BUBBLES ON SURFACES

DIFFUSIVE GROWTH & ELECTROLYSIS

Álvaro Moreno Soto

Bubbles on surfaces

diffusive growth & electrolysis

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I find, that if I just sit down to think ... the solution presents itself
A veces me siento a pensar ... y la solución se presenta sola

Professor Henry Jones (*Indiana Jones and The Last Crusade*)

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BUBBLES ON SURFACES

DIFFUSIVE GROWTH & ELECTROLYSIS

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O

Introduction

A wide variety of processes, both human-made and natural, involve the generation of bubbles. Bubbles appear to be the reason for the acceleration of life generation on Earth [1]. Bubbles are present in magmatic phenomena and affect the degassing of rhyolitic flows, consequently altering their characteristics [2, 3]. Bubbles are essential for the extraction of oil from reservoirs and their subsequent recovery [4]. Bubbles influence the flavour of beverages, such as champagne [5], beer [6] and other carbonated drinks [7]. Bubbles even appear in literature as metaphors of human life, e.g. the ‘Homo bulla’ [8]. As one can see, the diversity of fields in which bubbles play an influential role is remarkable and spreads over a broad range.

The question whether the appearance of bubble is desirable or not remains however unanswered. Some new technologies, such as drug deliverance in specific locations inside the body [9, 10] are based in the use of bubbles which entrap a determined drug. In such applications, the presence of bubbles is essential. Nonetheless, the generation of bubbles during electrolysis [11, 12] and catalysis [13, 14] is in the majority of cases detrimental, since those bubbles stick to the reacting surfaces and inhibit the chemical reactions.

When the lead singer of the famous band *The BeeGees*, Barry Gibb, stated ‘*but all bubbles have a way of bursting or being deflated in the end*’, he was referring to the fame period the band was going through at the moment. He was probably not thinking of the previously mentioned chemical reactions, in which, under steady conditions, bubbles of the order of nanometers, the so-called ‘nanobubbles’, can grow and strongly attach to the reacting surfaces,

remaining stable and, consequently, not dissolving nor bursting [15]. The quote applies remarkably well, though.

Despite the many different scenarios in which bubbles are generated and the complexity their growth or dissolution may entail, all of them share the mass transfer phenomenon between the gas/vapour contained inside them and the surrounding environment. We can differentiate different types of bubble-surrounding media. Bubbles can be formed either of gas, vapour or a mix of both, whereas the surrounding media can be solid, liquid or gaseous. The case of bubbles in solid media originates in the majority of cases from solids which absorb gases in their liquid phase and then rapidly solidify, entrapping the gas within them (e.g. the case of volcanic stones [16]). In gas media, bubbles need to be insulated by a thin material film such as soap [17]. Most commonly, bubbles are present in liquid phases, where they can be either separated from the media by a thin interface or directly in contact with the liquid environment. This thesis deals particularly with the last case: gas bubbles in a liquid with a direct interface between them. Since the bubbles are directly facing the liquid, they consist of a mix of gas and vapour. Throughout this thesis, we will discuss experiments in which the pressure of the gas phase is much higher than the vapour pressure of the liquid surrounding the bubbles. Other experiments will involve bubbles nucleating and growing for an extremely short time. In all those cases, the vapour phase can be neglected and we can reasonably assume that the bubbles will only consist of gas.

0.1 The origin of the nucleation of bubbles

Bubbles are naturally present in liquids when there is gas dissolved in them. These bubbles are formed by the slow accumulation of the dissolved gas molecules until a minimum number of them cluster together and form the new entity. This can be easily appreciated when water is left in a glass for a few hours: where there were no bubbles in the beginning, now we can see the presence of hundreds of small bubbles, normally attached to the walls of the glass. This is the case since bubbles tend to nucleate where the energy barrier to generate them is lowest. Generating a bubble in an unbounded liquid domain is very energy-demanding and only happens when such available energy is relatively high, e.g. in the case of boiling liquids [18]. In the majority of cases, bubbles form in crevices, breaks, cracks on surfaces... places where it is economic, energetically speaking, to generate a bubble [19]. The surface properties of the materials involved are also very influential. Preferred nucleation sites can be designed by locally adding hydrophobic components, such as black silicon [20–22], to a surface consisting of hydrophilic materials,

such as silicon. This will be the main structure that we will use throughout this thesis to generate bubbles: circular micropits of different sizes covered by black silicon and, therefore, super-hydrophobic etched in silicon substrates. We will refer to the specific experimental geometry and its properties in each chapter.

As previously mentioned, in some other cases, bubbles appear as a result of a chemical reaction. In many chemical processes, such as electrolysis [11, 23, 24] or catalysis [13, 14], bubbles nucleate and grow at the reacting surfaces. In the majority of cases, those bubbles attach to these surfaces, hence inhibiting the chemical process. The concern of the behaviour of such bubbles is self-justified and motivates the research of the fundamentals of bubble nucleation, growth/dissolution and eventual detachment during such chemical processes.

0.2 The diffusive growth of bubbles

In 1950, Epstein and Plesset [25] set down the mathematical analysis which was to become the basic reference regarding bubble growth in diffusion-driven regimes. Physically speaking, a change in the bubble volume is generated by an influx of mass towards the bubble. Assuming a perfectly spherical bubble of radius $R(t)$, this reasoning implies that

$$\frac{dm}{dt} = 4\pi R^2 \rho_g \frac{dR}{dt}, \quad (1)$$

where dm/dt is the mass transfer towards the bubble, t the time and ρ_g the gas density. The diffusive mass flux towards the bubble is determined by the concentration gradient and therefore,

$$\frac{dm}{dt} = 4\pi R^2 D \frac{dc}{dr}, \quad (2)$$

where D is the gas diffusivity in the liquid, c indicates the concentration of dissolved gas and r is the radial coordinate in a spherical coordinate system in which the origin coincides with the centre of the bubble. The concentration is related to pressure by the well-known Henry's law [26],

$$c(T, P) = k_H(T)P, \quad (3)$$

where T is the temperature, k_H is the so-called Henry's constant (dependent on each gas-liquid couple and a decreasing function of T) and P is the pressure.

In the diffusive regime, the concentration profile at each time and position is defined by the radially symmetric diffusion equation:

$$\frac{\partial c(r, t)}{\partial t} = D \nabla^2 c(r, t) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r, t)}{\partial r} \right). \quad (4)$$

Considering a single bubble in an infinite domain, the boundary conditions for solving (4) are defined as:

$$c(r, 0) = c_0, \quad r \gg R \quad (5a)$$

$$\lim_{r \rightarrow \infty} c(r, t) = c_0, \quad t > 0 \quad (5b)$$

$$c(R, t) = c_s, \quad t > 0 \quad (5c)$$

These boundary conditions establish that, at the beginning of the bubble growth, the solution has an homogeneous concentration $c_0 = k_H P_0$ which will depend on the temperature T_0 and the pressure P_0 at which the (saturated) solution was prepared (5a); very far away from the bubble, the concentration remains unaltered at all times (5b); and finally, the concentration at the bubble boundary remains constant at a value $c_s = k_H P_s$ which depends also on temperature T_s (which usually coincides with T_0) and pressure P_s at which we perform our experiments (5c). Solving equation (4) using these boundary conditions results in:

$$\left(\frac{\partial c}{\partial r} \right)_R = (c_0 - c_s) \left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right). \quad (6)$$

Finally, combining equations (1), (2) and (6) leads to the famous Epstein-Plesset equation that defines the change of the bubble radius in time:

$$\frac{dR}{dt} = \frac{D(c_0 - c_s)}{\rho_g} \left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right). \quad (7)$$

Depending on the concentration difference between the bubble interface and the bulk liquid and neglecting the effect of surface tension, we can list three different behaviours:

- $c_s > c_0$: the solution is undersaturated, the gas flow goes from the bubble to the bulk and consequently, the bubble shrinks, i.e. its radius decreases in time.
- $c_s = c_0$: equilibrium, the bubble radius remains constant and unaltered in time.
- $c_s < c_0$: the solution is supersaturated, the gas flows towards the bubble and therefore, the bubble grows, i.e. its radius increases in time.

