

## **The use of acoustoelectrochemistry to investigate bubble phenomena – Rectified diffusion**

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### **Abstract**

This paper describes the approach to bubble related phenomena using a novel 'acoustoelectrochemical' technique designed to investigate the physical and chemical effects of the acoustically induced motion of the bubble wall. In particular it describes the behaviour of a suspended gas bubble irradiated with sound of an appropriate frequency and pressure to induce oscillation.

The first electrochemical measurement of the growth of a bubble through rectified diffusion is demonstrated. The technique employed relies on the sensitivity of a scanning electrochemical microscope (SECM) deployed close to the gas/liquid interface of a bubble. The growth rate of the bubble (radius growth rate  $< 0.1 \mu\text{m s}^{-1}$ ) is reported, and compared to literature studies of the same phenomena.

### **Introduction**

The application of sound to liquids can have a wide variety of different effects. Many of these are associated with bubble activity within the media under investigation. As an example, power ultrasound can be employed to generate cavitation in liquids. In turn cavitation can have a range of physical and chemical consequences, ranging from the erosion of a solid surface<sup>1-3</sup> to the generation of highly reactive radicals<sup>4, 5</sup>. Subsequently these mechanisms can be usefully employed, for example, in the activation of catalysts or the destruction of organic waste materials<sup>6, 7</sup> respectively. However, the pressure amplitude required to generate such transient or inertial cavitation is normally in excess of  $10^5$  Pa under standard conditions in water.<sup>8</sup> This can be compared to the excitation of non inertial bubble oscillation, which may have some useful applications, that requires only small pressure amplitudes (10 – 100 Pa) to be applied with measurable electrochemical effects.<sup>9, 10</sup> Since the acoustic intensity in a linear plane wave is proportional to the square of the pressure, this represents a  $10^6$  to  $10^8$  reduction in the energy requirements of the system.<sup>8</sup>

It has been shown recently that it is possible to monitor the motion of the gas/liquid interface of a tethered bubble using a novel electrochemistry approach.<sup>9-11</sup> In this technique a microelectrode<sup>12</sup> (25  $\mu\text{m}$  diameter platinum) was positioned, using a micrometer and stage, close ( $\sim 5 - 10 \mu\text{m}$ ) to the gas/liquid interface of a large gas bubble (bubble equilibrium radius,  $R_0 \sim 2 \text{ mm}$ ). The position of the microelectrode with respect to the gas/liquid interface was determined by employing standard scanning electrochemical microscopy theory to analyse the negative feedback<sup>13, 14</sup> approach curves measured as the microelectrode approached the insulating bubble wall (employing  $\text{Fe}(\text{CN})_6^{3-}$  as a redox

agent). The motion of the gas liquid interface could then be followed as additional current resulting from the ensuing enhanced mass transfer due to forced convection.<sup>10</sup> This forced convection was produced by bubble oscillation as the result of acoustic irradiation of the liquid at the appropriate frequency and pressure ranges required to excite at the bubble wall either Faraday wave motion (a surface wave at  $f_p/2$  where  $f_p$  represents the drive frequency) or the excitation of bubble pulsation<sup>9</sup> at  $f_p$ . These studies have shown that this electrochemical technique is able to monitor the motion of the gas/liquid interface with high sensitivity. Motion below the  $\mu\text{m}$  scale could easily be detected by the microelectrode as enhancements in mass transfer.

The acoustoelectrochemical<sup>15</sup> approach to the study of bubble dynamics is clearly powerful. However, other bubble phenomena have yet to be investigated. One such process is termed rectified diffusion. Rectified diffusion is the growth or dissolution of a gas bubble driven into oscillation by an appropriate acoustic field. This process has been studied by a number of authors.<sup>8, 16, 17</sup> Experimental observations have shown that the bubbles grow at different rates depending on their size and exposure to sound.<sup>17</sup> Church produced a theory to describe the growth of gas bubbles due to mass transfer of material to the bubble wall and consideration of the dynamics of bubble oscillation.<sup>16</sup> These studies indicated that bubble growth could be accelerated by microstreaming (the circulation of the fluid close to the bubble wall) as the result of oscillation of the gas/liquid interface.

Clearly the sensitivities of the acoustoelectrochemical techniques reported earlier<sup>9</sup>, and the interest in the growth of gas bubbles through the process of rectified diffusion, lead one to the interesting question as to whether the same technique can be applied to measure rectified diffusion to high precision and accuracy. This is the subject of this manuscript.

