ABSTRACT

Following the evolution of an acoustic bubble near a surface is particularly difficult since its movement involves several time and space scales. Indeed, the bubble size may vary between a few micrometers and several hundreds of micrometers, but the surface/bubble distance is only in the nanometer range. On the other hand, the whole bubble life lasts a few acoustic cycles (therefore several hundreds of microseconds at 20 kHz) but the collapse occurs in the nanoseconds domain.

We will show that these difficulties can be overcome by performing ultrafast electrochemistry. Indeed, the current recorded at either a single or at an array of electrodes is directly proportional to the flux of electroactive material towards the electrode surfaces. The bubble oscillations strongly perturb this flux, which allows indirectly visualizing the evolution. Concomitantly, by using electrodes of micrometric diameters, single bubbles may be observed. The quantitative interpretation of the cavitation spikes gives the surface bubble/distance, and also confirms that the implosion velocity is very high (more than 100 ms$^{-1}$). Our model is therefore a first step towards a deeper rationalisation of the effects of ultrasound irradiation onto surfaces (cleaning, erosion, ...).

I) INTRODUCTION

There has been an increasing interest in cavitation studies over the last decades. On the one hand, bubble implosion in solution causes extremely high temperatures leading to sonoluminescence and sonochemistry effects. On the other hand, surface cavitation may have either positive effects such as cleaning properties and increased mass transport, or destructive ones such as those that cause erosion of pipes or damage to propellers. However, experimental data concerning the full characterisation of the bubble behaviour close to a surface are rare. The first photographic detection was carried out by Benjamin and Ellis, and then by Crum for an acoustic bubble driven at 60 Hz.$^\text{[1]}$ Lauterborn also studied the collapse of laser induced bubbles and the resulting erosion that occurs. These experimental approaches revealed the presence of a microjet and have been successfully simulated first by Plesset and Chapman first, and later by Blake.$^\text{[2]}$ However, the standard conditions useful for ultrasound applications in biology, chemistry and physics use kHz or MHz frequencies, and so differ significantly from the above experiments.

An alternative method of monitoring bubble activity is to use indirect techniques such as electrochemistry. Indeed, when a redox probe is added to the solution, the electrolysis current detected at an electrode is solely affected by events that occur within its diffusion layer $\delta$. An event occurring at a distance $h$ from the electrode surface will then be detected only provided that $h$ is smaller than $\delta$. However, with traditional millimetric electrodes, several bubbles may cavitate at the same time near the electrode. More importantly, the strong turbulences provoked by the bubble movements induce high current densities, and therefore ohmic losses in the solution filter the electrochemical information. In the following, we show that both problems can be solved using electrodes of micrometric dimensions together with a specific potentiostat able to monitor transients with a nanosecond resolution.
II ) BUBBLE EVOLUTION NEAR A SURFACE

1 ) Temporal behavior

When a 16 µm radius electrode is poised at a constant potential corresponding to reduction of Ru(NH$_3$)$_6^{3+}$, current traces such as those presented onto figure 1b are observed. In that case, the intense current spikes clearly attest that the bubble is oscillating at 20 kHz, the driving frequency of the sonic horn. We could also detect other bubbles oscillating at harmonics or subharmonics of the driving frequency. Moreover, before and after the series of spikes, the current is relatively constant. Using small electrodes, it is therefore very easy to separate the cavitation activity which is local and transitory from the acoustic streaming contribution which stems from a macroscopic constant flux of solution. When the horn to electrode/distance decreases (corresponding to an increase in the acoustic pressure), the cavitation shifts from stable (several acoustic cycles) to transient in a similar manner to what is observed in solution (figure 1d).

Figure 1. a ) Schematic of the non harmonic oscillations of a bubble near a surface. A, B and C correspond to the stages of bubble. Current traces with a 16 µm radius platinum electrode obtained when the solution is sonicated at 20 kHz: the sonic horn/electrode distance is 7 mm in b ) and 1.5 mm in d ). c ) Magnified view of a single spike (open circles) and the simulated current (line).

2 ) Spatial behaviour

In the bulk, the calculated equilibrium bubble radius is 150 µm for a single bubble in perfectly symmetrical conditions. At a surface, it is difficult to determine the size of the object evolving above the surface with a single electrode. To evaluate this parameter, we recorded simultaneously the signal for arrays of small electrodes with various gaps between the electrodes. We could sometimes detect a cavitation activity for distances as large as 800 µm, corresponding approximately to a bubble diameter in this range. Conversely, we also isolated bubbles having a diameter of less than 30 µm. These experiments reveal that there is a very wide distribution of bubble sizes onto the surface.