The three configurations are generally characterised by the saturation level, defined as

$$\zeta = \frac{c_0 - c_s}{c_s}. \quad (8)$$

Following this definition, undersaturation corresponds to $\zeta < 0$, equilibrium to $\zeta = 0$ and supersaturation to $\zeta > 0$. In this thesis, we will focus specially in the later case. Each case leads to a different solution of equation (7) and consequently, a different bubble behaviour.

0.3 Guide through this thesis

This thesis consists of nine different case scenarios which provide different fundamental knowledge regarding diffusive bubble growth in different configurations. Three different categories can be distinguished:

- In chapters 1-6, bubbles are generated in pressure-controlled supersaturated carbonated water. In this case, degassed ultra-pure water is saturated with a gas (typically CO_2) at a certain pressure P_0 . Afterwards, we proceed to decrease the pressure level to P_s , and, therefore and according to Henry's law (3), the solution becomes supersaturated and consequently, bubbles nucleate and grow.
- In chapters 7 and 8, bubbles are generated in two different ways and their respective growth compared. In one case, bubbles are generated as in the previous category. In the other, bubbles are generated by electrolysis, i.e. by a chemical reaction.
- In chapter 9, bubbles are generated by electrolysis.

Going through each chapter individually, Ch.1 focuses on the history effects during bubble growth and shrinkage (i.e. ζ is alternatively varied from positive to negative values) and contains an in-depth analysis of the variations of the concentration profile close to the bubble and its influence on the enhanced mass transfer towards the bubble during its growth after a shrinkage step. Ch.2 treats the long-term depletion effects caused by a succession of bubbles growing from a single spot as they remove the available dissolved gas in an area close to the bubble nucleation spot. Hence, subsequent bubbles grow in a domain with less available gas and consequently, their growth rate is strongly decreased. Ch.3 targets the onset of density-driven convection during diffusive bubble growth at low supersaturations. The reason behind this transition resides in the generation of a region that is gas depleted surrounding the bubble as it grows, which leads to the formation of a buoyant volume around the bubble. The different parameters affecting its appearance, such as the supersaturation level ζ and the initial saturation pressure P_0 are treated along with the long term effects of this convective onset. Ch.4 discusses the effects of confinement on the bubble growth caused by the attachment of a cylindrical wall around

the bubble nucleation site. The way in which convection sets in during the bubble growth, as well as the enhanced mixing that originates from bubble detachment in the confined space, are analysed in depth. Whereas Chs.2-4 provide a better understanding of how bubbles absorb the gas from their surrounding and how they deplete the medium in which they grow, Ch.5 on the other hand deals with the coalescence of two neighbouring bubbles that are diffusively growing from two nearby locations on a substrate. The mechanics of the coalescence and the achievement of an early bubble detachment are highlighted in this particular section. The last chapter of this category, Ch.6, explores the possibility of enhancing the mass transfer towards the bubble that results from the application of ultrasound at a certain frequency due to the so-called ‘rectified diffusion’. Here we turn towards a more applied perspective: we present a parametric scan of pressure amplitude and number of cycles applied by an ultrasound transducer and investigate in which conditions an early detachment, an enhanced growth or no particular event are achieved. Chs.5 and 6 constitute the foundation for much-needed future research which deals with the challenge of freeing surfaces from the presence of bubbles.

In the second category, Chs.7 and 8 compare the evolution of bubbles growing by electrolysis and the ones generated by pressure-controlled supersaturated conditions. Ch.7 targets the detailed fabrication of the substrates, which in this research consist of micromachined pillars on top of which a pit covered with black silicon is etched, and discusses the influence that the fabrication process has on the subsequent experiments, particularly focusing on the final detachment radii of bubbles. Ch.8 focuses on the study of the concentration boundary layer around the bubble and its evolution during a single bubble succession in a continuous electrolytic domain, comparing its evolution to the same succession generated in a pressure-controlled supersaturated solution. Three different growth regimes are distinguished in the electrolytic case, which makes the behaviour completely different to that of bubbles generated by a pressure drop.

To conclude, Ch.9 studies the nucleation rate of nanobubbles formed by electrolysis on nanoelectrodes and how they block the reacting sites. The surface block permits us measure the amount of time nanobubbles take to nucleate and grow until they start covering the electrode surface. The activation energy required to achieve bubble nucleation is also calculated and provides a means of satisfactorily approximate the bubble geometry.

The first half of this thesis, Chs.1-5, focuses on the fundamentals of bubble dynamics, and therefore, the gained knowledge cannot be directly associated with any present application. On the other hand, the second half, Chs.6-9, while also addressing the fundamentals of bubble dynamics, pays a primary

attention to real problems that scientist are dealing with nowadays and proposes several methods with the goal of improving chemical reactions. Figure 0.1 summarises the thesis layout in a blink.

Figure 0.1: Thesis outline: division in categories and corresponding chapters. The colours match the division in the fore edge of the book.

1

The history effect on bubble growth and dissolution. Experiments and simulations of a spherical bubble attached to a horizontal flat plate ^{*} [†]

The accurate description of the growth or dissolution dynamics of a soluble gas bubble in a super- or undersaturated solution requires taking into account a number of physical effects that contribute to the instantaneous mass transfer rate. One of these effects is the so-called history effect. It refers to the contribution of the local concentration boundary layer around the bubble that has developed from past mass transfer events between the bubble and liquid surroundings. In [27], a theoretical treatment of this effect was given for a spherical, isolated bubble. Here, we provide an experimental and numerical study of the history effect regarding a spherical bubble attached to a horizontal flat plate and in the presence of gravity. The simulation technique developed

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in this paper is based on a streamfunction–vorticity formulation that may be applied to other flows where bubbles or drops exchange mass in the presence of a gravity field. Using this numerical tool, simulations are performed for the same conditions used in the experiments, in which the bubble is exposed to subsequent growth and dissolution stages, using stepwise variations in the ambient pressure. Besides proving the relevance of the history effect, the simulations highlight the importance that boundary-induced advection has to accurately describe bubble growth and shrinkage, i.e. the bubble radius evolution. In addition, natural convection has a significant influence that shows up in the velocity field even at short times, although given the supersaturation conditions studied here, the bubble evolution is expected to be mainly diffusive.

