Immobilization of a bubble in water by nanoelectrolysis

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A surprising phenomenon is presented: a bubble, produced from water electrolysis, is immobilized in the liquid (as if the Archimedes’ buoyant force were annihilated). This is achieved using a nanoelectrode (1 nm to 1 \( \mu \)m of curvature radius at the apex) and an alternating electric potential with adapted values of amplitude and frequency. A simple model based on “nanoelectrolysis” (i.e., nanolocalization of the production of \( \text{H}_2 \) and \( \text{O}_2 \) molecules at the apex of the nanoelectrode) and an “open bubble” (i.e., exchanging \( \text{H}_2 \) and \( \text{O}_2 \) molecules with the solution) explains most of the observations.

Microbubbles have many applications: medicine (contrast agents,\(^1\) gas embolotherapy,\(^2\) blood clot lysis\(^3\)) or nuclear industry.\(^4\) Questions about their stability remain topical.\(^5\) \( \text{H}_2/\text{O}_2 \) microbubbles are easily generated by water electrolysis and their production is controlled by the electric potential. Recently, \( \text{H}_2 \) microbubbles have been used to rotate a microobject.\(^6\) Droplets may also be controlled by electrolysis.\(^7\) Many applications will result from a more effective control on the microbubbles and, especially, on each individual microbubble. Our preceding paper\(^8\) showed a first example of such control: the nanolocalization of the production of microbubbles at a unique point of a tip-shaped electrode, under precise values of the amplitude and the frequency of the alternating potential. This phenomenon will be called nanoelectrolysis (for bubble production). The relation between microbubble production and current intensity will be given in a forthcoming paper. The present paper describes a surprising phenomenon, which represents an example of control of a single microbubble: the immobilization of a bubble in the liquid (as if the Archimedes’ buoyant force were annihilated).

The experimental procedure is described in Ref. 8. Water electrolysis is performed using an aqueous solution containing \( 10^{-4} \) mol/L of \( \text{H}_2\text{SO}_4 \) and a periodic alternating applied potential, here of rectangular shape:\(^9\)

\[
V(t) = V_m \text{ for } 0 < t < T/2, \quad V(t) = -V_m \text{ for } T/2 < t < T \quad (T \text{ is the period and } \nu = 1/T \text{ the frequency}).
\]

The amplitudes \( V_m \) typically range from 2 V to 30 V. Two Pt electrodes are used and one of the two electrodes—called nanoelectrode—is tip-shaped, with a curvature radius, at the apex of the electrode, ranging from 1 nm to 1 \( \mu \)m. In the previous paper,\(^8\) we showed that, for definite values of the amplitude and the frequency of the potential, the microbubbles are produced at a single point, the apex of the nanoelectrode. We start in such conditions, so that microbubbles are successively generated at the apex of the electrode and then naturally go up towards the air–solution surface, owing to the Archimedes’ buoyant force. Let us now describe the observed phenomenon. Immediately after the production of a microbubble, if we rapidly increase the frequency (generally, up to at least 500 or 1000 Hz; and then, maintaining constant the frequency; \( V_m \) remaining always constant), then the microbubble remains immobile in the solution,\(^10\) at some distance from the electrode and nearly at the vertical of the apex of the electrode (Fig. 1). In addition, this configuration is stable, since the bubble remains at the vertical of the apex of the electrode and at the same distance from the electrode, when this electrode is moved in any direction with respect to the solution (see the video\(^11\)). This immobilization is observed during various minutes or hours (at constant amplitude \( V_m \) and frequency). The diameters \( D' \) of the immobilized bubbles typically range from some \( \mu \)m to 400 \( \mu \)m. This diameter may remain constant, in some cases, but very frequently decreases with time, as shown in Fig. 2, till the (optical) disappearance of the microbubble. As the diameter \( D' \) decreases with time (Fig. 3), we observe that the distance \( r_C \) between

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the center of the bubble and the apex of the electrode also decreases (Fig. 4). The evolution of the diameter decreasing rate \( \frac{dD'}{dt} \) as a function of the diameter is shown in Fig. 5, for three different experiments.

In order to understand such a strange phenomenon, we first note that the bubble cannot be considered as a closed system (i.e., with no exchange of matter with the solution) and its immobilization as a balance between the Archimedes’ buoyant force and a new force. Indeed, such a (downward) force should increase with the distance between the bubble and the apex of the electrode (in order to explain the stability of this equilibrium, shown in the video\(^{11} \)), which seems unrealistic. Our explanation is then based on a bubble considered as an open system, exchanging matter with the solution through its (immobile) surface. In this case, the new forces which might counterbalance the Archimedes’ one are the flux of momentum entering the bubble and the hydrodynamic forces. However, these forces are intimately associated with the fields of the pressures, velocities, and densities and the determination of these fields is a very complex coupled problem (involving hydrodynamics, diffusion, and mass fluxes kinetics at the bubble–solution interface). This problem is not treated here and will be investigated in the future by using computer simulations. As an approximation, hydrodynamics equations (concerning the pressures and the velocities) may be separated and, in the following, we show that a simplified model based on the mass balance, diffusion, and interface fluxes equations may explain—at least qualitatively—most of the above observations.