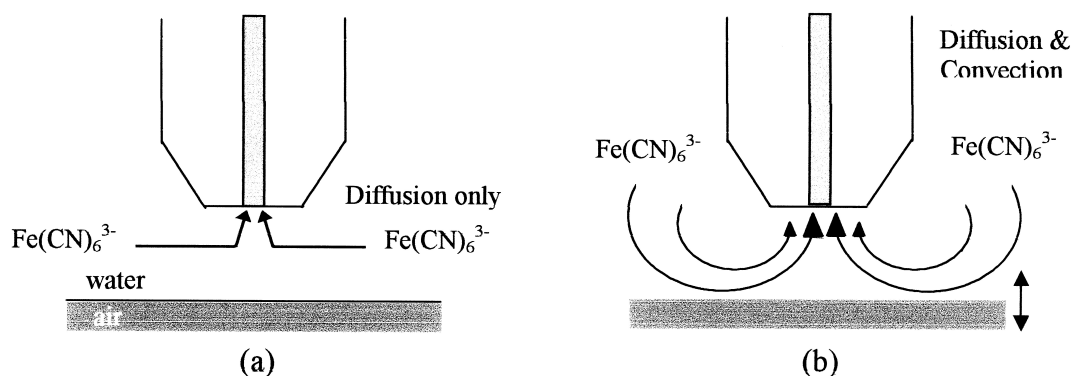


## Experimental

The experimental set-up has been reported previously.<sup>11</sup>  $K_3[Fe(CN)_6]$  (99.5% A.C.S. Reagent, Sigma), and  $Sr(NO_3)_2$  (99% A.C.S. Reagent, Aldrich) were used as received.

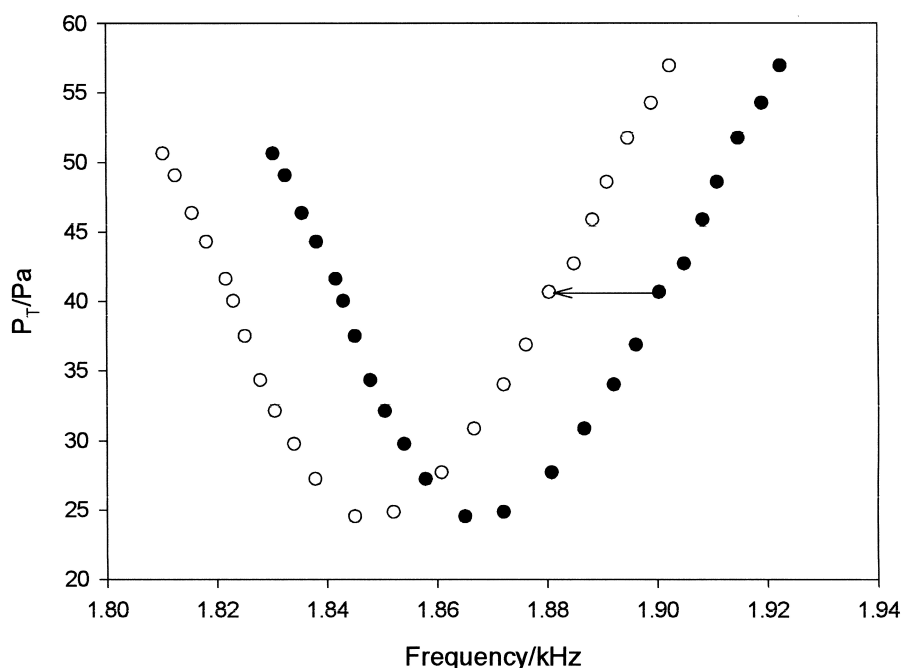
## Results and Discussion

In order to measure the growth of a large gas bubble ( $R_o \sim 2$  mm) a 25  $\mu m$  diameter Pt microelectrode (in 'torpedoed' configuration<sup>11</sup>) is positioned close to the gas/liquid interface of a tethered gas bubble. In this configuration the gas/liquid interface acts as an inert substrate and the current in stagnant solution (e.g. when the bubble is not irradiated with sound) is less than that expected for the same microelectrode positioned in the bulk solution. Hence this corresponds to a classic negative feedback situation in SECM<sup>13</sup> terminology. Figure 1a illustrates the physical model of the microelectrode and gas/liquid interface of the bubble under the conditions stated. However if the bubble is irradiated with sound of an appropriate frequency and pressure, then the oscillation of the bubble wall leads to enhanced mass transfer as the result of forced convection of the solution. This is termed microstreaming.<sup>8</sup> Figure 1b illustrates this situation.