1.1 Introduction

Mass transfer processes involving bubbles have gained a renewed interest over the last few years due to their relevance in modern microfluidic applications connected to topics such as carbon sequestration [28, 29]. Due to the small size of these bubbles they are spherical once they become smaller than the channel’s size and are detached from the channel’s wall. Thus, in general terms, the theory of [25] describing the diffusion-driven growth or dissolution of an isolated, spherical particle should be applicable. However, as discussed in [27], a number of effects not included in the Epstein & Plesset theory, e.g. flow around the bubble, must be taken into account to properly describe various experimental observations. Bubbles may also interact with nearby surfaces or they may contain more than one chemical species [30, 31]. Another effect that contributes to the diffusion-driven dynamics of a bubble is the so-called history effect, discussed in [27] and more recently in [32]. It has been shown that any recent history of growth and/or dissolution (triggered by past changes in ambient pressure) experienced by a particular bubble may leave, at least for some time, a non-negligible imprint on the current state of the concentration profile surrounding such a bubble. Consequently, the mass transfer rate is affected as well. In [27], a modification to the theory of Epstein & Plesset is proposed to take into account the history effect through a memory integral term for the case of spherical, isolated bubbles. Moreover, we applied this modified equation to calculate the bubble radius evolution when the bubble is subjected to some simple, yet relevant, pressure–time histories. It is worth mentioning that history effects are common to problems in which diffusion plays a central role, such as the viscous drag around a body or, closer to the present mass transfer problem, the heat transfer around a spheroid [33].

The primary goal of the present paper is to quantify the relative importance

of the history effect in a canonical, yet experimentally relevant, configuration that does not exhibit spherical symmetry, namely, that of a single spherical bubble tangent to a horizontal flat plate that grows and dissolves in response to changes in the ambient pressure and in the presence of gravity. In this configuration, the existence of the history effect may become noticeable with a simple experiment: let us consider such a spherical CO_2 bubble that dissolves when the pressure is above saturation (see figure 1.1). At a given time $t \approx 60$ s, the pressure is lowered to a new value still above saturation (figure 1.1(b)). Despite the pressure being at all times above saturation, after changing the pressure, the bubble is observed to grow for some time (figure 1.1(a)). Naturally, part of this growth is due to the expansion of the gas. Thus, to observe the effect purely due to diffusion, it is convenient to plot the ambient radius, R_0 . It is defined as the radius one would observe if the liquid surroundings were at the reference ambient pressure, P_0 , instead of the actual ambient pressure $P_\infty(t)$:

$$R_0(t) = R(t) \left(\frac{P_\infty(t)}{P_0} \right)^{1/3}. \quad (1.1)$$

Here, $R(t)$ is the measured bubble radius. Still, the ambient radius can be seen to grow until approximately $t \approx 100$ s, an effect purely driven by diffusion. Note that R_0 was referred to in [27] as the pressure-corrected radius R_{corr} . However, with the purpose of maintaining the standard nomenclature, R_0 will be used throughout this paper.

This phenomenon may be explained by examining the concentration of dissolved CO_2 near the bubble (figure 1.1(c)). Indeed, although the concentration at the bubble surface, given by Henry's law, responds instantaneously to pressure changes, there exists a boundary layer around the bubble where the concentration of CO_2 is higher than the instantaneous saturation one, as a result of the dissolution stage that took place before the pressure drop. In the example depicted in figure 1.1(c), it can be seen how the concentration gradient at the bubble's top is actually positive at $t = 65$ s, which explains the growth of the ambient radius. In this figure, numerical simulations such as the ones described in §§1.3–1.5 have been used to compute the concentration field along the z axis. These simulations are validated by comparing the predicted bubble radius with the experimental one (see figure 1.1(a)).

This simple example illustrates that, to properly describe the time evolution of the bubble radius observed in experiments, the history effect must be taken into account. However, a question that was left open in previous work [27] was the relative importance of this effect in a realistic experimental condition where other effects such as the interference with a wall and natural convection may greatly influence the diffusion-driven bubble dynamics, as was shown by [34].

With this idea in mind, another objective of the present work is to propose a numerical approach able to accurately describe the evolution of a bubble attached to a horizontal flat plate and growing/dissolving in the presence of a gravitational field.

While this work only deals with bubbles composed of a single soluble gas, it is important to realise that the history effect is omnipresent in multicomponent bubbles. In [27], the history effect was described as ‘the acknowledgement that at any given time the mass flux across the bubble is conditioned by the preceding time history of the concentration at the bubble interface’. Thus, in dissolving/growing multicomponent bubbles, the flow rate of a particular species across the bubble interface will likely be different from the rest. The species composition inside the bubble will thus change over time, which amounts to time-dependent partial pressures and hence time-dependent interfacial concentrations. It is possible to artificially discern the contribution of the history effect numerically, as was done by [32] for the case of a dissolving two-gas bubble. Isolating the history effect experimentally, on the other hand, is anticipated to be much harder.

Finally, it is worth mentioning that the history effect is naturally present in the evaporation of multicomponent drops. [35] have recently developed a formulation that includes a memory integral to describe the diffusion-driven dynamics of multicomponent drops in the presence of a solvent, a phenomenon of relevance in modern techniques of chemical analysis [36]. In this problem, the faster or slower dissolution of one of the components yields a time-varying composition at the drop’s interface, which makes the inclusion of the history integral in Fick’s law essential, even when the ambient pressure remains constant.

The paper is structured as follows: §1.2 presents the experimental results that illustrate the effect of history in the growth–dissolution of CO_2 bubbles tangent to a flat plate. §1.3 presents the general mathematical formulation of the problem and sheds light on the importance of the different physical effects involved in the experiments. In §1.4, a formulation based on the streamfunction–vorticity method is described to simulate the mass transfer and flow field around the bubbles. The simulation results are then presented and discussed in §1.5. Finally, §1.6 summarises the main conclusions.

1.2 Experimental characterisation of the history effect

We have carried out experiments to support our theoretical and numerical analyses by subjecting single bubbles to well-controlled, step-like pressure

Figure 1.1: Dissolution of a CO_2 spherical-cap bubble tangent to a flat chip immersed in a CO_2 -water solution under pressurised conditions (see later figure 1.9). The bubble is subjected to (b) a pressure jump $P_\infty(t)$, from $P_\infty(0) = P_0 = 7.4$ bar to 6.5 bar. Both pressures are above the saturation pressure, $P_{sat} = 6.1$ bar (according to simulation). Panel (a) shows the evolution in time of the measured bubble radius $R(t)$ (white markers) and ambient radius $R_0(t)$ (dark markers). The former is compared to simulation, which in addition was employed to depict (c) the concentration profile along the z -axis above the bubble at three different instants in time. The employed experimental and numerical techniques are detailed in the main text.

jumps that super- or undersaturate the liquid alternatively. This way, we can make bubbles grow and shrink under repeatable conditions to expose the history effect. It becomes apparent through the differences in the responses to successive identical pressure–time histories.

1.2.1 Experimental set-up and procedure

Although the experimental set-up has been described in a previous work [37], a brief description is included here for convenience. The facility is fed with water that is demineralised in a purifier (MilliQ A10) and degassed by making it flow through a filter (MiniModule, Liquicel, Membrana). This water enters into the mixing chamber (see figure 1.2), that has been previously flushed with CO_2 to purge the air from the system. There the water is stirred in the presence of CO_2 , kept at the desired saturation pressure, for approximately 45 minutes. Finally, the experimental tank is pressurised with CO_2 at this same pressure and then slowly flooded with the carbonated water, so bubbles do not appear during the filling. This preparation procedure ensures that in the experimental tank there are no other gas species present within the liquid or gas phases apart from CO_2 (at least in quantifiable amounts).