In our previous paper,\(^8 \) we showed that the bubble production is nanolocalized (at the apex of the nanoelectrode) when the potential \( \nu \) (applied to the dielectric layer, at the electrode–electrolyte interface) reaches a threshold value \( \nu_0 \). Similarly, we expect that the chemical reactions of electrolysis will be also nanolocalized for a (lower) threshold value \( \nu_0 \). According to our model,\(^8 \) this implies that, in the potential amplitude–frequency plane, the domain for the nanolocalization of the electrolysis reactions is shifted toward higher frequencies, with respect to that for the nanolocalization of bubble production. Thus, after the increase in frequency needed for the immobilization of the bubble, the new present amplitude–frequency values correspond to conditions of no bubble production,\(^8 \) but we here assume that they correspond to nanolocalization conditions for the electrolysis reactions: i.e., these reactions still occur and are nanolocalized at the apex of the electrode, although the rate of production of \( \text{H}_2 \) and \( \text{O}_2 \) molecules is not enough to generate bubbles. These molecules, produced at the apex of the electrode, thus remain and diffuse in the solution, without generating any bubble. In our model, the immobilized bubble is considered as an open system, which may exchange \( \text{H}_2 \) and \( \text{O}_2 \) molecules with the solution through its surface. The whole system (solution and bubble) is considered in a steady state.

The bubble contains \( \text{H}_2 \) and \( \text{O}_2 \) molecules, and the general model for a bubble containing these two components is given in the supplementary material.\(^11 \) This model shows that, in the steady state (and for not too small diameters), the bubble contains nearly the same number of moles of \( \text{H}_2 \) and \( \text{O}_2 \) (although the production of \( \text{O}_2 \) molecules is lower than that of \( \text{H}_2 \), and the solubility of \( \text{O}_2 \) is higher than that of \( \text{H}_2 \); this is due to the low diffusion coefficient of \( \text{O}_2 \)).\(^11 \) In the following, for
the sake of simplicity, we present the model for a bubble containing only one component, e.g., $H_2$. Let us use the subscript $i = 1$ to denote the $H_2$ component in the solution and the subscripts $i = 2, 3, \ldots$ for the other components of the solution (such as $O_2$, $H_2O$, $H^+$, ...). The diffusion flux of $H_2$ is given by Fick’s law:

$$j_1 = \rho_1 (\nu_1 - v) = -D_1 \text{grad} \rho_1 \tag{1}$$

($\rho_1$ and $\nu_1$ are, respectively, the volume mass density and the velocity of the component $i$; $v$ is the barycentric or convection velocity defined by $\rho \nu = \rho_1 \nu_1 + \rho_2 \nu_2 + \ldots$, $\rho$ being the mass density of the solution; $D_1$ is the diffusion coefficient = $4.6 \times 10^{-9}$ m$^2$/s for $H_2$ in water at 20°C). In the solution, the $H_2$ mass balance equation leads to

$$\frac{\partial \rho_1}{\partial t} + \text{div}(\rho_1 \nu_1) = m_1 \delta \tag{2}$$

($m_1$ is the mass production per unit time at the apex of the electrode, which is considered as the origin point; $\delta$ is the Dirac measure—in space—at this origin point; $m_1$, averaged on a period, is considered constant in this simple model) leads to

$$-D_1 \Delta \rho_1 + v \cdot \text{grad} \rho_1 = m_1 \delta \tag{3}$$

(with the help of Eq. (1), $\frac{\partial \rho_1}{\partial t} = 0$—steady state—and $\text{div} \nu = 0$—incompressibility).

At each point of the surface $S$ of the bubble, the flux of $H_2$ entering the bubble is

$$j_S = \rho_1 (\nu_1 - v_S) \cdot n = \rho (v - v_S) \cdot n \tag{4}$$

(assuming only exchanges of $H_2$ between the bubble and the solution; $n$ is the unit vector normal to $S$, oriented towards the interior of the bubble; $v_S$ is the normal velocity of the surface, parallel to $n$; obviously, $v_S = 0$ for an immobile bubble), which gives, according to Eq. (1)

$$-D_1 \partial_n \rho_1 = (1 - \frac{\rho_1}{\rho}) j_S \approx j_S. \tag{5}$$

We assume that the exchange of $H_2$ between the solution and the bubble is controlled by the simple kinetic law

$$j_S = K (\rho_1 - H p'), \tag{6}$$

where $p' = p_a + \frac{2\gamma}{R'}$ is the pressure in the bubble ($p_a$ the atmospheric pressure, $\gamma$ the surface tension, $R' = D'/2$ the bubble radius), $H$ the Henry’s constant, and $K$ the mass transfer coefficient ($\gamma = 7.28 \times 10^{-2}$ N/m, the water–air value at 20°C; $H = 1.62 \times 10^{-3}$ kg/(m$^3$ atm) for $H_2$ in water at 20°C (Ref. 12)).

