at the gas–liquid interface at significant levels. Furthermore, the bulk may have been depleted of trace surfactants over the course of the session due to adsorption onto previously blown bubbles and at the top surface of the cell. An additional contribution could be due to the first particles to drop onto the bubble sweeping surfactant on the bubble surface out of the way of following particles [*cf.* Manor, *et al.*, 2008].

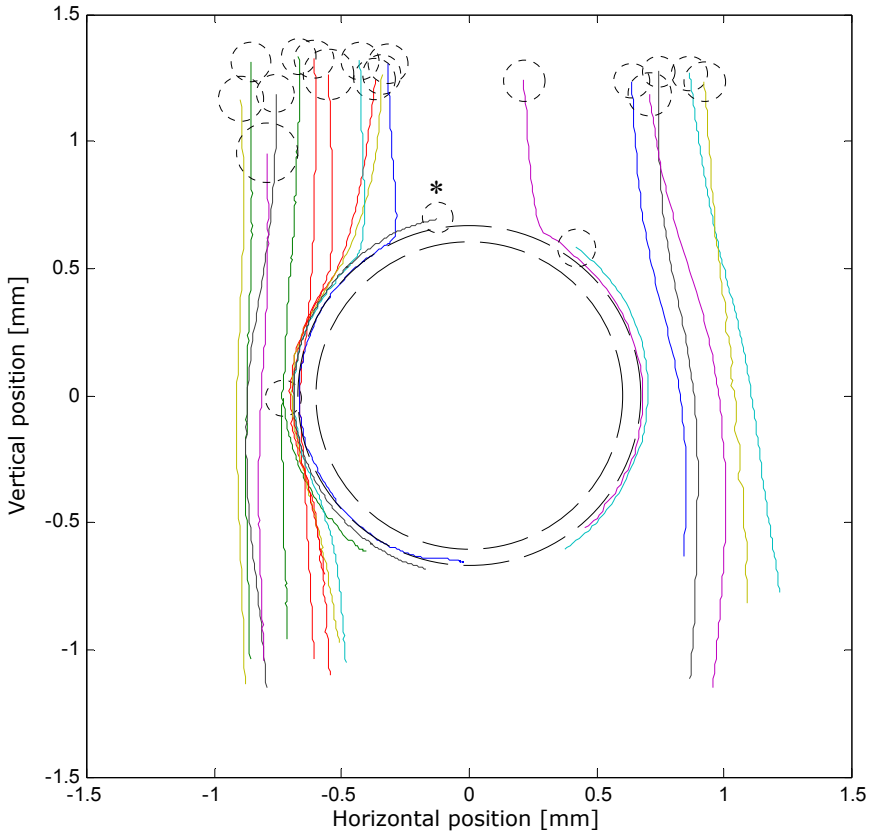

Figure 3: Trajectories of spherical particles falling under gravity onto or around a stationary near-spherical bubble. The coloured traces indicate trajectories of individual particles, all lying approximately in the plane through the centre of the bubble. Each particle size is indicated by a dotted outline. The two dashed outlines indicate the corresponding range of bubble size. The co-ordinates have their origin at the bubble centre.