Placed at the centre of the experimental tank there is a silicon chip, treated

Figure 1.2: Sketch of the experimental set-up. See [37] for a detailed description.

to become hydrophilic, with a black-silicon hydrophobic pit ($50 \mu\text{m}$ in radius) at its centre. The role of this pit is to force a single bubble to nucleate at a fixed location in a repeatable way. Furthermore, in order to avoid slight temperature variations to affect the diffusion-driven bubble dynamics, the measurement tank is kept at a constant temperature by means of an external chiller.

Once the measurement tank is filled with the carbonated water, the following experimental procedure is followed:

1. The pressure is lowered below the saturation value, until a bubble nucleates at the pit and grows up to the desired size, R_i .
2. The tank pressure is set again to the saturation value. Then, the pressure is finely adjusted manually until the bubble size does not vary in an observable way for approximately five minutes. The pressure at which this occurs will be hereafter the one used in the calculations as the saturation pressure. Notice that this procedure allows us to determine the saturation pressure with more accuracy than that given by the pressure controller during the mixing process.
3. At time t_1 (see figure 1.3), the pressure is lowered by a given amount, Δp_1 , during a prescribed time $T = t_2 - t_1$. This turns the liquid supersaturated, which leads to bubble growth.

1. The history effect on bubble growth and dissolution

Figure 1.3: Experimental procedure during which the bubble is exposed to two identical supersaturation–undersaturation cycles. The lower plot shows the pressure that the bubble is subjected to, whilst the upper one illustrates its radius time evolution. In few words, once a bubble is stabilised at a given radius R_i , it is forced to a growth cycle for a prescribed time T and then to a dissolution cycle down to a size slightly smaller than R_i ($t = t_{3a}$), such that a short time T_s after the pressure returns to the initial level P_0 ($t = t_{3b}$), the combination of previous gas expansion (during $t_{3a} - t_{3b}$) and history lead the bubble size to the initial radius ($t = t_4$). An identical pressure cycle is immediately imposed, which results in a different time-evolution of the bubble radius due to the history effect.

4. Subsequently, at time t_2 , the pressure is increased by an amount Δp_2 , which causes undersaturation and the bubble to shrink.
5. When the bubble becomes slightly smaller than R_i at time t_{3a} , the pressure is gradually set back to the saturation level P_0 ($t = t_{3b}$) by means of a pressure drop Δp_3 . During this short period ($t_{3a} - t_{3b}$) the bubble expands and grows.
6. During a short time T_s after t_{3b} , the pressure remains at saturation but the bubble keeps growing and attains the initial size R_i at t_4 due to the history effect (portrayed in figure 1.1). At this point (t_4), growth step (3) and subsequent dissolution step (4) are immediately repeated at identical Δp_1 and Δp_2 respectively.

It is imperative to realise that the pressure and bubble size conditions at t_4 , just before the pressure jump, are identical to the initial conditions at t_1 . Namely, $R(t_4) = R(t_1)$, $P_\infty(t_4) = P_\infty(t_1)$ and $dP_\infty(t_4)/dt = dP_\infty(t_1)/dt = 0$. The zero-pressure time derivative condition is extremely important to ensure

Figure 1.4: Results for experiment 1, showing the time-histories of (a) the measured bubble radius R in response to (b) the imposed pressure $P_\infty(t)$. In (c), the rate of growth of the ambient radius R_0 , defined in (1.1), is plotted for the two growth cycles. The time axis is initialised at t_1 or t_4 accordingly.

that the bubble is not under the effect of any previous pressure-induced volumetric expansion or compression at the time when Δp_1 is suddenly imposed. Note that the sole purpose of the pressure change between t_{3a} and t_{3b} and subsequent stabilisation period (t_{3b} and t_4) is precisely to enforce this last condition. This complex procedure allows us to directly isolate and quantify the history effect through direct comparison. Any differences between the first growth rate (during t_1 – t_2) and second growth rate (t_4 – t_5) must be purely attributed to the history effect. The differences arise because at t_1 the bubble is in equilibrium with its surroundings (uniform concentration field) and the contribution of history term is essentially negligible. At t_4 , however, the concentration field surrounding the bubble has evolved. It is no longer uniform, and the bubble is no longer in equilibrium: thus, the contribution of the history term is now larger.

1.2.2 Experimental results and discussion

In this subsection we present the results of four experiments that manifest the effects of history in bubble growth and shrinkage. Three of the experiments were carried out as described above, while in the fourth the order of the growth and shrinkage stages was swapped, i.e. first shrinking and then growing.

In the experiments where the bubble is first made to grow (figures 1.4 to 1.6), the most apparent difference between the two growth stages is the somewhat larger bubble size achieved at the end of the second stage (see panels

1. The history effect on bubble growth and dissolution

Figure 1.5: Results for experiment 2 (see caption of figure 1.4). The range of pressures is slightly different to the ones exposed in figure 1.4. However, the history effect is repeatable.

Figure 1.6: Results for experiment 3 (see caption of figure 1.4).

Figure 1.7: Results for experiment 4 (see caption of figure 1.4). This time, the direction of the pressure jumps is inverted thereby replacing the two growth stages observed in experiments 1–3 with two dissolution stages.

labelled as (a)). This is a consequence of a more important effect, namely the higher growth rate found during the first instants of the second stage, as predicted by the modified Epstein & Plesset equation with history effects provided in [27]. To illustrate this point, panels (c) show the time derivative of the ambient bubble radius. In all cases the growth rate during the second stage lies above that of the first one, although both curves eventually converge at longer times, when the memory of the previous dissolution stage damps out. As demonstrated in [27], the CO_2 accumulated around the bubble during a dissolution stage yields a steeper concentration gradient at the interface that, in turn, leads to a faster growth rate at short times once the pressure is reduced and the liquid is supersaturated again. As the growth progresses, the influence of the initial concentration profile becomes weaker and both growth rates converge to the same curve.

As demonstrated in [27], the CO_2 accumulated around the bubble during a dissolution stage yields a steeper concentration gradient at the interface that, in turn, leads to a faster growth rate after a short transient time once the pressure is dropped and the liquid is supersaturated again. As the growth progresses, the influence of the initial concentration profile becomes weaker and both growth rates converge to the same curve. During the very early times after the pressure drop (up to approximately ten seconds later), the contribution of the history effect on mass transfer is masked by the large growth rates induced by the sudden decrease of the interfacial concentration (induced by this pressure drop via Henry’s law) that leads to a steep interfacial concentration gradient. The change in growth rates between the first and

second cycles is experimentally indiscernible. This does however agree with theory, as one may observe from the numerically computed rates in figure 3 of [27].

It is interesting to compare this behaviour with that found when the bubble is forced to first dissolve and then to grow (figure 1.7). Although unavoidable experimental limitations of the control of the pressure in the facility in this case result in a somewhat noisier time derivative of the ambient radius, the same qualitative behaviour is found. Namely, the magnitude of the rate of change of the radius is larger in the second dissolution stage, thus leading to a smaller radius at the end of this stage. Analogously to what occurred in experiments 1–3, this is a consequence of the local depletion of CO_2 near the bubble caused by the intermediate growth stage.