As a simple model, we use the $\rho_1$ field produced only by diffusion (i.e., satisfying to Eq. (3) with $v = 0$), without taking into account the presence of the bubble (i.e., the condition Eq. (5))

$$\rho_1 = \frac{m_1}{4\pi D_1} \frac{1}{r} \tag{7}$$

where $r$ is the distance to the origin point $O$ (which is the apex of the electrode). If $r_0$ denotes the distance at which $\rho_1(r_0) = H p_a$ (corresponding to the equilibrium of $H_2$ between the solution and $H_2$ gas at the atmospheric pressure), Eq. (6) takes the form

$$j_S = KH p_a (r_0 - (1 + \frac{2\gamma}{R'}) \tag{8}$$

where $\gamma = \frac{2\gamma}{p_a}$. A simple calculation then gives the variation of the mass $m'$ of the bubble

$$\frac{dm'}{dt} = \int_S j_S \, da = j_S(r_C) a_S, \tag{9}$$

where $da$ is the area measure, $a_S = 4\pi R'^2$ the area of $S$, and $j_S(r_C)$ the value of $j_S$ (from Eq. (8)) at $r = r_C$ (and for the radius $R'$; $C$ is the center of the bubble, $r_C$ the distance OC). Eq. (9) expresses that the mass or the diameter of a bubble (the center of which is) situated at $r_C = r_0/(1 + \frac{2\gamma}{R'})$ remains constant, whereas that of a bubble situated at $r_C > r_0/(1 + \frac{2\gamma}{R'})$ (respectively, at $r_C < r_0/(1 + \frac{2\gamma}{R'})$) decreases (respectively, increases).

Note that, although Eq. (5) is not strictly satisfied with the approximate expression Eq. (7), it is however “qualitatively” satisfied if $r_T$ (i.e., the distance OT) is equal to $r_0/(1 + \frac{2\gamma}{R'})$, $T$ being a point of $S$ such that OT is tangent to $S$ (see Fig. 6). Indeed, at $T$, we have $\partial_n \rho_1 = n \cdot \text{grad} \rho_1 = 0$ (since $\text{grad} \rho_1$ is directed from $T$ to $O$, according to Eq. (7)) and $j_S = 0$ (since $r_T = r_0/(1 + \frac{2\gamma}{R'})$), so that Eq. (5) is satisfied at $T$, i.e., on the horizontal circle $\Gamma$ of $S$ generated by these points $T$. Let us denote $S_-$ the part of $S$ situated below the circle $\Gamma$, and $S_+$ that situated above $\Gamma$.
satisfied. Thus, $H_2$ molecules enter the bubble through $S_-$ ($j_S > 0$) and leave the bubble through $S_+$ ($j_S < 0$). Note that the main assumption is here the approximate expression Eq. (7) (which does not take into account either the velocity field or the presence of the bubble).

A first consequence of this situation is that $r_C > r_0/(1 + 2r_0/m)$ (since $r_C > r_T$) which, as noted above, indicates that the diameter of the bubble decreases with time. This is consistent with the experiments, since bubbles decreasing in diameter with time are the most frequently observed. Another consequence is the following relation between $r_C$ and $R'$

$$r_C = \sqrt{R'^2 + \left(\frac{r_0}{1 + \frac{2r_0}{m}}\right)^2}$$  \tag{10}

(according to the value of $r_T$; see Fig. 6), which is in agreement with the observations: see Fig. 7, drawn with $r_0 = 9.5$ $\mu$m, for comparison with the experimental points of Fig. 4. Note that, for comparison with Eq. (10), with $r_0 = 9.5$ $\mu$m (continuous line), for comparison with the experimental points of Fig. 4 (dots). The dashed line represents the equation $r_C = D'/2$.

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9A potential of sinusoidal shape may also be used.
10If the increase in frequency is not sufficiently rapid, the bubble will continue to go up and will not be immobilized.
11See, as supplementary material, (1) video showing the immobilization of a bubble (experiment of Fig. 1) and the stability of this configuration when the electrode is moved (recording speed 100 images/s, reading speed 10 images/s), and (2) general model for a bubble containing $H_2$ and $O_2$.
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