**Figure 1a.** Illustration of the approach of a microelectrode to a gas/liquid interface of a gas bubble. As no  $Fe(CN)_6^{3-}$  can enter the gas phase of the bubble hindered diffusion predominates in the stagnant case. **1b.** Illustration of an oscillating boundary inducing fluid flow and enhanced mass transfer to the microelectrode.

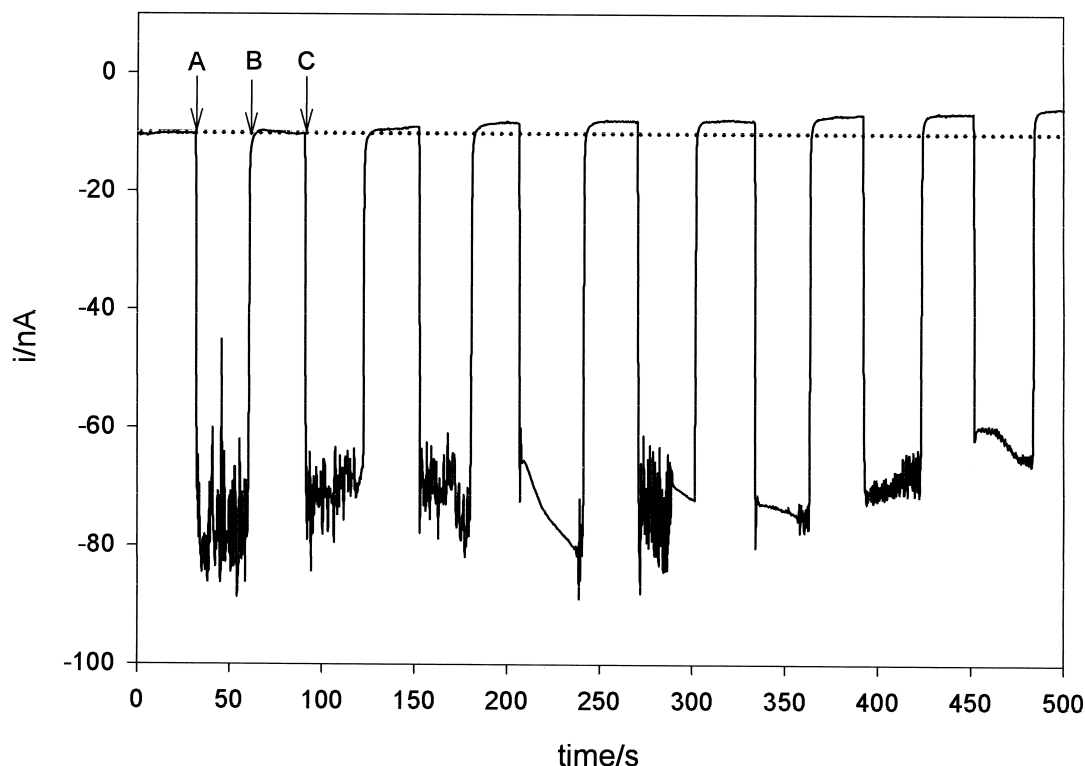
It must also be remembered that the exchange of gas across the gas/liquid interface is extremely important for a number of industrial and global processes.<sup>8</sup> In bubbles this gas exchange effectively changes the size of the gas bubble and leads to growth or dissolution depending on the size of the bubble. The effects of rectified diffusion on the size of a large gas bubble can be investigated using the acoustoelectrochemical experiments described here and elsewhere.<sup>18</sup> It is possible using the acoustoelectrochemical approach to measure the threshold pressure for the onset of Faraday waves as a function of frequency around the resonant frequency of the gas bubble. While these experiments were being performed it was noted that the resonant frequency of the gas bubble fell over a period of time. Figure 2 shows the pressure threshold for the onset of Faraday wave motion of a bubble wall (●) as a function of frequency. However, after prolonged exposure to sound irradiation producing Faraday wave motion, the threshold was noted to fall by 20 Hz (shown as a predicted threshold data set (○)). This corresponds to an increase in the bubble radius of  $\sim 18$   $\mu m$  over the duration of the experiment. Although this is a relatively small change relative to the initial size of the gas bubble (1%, given that  $R_o \sim 1.707$  mm) it is clearly detectable with the acoustoelectrochemical technique employed.



**Figure 2.** Plot showing the threshold pressure ( $P_T$ ) for the onset of Faraday wave motion of the bubble wall as a function of frequency (●). This threshold pressure was determined by the acoustoelectrochemical technique described previously. (○) represents the shifted pressure threshold caused by bubble growth calculated from measurements of the frequency shift of a point on the pressure threshold curve.