Besides illustrating the history effect in the growth and dissolution of bubbles, these experiments will serve as benchmark cases for the numerical simulations described in the following sections. These numerical analyses will allow us to quantify the relative importance of the different physical effects that play a role in the processes illustrated in figures 1.4 to 1.7 which, besides diffusion, include surface tension, boundary-induced advection and natural convection.

In the theory that follows, we will assume that the bubble remains strictly spherical at all times. Two experimental snapshots depicting the upper and lower extremes in bubble size are provided in figure 1.8. The bubble is actually attached to a cylindrical pit of $50\text{ }\mu\text{m}$ diameter and $30\text{ }\mu\text{m}$ depth. The gas volume contained inside the pit can be neglected compared to the total volume of the gas bubble. In the experiments in which the cycles start with a growth phase, where $R > 200\text{ }\mu\text{m}$, the bubble remains spherical, as observed in figure 1.8(a). Only at the smallest radii during the experiments starting with a dissolution phase, we observe a spherical cap, figure 1.8(b). However, the assumption of perfectly spherical bubble at all time yields a relative error of less than 3 % as compared to the actual gas volume of the spherical cap and the pit. Therefore, the assumption of strictly spherical gas bubble for the analysis is more than justified.

1.3 Numerical analysis: problem formulation

Our goal is to accurately predict the time evolution of the radius of a spherical CO_2 bubble adhered to a horizontal flat plate in a CO_2 -water solution under the action of gravity and variable ambient pressure, as sketched in figure 1.9. In this section we formulate the mass transfer problem, which involves a non-stationary boundary and that must be coupled with the equations of motion for the liquid assuming axisymmetry around the vertical axis.

Figure 1.8: Bubble snapshots at both extremes of the bubble size range measured during our experiments. The largest radius is (a) $R = 358 \mu\text{m}$, corresponding to the maximum radius attained during experiment 1 (see later figure 1.4), whereas (b) $R = 92 \mu\text{m}$ is the smallest radius, obtained during the dissolution experiment 4 (see figure 1.7). The radius is computed by means of the light-blue circumference fitted to the bubble contour. The horizontal red line marks the height of the bubble-substrate contact line, below which there is the reflection of the bubble on the substrate surface.

Figure 1.9: Sketch of a spherical CO_2 bubble adhered to a flat plate. The relevant parameters and functions used in the formulation of the mass transfer problem are also indicated.

1.3.1 Mass transfer problem

The transport of dissolved gas species in the liquid is governed by the following mass transport equation, usually referred to as the advection–diffusion equation,

$$\frac{\partial C}{\partial t} + \mathbf{U} \cdot \nabla \mathbf{C} = D_m \nabla^2 C, \quad (1.2)$$

where $C(\mathbf{x}, t)$ is the molar concentration field, $\mathbf{U}(\mathbf{x}, t)$ is the velocity vector field and D_m is the mass diffusion coefficient. The initial concentration of dissolved gas is assumed to be uniform throughout the liquid and equal to C_∞ , equal to the gas concentration in the far field. The boundary condition of zero-mass flux holds across the impermeable wall. The concentration boundary condition at the bubble surface, $C_i(t)$, is given by Henry’s law,

$$C_i(t) = k_H P_g(t), \quad (1.3)$$

where k_H is Henry’s (molar-based) solubility constant and $P_g(t)$ is the total gas pressure inside the bubble. A constant temperature environment T_∞ is assumed, i.e. k_H remains constant, while the ambient pressure $P_\infty(t)$ is set to vary with time t . The bubble gas volume is related to the gas content and pressure via the equation of state for an ideal gas,

$$\frac{4}{3}\pi R^3 P_g = n R_u T_\infty, \quad (1.4)$$

where $n(t)$ is the number of gas moles inside the bubble and R_u denotes the universal gas constant. The total gas pressure inside the bubble, P_g , considering liquid-gas surface tension γ_{lg} , but neglecting inertial and viscous effects inside the gas phase, is given by

$$P_g = P_\infty + 2\gamma_{lg}/R. \quad (1.5)$$

The mass transfer problem is closed with Fick’s first law, which sets the molar flow rate of gas across the bubble surface S to be

$$\dot{n} = D \int_S \nabla C \cdot \hat{\mathbf{n}} dS, \quad (1.6)$$

where dS is an infinitesimal area element of the bubble surface, and $\hat{\mathbf{n}}$ is the outward-pointing unit normal from the bubble surface.

Equations (1.2)–(1.6) represent the mass transfer problem equations. These must be coupled with the equations of motion from which the velocity field $\mathbf{U}(\mathbf{x}, t)$ may be computed.

1.3.2 Modelling density-driven natural convection

The dissolved gas concentration profile around the bubble implies a non-uniform density field of the surrounding liquid-gas solution which may trigger the onset of ‘density-induced natural convection’ [38]. The change in solution density may be quantified through the concentration expansion coefficient, λ , usually defined as [39]

$$\lambda = \frac{1}{\rho_l} \frac{\partial \rho}{\partial C}, \quad (1.7)$$

where ρ_l is the density of the pure solvent. Any change in the solution density is therefore assumed proportional to the change in dissolved gas concentration. For dilute, monosolute solutions, the concentration expansion coefficient is approximately given by (see Appendix 1.A)

$$\lambda \approx \frac{M_g}{\rho_l} - \bar{V}_g^\infty, \quad (1.8)$$

where M_g is the gas molar mass and $\bar{V}_g^\infty$ is the (temperature dependent) partial molar volume of the solute in the solvent at infinite dilution. For CO₂ gas in pure water, $\bar{V}_g^\infty \approx 34.2 \text{ cm}^3/\text{mol}$ [40], which results in $\lambda \approx 9.8 \text{ cm}^3/\text{mol}$.

The variations in density considered here are small, of the order of 0.1 %. However, these variations are sufficiently large to have a non-negligible effect on the motion of the flow. Consequently, it was deemed appropriate to take this effect into account via the Boussinesq approximation. This essentially results in the inclusion of a non-uniform buoyancy term imposed by the local dissolved gas concentration into the Navier-Stokes equation (1.12). The Boussinesq approximation allows for the flow to be regarded as incompressible when treating the continuity equation. Therefore, the incompressibility condition,

$$\nabla \cdot \mathbf{U} = 0, \quad (1.9)$$

always holds. Moreover, the density $\rho(\mathbf{x}, t)$ of the liquid-gas solution shall be approximated as constant, $\rho(\mathbf{x}, t) = \rho_l$, in both the inertial and viscous terms of the momentum equation. However, we shall allow small variations in density in the body force (gravity) term. The density field $\rho(\mathbf{x}, t)$ may then be expressed as

$$\rho(\mathbf{x}, t) = \rho_l + \rho^*(\mathbf{x}, t) \quad (1.10)$$

where $\rho^*(\mathbf{x}, t)$ is the density perturbation field arising from the non-uniform concentration field and, evidently, $|\rho^*| \ll \rho_l$. Similarly, the pressure field in the solution may be decomposed into

$$P(\mathbf{x}, t) = P_\infty(t) + P_h(\mathbf{x}) + P^*(\mathbf{x}, t). \quad (1.11)$$

Here P_h is the background hydrostatic pressure, $\nabla P_h = \rho_l \mathbf{g}$, where $\mathbf{g}$ denotes the gravitational acceleration, and $P^*(\mathbf{x}, t)$ is the pressure perturbation arising from the fluid motion. It likewise follows that for our experiments, $P_h \ll P_\infty$ and $|P^*| \ll P_\infty$.