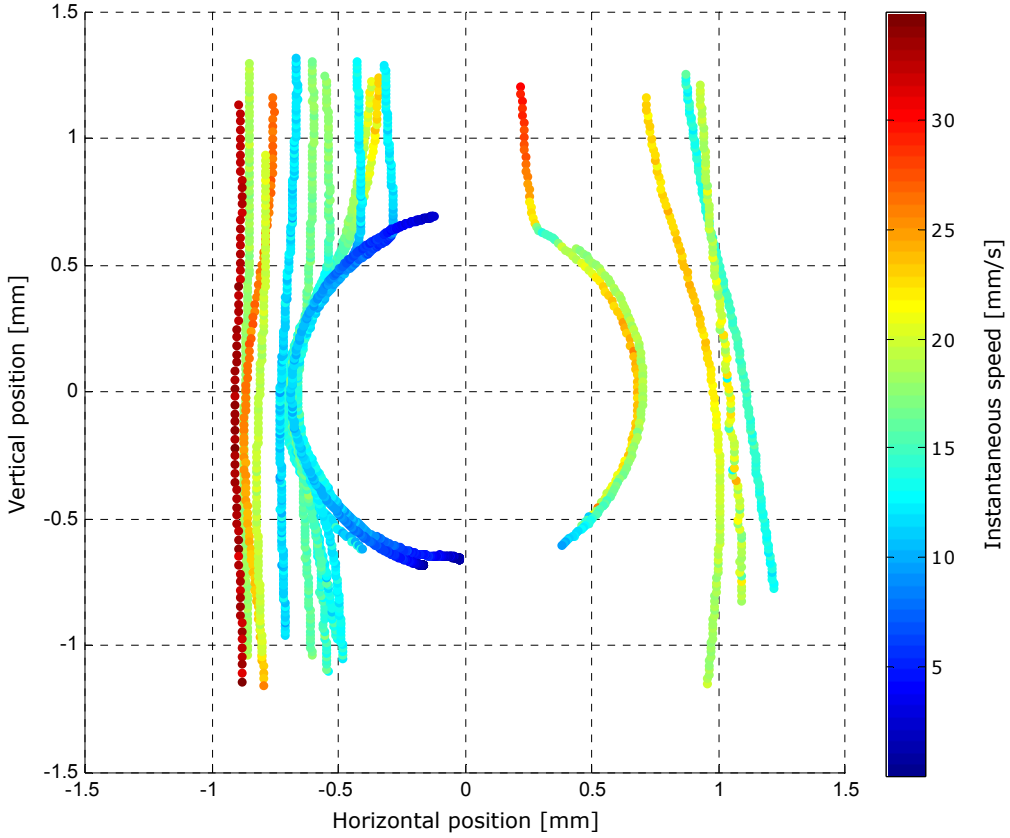

Figure 4: Particle trajectories around a bubble, coloured by their instantaneous speed.