The last parameter to evaluate is the electrode/bubble distance. At a constant potential, the diffusion layer δ reflects either the acoustic streaming flow or the bubble movement, and cannot be controlled by the experimentalist. To this respect, the advantage of cyclic...
voltammetry is to allow adjusting precisely $\delta$ by properly choosing the scan rate $v$ of the linear ramp of potential applied to the electrode. Indeed, in this technique, $\delta$ is given by:

$$\delta \approx \sqrt{\frac{DV}{RTF}}$$

where $D$ is the diffusion coefficient, $R$ the perfect gas constant, $T$ the temperature and $F$ the Faraday constant. $2800 \text{ Vs}^{-1}$ corresponds hence to a diffusion layer of approximately 150 nm. Furthermore, this scan rate also allows to register more than 10 acoustic cycles. Figure 2 represents the voltammograms obtained simultaneously for an array of two 29 $\mu$m diameter electrodes separated by 206 $\mu$m. Cavitation appears here simultaneously revealing a bubble much larger than the electrodes. In these voltammograms, an important depletion in the voltammetric peaks is observed before the cavitation spikes. This important information attests that the bubble expansion may prevent the growth of the diffusion layer simultaneously for two electrodes separated by a relatively large distance. The bubble must then be in the near proximity of the surface over a 206 $\mu$m distance, which to our opinion reveal that the bubble is flat and not spherical nor toroidal.

![Figure 2](image_url)

**Figure 2.** Cyclic voltammograms recorded simultaneously for two electrodes separated by 206 $\mu$m. The voltammetric wave corresponds to reduction of Fe(CN)$_6^{3-}$. Circles: voltammograms under silent conditions. Solid lines: voltammogram under sonication at 20 kHz.

All these observations lead us to the conclusion that the cavitation spikes are not due to a microjet as was anticipated previously. In that case, the current should intuitively drop with the distance from the microjet, so that observing comparable behaviour at large distances would be impossible. In our view, the cavitation spikes simply reflect the possibility or not for the mediator to diffuse towards the electrode when the bubble discovers its surface. The quantitative description based onto these qualitative observations is given in the following.

### III ) ANALYSIS OF THE BUBBLE MOVEMENTS

We present below a quantitative model that allows extracting the electrode/bubble distance $x_0$ from the current trace presented in figure 1b. Only two physical states are considered for the bubble. In the first one, the bubble is expanded and diffusion of the redox mediator towards the electrode is hindered. In the second one (which lasts a time $t_0$), the bubble is contracted and diffusion towards the electrode is possible within the $x_0$ width thin layer of solution. The switch between these two states is supposed to be instantaneous, so that this model is valid only for very fast collapses. This very simplified picture therefore describes with only onto two parameters a very complex phenomenon. Each of the spikes of figure 1b was analysed, and more than half of the peaks gave a very good fitting with this simplified theory. $x_0$ was evaluated to be between 50 and 100 nm. It is possible that the misfit obtained for a few cavitation peaks using this simplified theory stems from a different electrode/bubble distance before and after the collapse. Times $t_0$ extracted from the peak simulations confirm that most of the time the bubble is expanded, and are compatible with implosion velocities above 100 $\text{ms}^{-1}$. Furthermore, there is a small but non negligible steady-state current between the cavitation spikes. In these relatively long time scales, this current is compatible with a slow drift of the bubble towards the solution before the implosion, at a velocity in the $10^{-4}$ $\text{m.s}^{-1}$ range (this drift is independent from the violent collapse so that both analysis can be decoupled).

### IV ) THEORETICAL AND PRACTICAL DEDUCTIONS

Implosion occurs when all the pressure contributions outside the bubble become larger than the interior ones, namely:
\[ P_A + P_H + \frac{2\sigma_S}{R_B} > P_V + P_G + \sigma_V \quad (2) \]

where \( P_A \) is the acoustic pressure, \( P_H \) the hydrostatic pressure, \( \sigma_S \) the surface tension, \( R_B \) the bubble radius, \( P_V \) the vapour pressure and \( P_G \) the gas pressure inside the bubble. \( \sigma_V \) is a surface friction term involving the shear stress imposed onto the surface by the liquid movement. This term is then peculiar to surfacic cavitation.

In our conditions, four terms can be neglected so that inequality (2) reduces to:

\[ P_A > \sigma_V \quad (3) \]

In our view, collapse can then not occur at \( x_0 = 0 \) since this would involve a non-zero velocity of the fluid onto the surface, which is physically impossible. A slow bubble drift then occurs until inequality (3) can be satisfied. Then, conditions are met for a very fast collapse.\(^5\) For smaller horn to electrode distances, the local acoustic pressure is much higher, so that \( x_0 \) and \( t_0 \) are smaller, in agreement with our analysis.

By reaction, the shear stress also acts onto the surface, and is responsible for depassivation or erosion. Our model is then a first step towards a deeper interpretation of the ultrasound effects onto surfaces.

References.