1.3.3 Equations of motion in terms of the streamfunction and vorticity

Making use of (1.10) and (1.11), the Navier-Stokes momentum equation may be written as

$$\frac{\partial \mathbf{U}}{\partial t} + (\mathbf{U} \cdot \nabla) \mathbf{U} = -\frac{\nabla P^*}{\rho_l} + \nu \nabla^2 \mathbf{U} + \frac{\rho^* \mathbf{g}}{\rho_l}, \quad (1.12)$$

where ν is the kinematic viscosity of the liquid. Since the flow is axisymmetric around the vertical (z) axis, if we are able to define an orthogonal set of coordinates η, ξ, ϕ where ϕ is the angle of rotation around the vertical axis, then the velocity field has only two components, $\mathbf{U} = U_\eta(\eta, \xi) \hat{\mathbf{e}}_\eta + U_\xi(\eta, \xi) \hat{\mathbf{e}}_\xi$, and the whole problem may be treated as two-dimensional. The vorticity field Ω is then also unidirectional and a vorticity scalar, Ω , exists:

$$\Omega = \Omega \hat{\mathbf{e}}_\phi = \nabla \times \mathbf{U}. \quad (1.13)$$

Taking the curl of (1.12) eliminates the pressure term and the vorticity scalar transport equation is obtained:

$$\frac{\partial \Omega}{\partial t} + \mathbf{U} \cdot \nabla \Omega = \Omega \hat{\mathbf{e}}_\phi \cdot \nabla \mathbf{U} - \nu \nabla \times (\nabla \times (\Omega \hat{\mathbf{e}}_\phi)) \cdot \hat{\mathbf{e}}_\phi + \frac{1}{\rho_l} (\nabla \rho^* \times \mathbf{g}) \cdot \hat{\mathbf{e}}_\phi. \quad (1.14)$$

It follows from Eq. (1.7) that $\nabla \rho^* = \lambda \rho_l \nabla C$, so the vorticity transport equation becomes

$$\frac{\partial \Omega}{\partial t} + h_\phi \mathbf{U} \cdot \nabla (\Omega / h_\phi) = \mathcal{L}^2 \Omega + \lambda (\nabla C \times \mathbf{g}) \cdot \hat{\mathbf{e}}_\phi. \quad (1.15)$$

Here, we have made use of the following linear operator:

$$\mathcal{L}^2 = \frac{1}{h^2} \left[\frac{\partial}{\partial \xi} \left(\frac{1}{h_\phi} \frac{\partial}{\partial \xi} (h_\phi \Omega) \right) + \frac{\partial}{\partial \eta} \left(\frac{1}{h_\phi} \frac{\partial}{\partial \eta} (h_\phi \Omega) \right) \right], \quad (1.16)$$

where h_ϕ denotes the scale factor in the $\hat{\mathbf{e}}_\phi$ direction and h the scale factor in both the $\hat{\mathbf{e}}_\xi$ and $\hat{\mathbf{e}}_\eta$ directions. The coordinate system and scale factors will be introduced quantitatively in §1.4. Incompressibility, along with the

axisymmetric nature of the flow, allow for the velocity field to be expressed in terms of a scalar streamfunction, Ψ :

$$\mathbf{U} = \nabla \times (\Psi/h_\phi \hat{\mathbf{e}}_\phi). \quad (1.17)$$

Combining (1.13) and (1.17) results in the following equation for the streamfunction,

$$\mathcal{L}^2(\Psi/h_\phi) = -\Omega. \quad (1.18)$$

In §1.4, it will be shown how the fluid motion may be obtained by simultaneously solving Ψ from (1.18) and Ω from (1.15) numerically by employing a streamfunction–vorticity method in dynamic tangent-sphere coordinates. It will be seen that the boundary conditions for Ψ and Ω can be determined from those for $\mathbf{U}$ through careful analysis. From the physical point of view, the velocity field must satisfy the kinematic and dynamic (zero-shear stress) boundary conditions along the moving bubble boundary, in addition to the no-slip condition at the wall.

1.3.4 On the parameters and time scales of the problem

This subsection intends to shed light on the physics governing the diffusion-driven growth and dissolution of a bubble attached to a flat plate. More specifically, the goal is to prove that the concentration and velocity fields evolve over very disparate time scales, which will allow for an efficient procedure to numerically solve the problem formulated in previous subsections.

The processes involved in this problem introduce four characteristic time scales: t_s for bubble growth and dissolution, t_m for mass diffusion of the dissolved gas, t_v for viscous diffusion of momentum and t_b for the density-induced convection. Let U denote the characteristic flow velocity. When the advection induced by the moving boundary dominates over natural convection, then U is the interface velocity $U_s \sim \dot{R}$. When convection overcomes boundary-induced advection, then U becomes the convection velocity U_b . The characteristic length scale is the bubble radius R . For mass-diffusion-controlled growth driven by a molar concentration difference ΔC between the bubble boundary and the bulk fluid, the flow behaviour may be characterised using three dimensionless parameters. These are the Jakob [41] and Grashof numbers for mass transfer, in addition to the Schmidt number, defined as follows:

$$Ja = \frac{M_g |\Delta C|}{\rho_g}, \quad Gr = \frac{\lambda |\Delta C| g R^3}{\nu^2}, \quad Sc = \frac{\nu}{D_m}, \quad (1.19a-c)$$

where ρ_g is the density of the gas bubble and g is the magnitude of the acceleration due to gravity. The Jakob number, Ja , may be regarded as a measure

of the driving force for bubble growth induced by the concentration difference and gas solubility. The Grashof number, Gr , represents the ratio of buoyancy (convection) and viscous forces. The Schmidt number, Sc , is the ratio of momentum and mass diffusivities.

Here we shall consider bubble growth or dissolution that is primarily driven by mass diffusion. We may then use the approximate result obtained by [25] or [42] to estimate bubble growth as

$$R \sim Ja\sqrt{D_m t}. \quad (1.20)$$

It then follows that the bubble growth time scale and boundary-induced advection velocity scales are

$$U_s = \dot{R} \sim \frac{Ja^2 D_m}{R}, \quad t_s = \frac{R}{U_s} \sim \frac{R^2}{Ja^2 D_m}. \quad (1.21a, b)$$

The magnitudes of the terms in the mass transport equation (1.2) are

$$\frac{\partial C}{\partial t} \sim \frac{|\Delta C|}{t_m}, \quad \mathbf{U} \cdot \nabla C \sim \frac{U|\Delta C|}{R}, \quad D\nabla^2 C \sim \frac{D_m|\Delta C|}{R^2} \quad (1.22a-c)$$

where t_m is the characteristic time required for a significant concentration change over characteristic length scale R . Similarly, taking $\Omega \sim U/R$, the magnitudes of the terms in the vorticity transport equation (1.15) are

$$\frac{\partial \Omega}{\partial t} \sim \frac{U}{R t_v}, \quad \mathbf{U} \cdot \nabla \Omega \sim \frac{U^2}{R^2}, \quad \nu \mathcal{L}^2 \Omega \sim \frac{\nu U}{R^3}, \quad \lambda \nabla C \times \mathbf{g} \sim \frac{\lambda |\Delta C| g}{R}, \quad (1.23a-d)$$

where similarly t_v refers to the time required for a significant vorticity change over the same characteristic length scale R . For $Sc \sim 1$ or $Sc \gg 1$, the characteristic convection velocity and time scale may be obtained from a balance between the viscous term (1.23c) and the buoyancy term (1.23d) in the vorticity transport equation,

$$U_b \sim \frac{\lambda |\Delta C| g R^2}{\nu}, \quad t_b = \frac{R}{U_b} \sim \frac{\nu}{\lambda |\Delta C| g R}. \quad (1.24a, b)$$