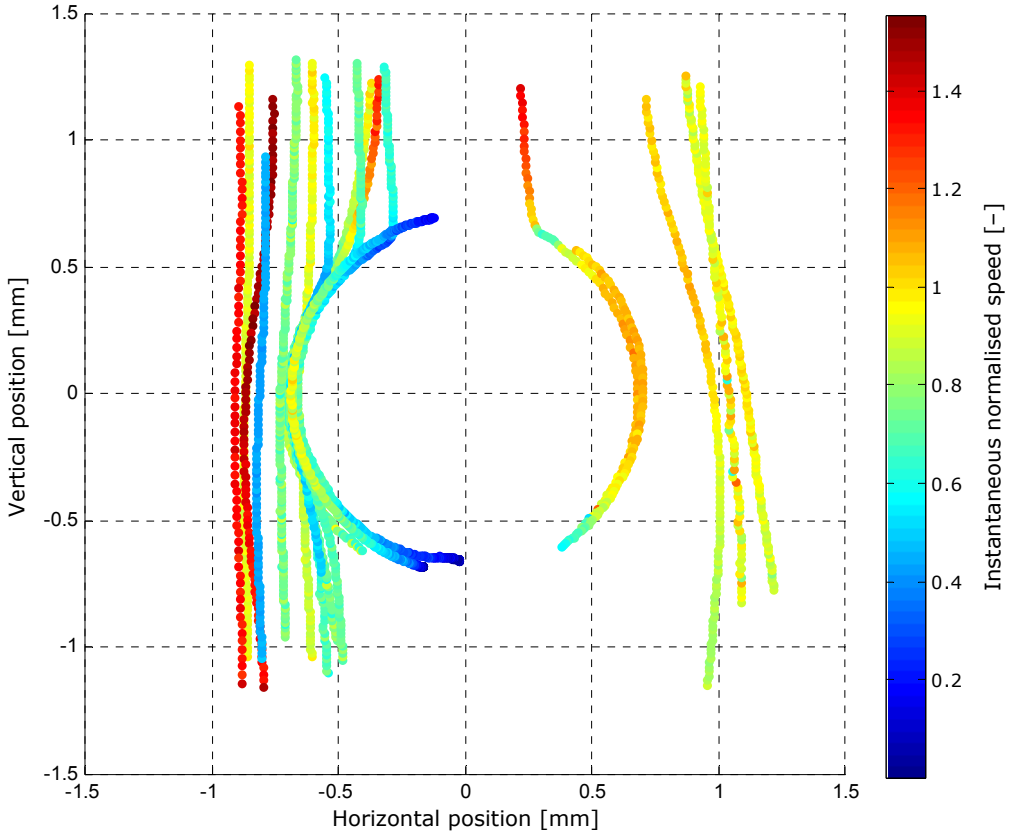

Figure 5: Particle trajectories around a bubble, coloured by their instantaneous speed normalised by the respective Stokes velocity (dimensionless ratio).

'Jump in' events

Six of the fifteen observed attachments manifested events in which the particle 'jumped in' slightly toward the centre of the bubble after a short period of sliding. A good example of this behaviour is shown by the particle in **Figure 6**, whose trajectory is marked with an asterisk in **Figure 3**. Thus the initial sliding occurs as if lubricated by a thin liquid film, before rupture, formation of a 'three-phase contact line' (TPCL), and rapid growth of the contact line to a stable position.

Such a 'jump-in' has previously been reported by Nguyen & Evans [2004], where the magnitude of the jump-in was approximately 15 µm and occurred after 50 ms. The sequence shown in **Figure 6** corresponds to a jump-in distance of just 5 µm and occurred after sliding for approximately 62 ms. The duration of the jump-in event was approximately 2 ms.

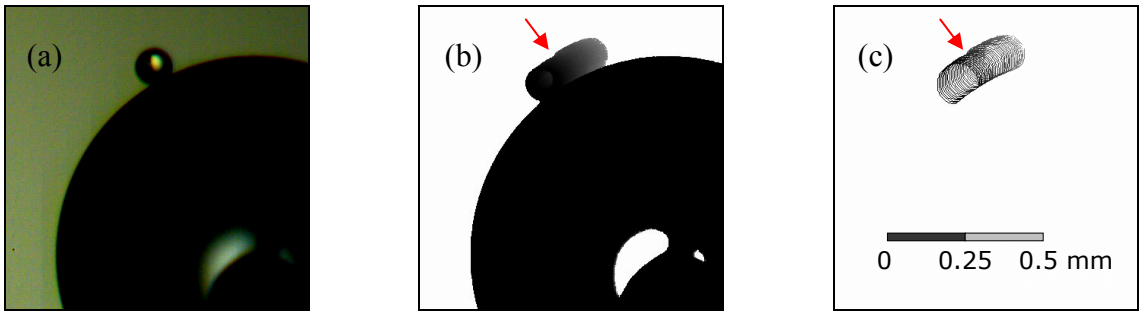

Figure 6: Sequence of images illustrating an observed 'jump in' event upon attachment. (a) Particle at the surface of the bubble during the attachment event. (b) Superimposed silhouettes spanning 35 ms, showing the transition from sliding on the surface to motion after attachment. Silhouettes from earlier times are shown in a lighter shade. (c) Outlines of the exposed portion of the particle over the same period. The particle was approximately 130 µm in diameter, while the bubble had a diameter of approximately 1.3 mm.