Considering the physical conditions of the experiment, it seems likely that the growth of the bubble is due to rectified diffusion of dissolved gas in the liquid phase transferring into the gas phase of the bubble. In order to measure the rate of growth of the bubble by rectified diffusion, an experiment was performed to measure the rate of growth of the bubble as a function of exposure to sound irradiation. Initially a bubble was trapped on a solid support and the threshold pressure curve for Faraday wave motion determined as described previously. The microelectrode was then moved away from the interface to allow room for bubble expansion. However, negative feedback conditions were still employed allowing the initial distance between the microelectrode tip and the bubble wall to be estimated at  $\sim 20 \mu\text{m}$ .<sup>14</sup> A sound frequency and pressure were selected so as to ensure Faraday wave motion of the interface over a prolonged period of time. The bubble was then exposed to alternate 30 s periods of sound irradiation followed by silent conditions. This procedure ensured that the exposure of the bubble to sound was controlled and an accurate measurement of the growth of the bubble (as determined by a reduction in the microelectrode tip to bubble distance) could be ascertained. This measurement was made possible by determining the current passed at the microelectrode under silent conditions, and comparing it to the predicted negative feedback curve from SECM theory under the appropriate physical conditions of the system.<sup>14</sup> Figure 3 shows the current recorded as a function of time as the experiment was performed. The region denoted between 'A' and 'B' indicates a sound irradiation period while the region between 'B' and 'C' a silent period. Several points should be denoted from the figure. First, the current passed at the microelectrode in the presence of sound is enhanced by microstreaming caused by the motion of the bubble wall (see figure 3 region between 'A' and 'B'). Second, as the experiment continues the mass transfer enhancement in the presence of sound can be noted to tend to decrease with increased exposure time of the

bubble (presumably due to the small microelectrode to bubble distance inhibiting fluid motion). Third, in the silent periods (see figure 3 region 'B' to 'C') between the sound irradiation of the bubble the current passed at the microelectrode was observed to decrease as the exposure time of the bubble to sound was progressively increased. These observations are consistent with the bubble to microelectrode distance diminishing as the bubble was exposed to sound. This decrease in distance is attributed to growth of the bubble through rectified diffusion. It is also possible from these experiments to estimate



**Figure 3.** Plot of current versus time detected by a 25  $\mu\text{m}$  Pt microelectrode positioned at approximately 20  $\mu\text{m}$  from the bubble wall where a sound field of 2.08 kHz at 51.74 Pa (measured in the bubble location in the absence of the bubble) was alternated between off and on in 30 s intervals. The solution used was an aerobic solution of 5 mmol  $\text{dm}^{-3}$   $\text{Fe}(\text{CN})_6^{3-}$  in 0.2 mol  $\text{dm}^{-3}$   $\text{Sr}(\text{NO}_3)_2$ . The solution temperature was 18–22  $^{\circ}\text{C}$ . 'A' indicates sound irradiation, 'B' termination of sound irradiation and 'C' initiation of sound irradiation for second period. The dotted horizontal line indicates the expected current under silent conditions if the bubble were not to change in size during the experiment.

the rate of bubble growth under the conditions stated. In order to do this the currents in the silent periods were compared to the standard SECM theory for a negative feedback system and the absolute bubble to microelectrode tip distance calculated as a function of exposure time. The rate of growth of the bubble radius was determined to be 0.0371  $\mu\text{m s}^{-1}$  under the conditions stated. This can be compared to other experiments<sup>17</sup> where growth rates of  $\sim 0.5 \mu\text{m s}^{-1}$  were measured. However, this was for bubbles in a 26.6 kHz sound field of 0.3 bar. Considering these conditions it is unsurprising that the growth rate reported here is less than that determined by Eller. Clearly the acoustoelectrochemical technique is sensitive enough to measure such slow growth rates (although for the acoustoelectrochemical technique to work, microstreaming (and any associated augmentation of bubble growth rates) must be present).

## Conclusions

The acoustoelectrochemical technique has been shown to be able to measure the rate of bubble growth due to rectified diffusion of gas from the liquid to gas phase. The bubble radius growth rate determined using this technique was  $0.0371 \mu\text{m s}^{-1}$  under the conditions stated. This is considerably smaller than previously determined but at lower frequency and acoustic pressure amplitude.

## Acknowledgements

The authors thank the EPSRC (Grant GR/M24615/01) for support. TGL would like to thank the Royal Society Leverhulme trust for a Senior Research Fellowship

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