The ratio of velocities is given by $U_b/U_s = Gr Sc/Ja^2$. The ratio of the advection term (1.22b) and the diffusive term (1.22c) in the mass transport equation yields a Péclet number, $Pe = UR/D$. The ratio of the advection term (1.23b) over the diffusive term (1.23c) in the vorticity transport equation similarly yields a Reynolds number, $Re = UR/\nu$. Neglecting natural convection, setting $U = U_s$ gives $Pe = Ja^2$ and $Re = Ja^2/Sc$. Likewise, natural convection

dominating over boundary-induced advection, $U = U_b$, results in $Pe = Gr Sc$ and $Re = Gr$.

From the above analysis, we may conclude that mass and momentum diffusion will clearly dominate over advection and natural convection provided $Gr Sc < 1$ and $Ja < 1$ (i.e. Pe and Re are small). In such a case, the mass diffusion and viscous time scales are the leading time scales in the mass transport and vorticity transport equations respectively. The unsteady term in each transport equation may then be balanced by the corresponding diffusive term, yielding

$$t_m \sim \frac{R^2}{D_m}, \quad t_v \sim \frac{R^2}{\nu}. \quad (1.25a, b)$$

The ratios between the mass diffusion time scale and the other time scales are

$$\frac{t_m}{t_s} = Ja^2, \quad \frac{t_m}{t_b} = Gr Sc, \quad \frac{t_m}{t_v} = Sc. \quad (1.26a-c)$$

As reference for the conditions explored in this work, a CO_2 gas bubble with $R = 0.25$ mm growing in a 15% supersaturated CO_2 -water solution at 5 bar and 293 K, with $\lambda = 9.8$ cm³/mol, results in $Ja = 0.12$, $Gr = 0.038$ and $Sc = 523$. The Rayleigh number is $Gr Sc = 19.6$. Under these conditions, intentionally similar to those of our experiments, equation (1.26) translates to

$$t_s > t_m \sim t_b \gg t_v. \quad (1.27)$$

The vorticity/velocity field around a bubble evolves at a time scale t_v provided by the viscous diffusion of momentum. This time scale is much faster than the time scale t_m of mass transfer, i.e. the time required to observe a significant change in the concentration field surrounding the bubble. Likewise, the time scale t_s in which a substantial change in the bubble radius may be observed is significantly larger than t_m . This means that the thin boundary layer approximation (valid when $t_s \ll t_m$, i.e. $Ja \gg 1$), while suitable for treating the fast growth of bubbles in highly supersaturated liquids [43], is clearly not applicable here.

The time scale of interest is of course t_m . Let us neglect density-driven convection for the moment. At every time step of this slow time scale t_m , provided $t_m \gg t_v$ ($Sc \gg 1$), viscous action ensures that the flow always reaches (over a much faster time scale t_v) a steady-state solution. In other words, at every time step of t_m , the advection term in the mass transport equation may then be computed from the steady-state vorticity (hence velocity) solution imposed by the instantaneous concentration field and interface velocity. We shall refer to it as the quasi-steady advection approximation. It is worth pointing out that bubbles of other gases with solubility parameter, Λ , smaller

than that of CO_2 (such as nitrogen or oxygen) can be described as well with this approximation, as t_m will be even much smaller than t_s . In these cases, the history effect – which is a diffusive effect – will be even more apparent since boundary-driven advection will have a smaller influence.

Considering now density-driven convection, provided $t_b \gg t_v$ ($Gr \ll 1$), then viscosity is able to establish a quasi-steady velocity field in a time much shorter than that taken by buoyancy to induce changes in the flow. In other words, although buoyancy must be taken into account to properly compute the velocity field around the bubble, it does not affect the validity of the quasi-steady advection approximation. This knowledge will now be used in the next section when implementing the equations into a numerical model.

1.4 Numerical analysis: implementation

1.4.1 Non-dimensionalisation

We begin by introducing the dimensionless time, radius and Cartesian coordinates, ambient pressure and mole number:

$$\tau = \frac{D_m}{R_i^2} t, \quad a = \frac{R}{R_i}, \quad \tilde{\mathbf{x}} = \frac{\mathbf{x}}{R_i}, \quad p = \frac{P_\infty}{P_0}, \quad \mu = \frac{R_u T_\infty}{4/3\pi R_i^3 P_0} n. \quad (1.28a-d)$$

In this work we have chosen the characteristic radius R_i to be the initial radius $R(t=0)$. Similarly, the characteristic ambient pressure P_0 corresponds to the initial liquid pressure, $P_\infty(0)$, whereas the mole number n is made dimensionless with that contained in a bubble of radius R_i , immersed in a liquid at pressure P_0 and in the absence of surface tension. Note that the time scale of choice has been that of mass diffusion, t_m , presented in (1.25a). Additionally, the molar concentration field C and the interfacial molar concentration C_i may be non-dimensionalised through

$$c = \frac{C - C_\infty}{k_H P_0}, \quad c_i = \frac{C_i - C_\infty}{k_H P_0}. \quad (1.29a, b)$$

The dimensionless counterparts of the vorticity scalar, velocity and streamfunction are

$$\omega = \frac{R_i^2}{D_m} \Omega, \quad \mathbf{u} = \frac{R_i}{D_m} \mathbf{U}, \quad \psi = \frac{1}{R_i D_m} \Psi. \quad (1.30a-c)$$

Lastly, let us present the following dimensionless parameters and dimensionless numbers:

$$\Upsilon = \frac{C_\infty}{k_H P_0}, \quad \Lambda = k_H R_u T_\infty, \quad \sigma = \frac{2\gamma l g}{R_i P_0}, \quad Gr_0 = \frac{\lambda k_H P_0 g R_i^3}{\nu^2}. \quad (1.31a-d)$$

The parameter Υ refers to the initial saturation level of the solution, Λ is a solubility parameter, σ is the surface tension parameter, while Gr_0 is a reference Grashof number, $Gr_0 = Gr k_H P_0 / |\Delta C|$.