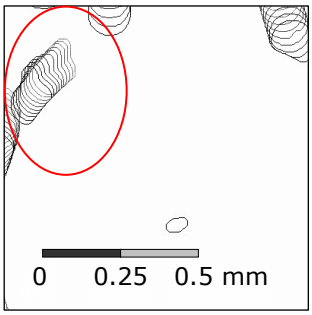

Figure 7: Superimposed outlines spanning 10 ms showing a 'jump in' event upon attachment of a particle with satellite protuberance, with sudden change in orientation.

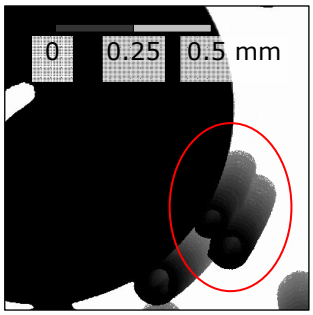

Figure 8: Superimposed silhouettes spanning 15 ms showing a 'jump in' event upon attachment of a particle doublet on the underside of the bubble.

Figure 7 shows a particle that was formed with a protrusion in the manufacturing process. After first sliding with no change in orientation it experiences a sudden anticlockwise rotation. This could be caused by preferential expansion of the TPCL at the leading edge (due to hydrodynamics or surface non-uniformity), or possibly the initial film rupture and TPCL formation occurred towards the front of the sliding particle.

Figure 8 represents an especially interesting observation, as it depicts a jump-in event occurring on the underside of the bubble. Considering streamline flow, most

researchers presume that attachment can only occur for angles within 90° of the zenith, *i.e*. between the top of the bubble and its horizontal 'equator' [*e.g*. Wang*, et al.*, 2003; Yoon & Luttrell, 1989], or even restricted to a narrower range of angles, due to fore-and-aft asymmetry of the flow [Nguyen & Schulze, 2004: 139ff., 271ff.]. A mechanism that would allow a particle (even a doublet) to attach beneath the 'equator' requires further consideration.

The duration of the sliding period before 'jump-in' ranged from approximately 6 ms to 70 ms in the present system. These are of the same order of magnitude as induction times reported in comparable studies [Laskowski*, et al.*, 1992; Nguyen & Evans, 2004]. It is not clear how this variation can be explained by the 'latitudinal' angle of first contact, and our investigations are ongoing.

The final important feature of the 'jump in' events is that they were not observed in all cases of attachment. The presumed meaning of this fact is that in some cases the 'jump in' distance was too small to be seen at the magnification employed. (The nominal resolution limit of the present set-up is approximately 3 μm. However, the sensitivity is improved by using MATLAB to compute the centroid of the particle in fractional pixel units based upon the silhouette area, providing a precision down to 1 μm.) If the particles were identical then the stable position of the TPCL would be expected to be the same. Therefore the above observations could be due to either kinetic effects (and the divergence between approaching and receding contact angles), or non-uniformity among the particles, or surface heterogeneities.

Conclusions

We are confident that the present experimental approach has several advantages over alternative techniques, because the particle is able to move freely, and behaviour is able to be directly observed. These observations provide insights that will lead to improved accuracy of model predictions. The particle trajectories and velocities observed so far do not indicate a significant slow-down upon attachment, which we tentatively attribute to a highly mobile bubble surface in the present system. A number of attached particles exhibited a 'jump-in' during the sliding period, which is interpreted as the attachment event. However, other particles that did attach did not exhibit a noticeable 'jump in'. The induction times determined based on the 'jump-in' events ranged from 6 ms to 70 ms.

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BRIEF BIOGRAPHY OF PRESENTER

Dr. David Verrelli completed a Bachelor of Arts and a Bachelor of Engineering (Chemical) at Monash University. Subsequently he worked in research and consulting in the fields of medical filtration, water supply & treatment, and hydrological modelling. Dr. Verrelli returned to study for a PhD at the University of Melbourne, on the production and dewaterability of drinking water treatment sludges. This was completed in 2009. Since late 2009 Dr. Verrelli has been employed by CSIRO, collaborating on experimental research into flotation modelling.