1.4.2 The tangent-sphere coordinate system

The problem can be conveniently recast in dimensionless tangent-sphere spatial coordinates (η, ξ, ϕ) , where

$$\tilde{x} = 2a \frac{\eta}{\eta^2 + \xi^2} \cos \phi, \quad \tilde{y} = 2a \frac{\eta}{\eta^2 + \xi^2} \sin \phi, \quad \tilde{z} = 2a \frac{\xi}{\eta^2 + \xi^2}. \quad (1.32a-c)$$

The contours of η and ξ satisfy the following inverse relations [44, 45]:

$$\tilde{x}^2 + \tilde{y}^2 + \tilde{z}^2 = (2a/\eta) \sqrt{\tilde{x}^2 + \tilde{y}^2}, \quad \tilde{x}^2 + \tilde{y}^2 + \tilde{z}^2 = (2a/\xi) \tilde{z}. \quad (1.33a, b)$$

These coordinates, represented in figure 1.10, scale with the dimensionless radius of the bubble, $a(\tau)$. The scale factors are defined as

$$\tilde{h} = \frac{h_\eta}{R_i} = \frac{h_\xi}{R_i} = \frac{2a}{\eta^2 + \xi^2}, \quad \tilde{h}_\phi = \frac{h_\phi}{R_i} = \frac{2a\eta}{\eta^2 + \xi^2}. \quad (1.34a, b)$$

The partial time derivative of any scalar function f described by fixed Cartesian coordinates (x, y, z) expands as the material derivative when described by our $R(t)$ -scaling spatial coordinates (η, ξ) . Taking the partial derivative of f with respect to time τ , we find

$$\frac{\partial}{\partial \tau} f(\tilde{x}, \tilde{y}, \tilde{z}, \tau) = \frac{D}{D\tau} f(\eta(\tau), \xi(\tau), \tau) = \frac{\partial f}{\partial \tau} + \eta' \frac{\partial f}{\partial \eta} + \xi' \frac{\partial f}{\partial \xi}. \quad (1.35)$$

The prime notation ($'$) denotes $d/d\tau$. The terms containing η' and ξ' represent the apparent advection of a quiescent fluid relative to our time-varying coordinate system. Let us define the *a priori* unknown corresponding (dimensionless) apparent velocity field as $\mathbf{u}_{rel}(\eta, \xi, \tau) = u_{rel,\eta} \hat{\mathbf{e}}_\eta + u_{rel,\xi} \hat{\mathbf{e}}_\xi$. The advection term on f would then be

$$(\mathbf{u}_{rel} \cdot \hat{\nabla}) f = \frac{u_{rel,\eta}}{\tilde{h}} \frac{\partial f}{\partial \eta} + \frac{u_{rel,\xi}}{\tilde{h}} \frac{\partial f}{\partial \xi}, \quad (1.36)$$

where the operator $\hat{\nabla} = R_i \nabla$ is dimensionless. Comparing (1.35) and (1.36) immediately reveals that $u_{rel,\eta} = \tilde{h} \eta'$ and $u_{rel,\xi} = \tilde{h} \xi'$. Thus, the dimensionless velocity field of our scaling coordinate system (relative to any fixed point in the physical domain) is just equal to $-\mathbf{u}_{rel} = -(\tilde{h} \eta' \hat{\mathbf{e}}_\eta + \tilde{h} \xi' \hat{\mathbf{e}}_\xi)$. Differentiating (1.33a) and (1.33b) independently with respect to τ , one finds that

$$\eta' = a' \eta / a, \quad \xi' = a' \xi / a. \quad (1.37a, b)$$

Figure 1.10: Contourlines of the tangent-sphere η , ξ coordinates, plotted in the $y = 0$ ($\phi = 0$) Cartesian plane. $\eta = 0$ lies on the z -axis, $\eta \rightarrow \infty$ at the contact point. The horizontal wall lies on the $\xi = 0$ isosurface, while the bubble surface is always mapped by $\xi = 1$. The separation of the plotted contours is uniform ($\Delta\eta = \Delta\xi = 0.1$).

1.4.3 Streamfunction–vorticity formulation

The streamfunction satisfies the following equation,

$$\tilde{\mathcal{L}}^2(\psi/\tilde{h}_\phi) = -\omega, \quad (1.38)$$

which makes use of the dimensionless operator $\tilde{\mathcal{L}}^2 = R_0^2 \mathcal{L}^2$, and (1.38) may be rewritten in terms of the coordinates η and ξ as

$$\frac{\eta^2 - \xi^2}{2a\tilde{h}_\phi^2} \frac{\partial \psi}{\partial \eta} + \frac{\eta\xi}{a\tilde{h}_\phi^2} \frac{\partial \psi}{\partial \xi} + \frac{1}{\tilde{h}^2\tilde{h}_\phi} \left(\frac{\partial^2 \psi}{\partial \eta^2} + \frac{\partial^2 \psi}{\partial \xi^2} \right) = -\omega. \quad (1.39)$$

Boundary conditions are derived and explained in Appendix 1.B. These are

$$\psi(\eta, 0) = 0, \quad \psi(\eta, 1) = -\frac{2a^2 a'}{\eta^2 + 1}, \quad \psi(0, \xi) = -2a^2 a', \quad \psi(\infty, \xi) = 0. \quad (1.40a-d)$$

Once $\psi(\eta, \xi)$ is known, from the definition in (1.39), the dimensionless velocity components may be computed by numerically differentiating ψ according to

$$u_\eta = \frac{1}{\tilde{h}_\phi \tilde{h}} \frac{\partial \psi}{\partial \xi}, \quad u_\xi = -\frac{1}{\tilde{h}_\phi \tilde{h}} \frac{\partial \psi}{\partial \eta}. \quad (1.41a, b)$$

Expressions for the velocity field in the Cartesian reference frame are included in Appendix 1.C. The dimensionless vorticity transport equation reads

$$\frac{\partial \omega}{\partial \tau} + \tilde{h}_\phi \mathbf{u} \cdot \hat{\nabla} \left(\frac{\omega}{\tilde{h}_\phi} \right) = Sc \tilde{\mathcal{L}}^2 \omega + Gr_0 Sc^2 (\hat{\nabla} c \times \hat{\mathbf{g}}) \cdot \hat{\mathbf{e}}_\phi, \quad (1.42)$$

where $\hat{\mathbf{g}} = \mathbf{g}/g$. The Rayleigh number $Gr_0 Sc$ represents the ratio between the reference buoyant transport of momentum and diffusive transport of mass. In (η, ξ) coordinates, the vorticity transport equation becomes

$$\frac{\partial \omega}{\partial \tau} = L \frac{\partial \omega}{\partial \eta} + M \frac{\partial \omega}{\partial \xi} + P \left(\frac{\partial^2 \omega}{\partial \eta^2} + \frac{\partial^2 \omega}{\partial \xi^2} \right) + Q + S\omega, \quad (1.43a)$$

where L, M, P, Q and S are time- and space-dependent coefficients given by

$$L = -Sc \frac{\eta^2 - \xi^2}{2a\tilde{h}_\phi} - \frac{a'\eta}{a} - \frac{u_\eta}{\tilde{h}}, \quad M = -Sc \frac{\xi\eta}{a\tilde{h}_\phi} - \frac{a'\xi}{a} - \frac{u_\xi}{\tilde{h}}, \quad (1.43b, c)$$

$$P = \frac{Sc}{\tilde{h}^2}, \quad Q = -Gr_0 Sc^2 \left(\frac{\eta^2 - \xi^2}{2a} \frac{\partial c}{\partial \eta} + \frac{\eta\xi}{a} \frac{\partial c}{\partial \xi} \right), \quad (1.43d, e)$$

1. The history effect on bubble growth and dissolution

$$S = -\frac{Sc}{\tilde{h}} \frac{\eta^2 + 2\xi^2 + \xi^4/\eta^2}{(\eta^2 + \xi^2)^2} - \frac{1}{\tilde{h}\eta} \frac{u_\eta(\eta^2 - \xi^2) + 2u_\xi\eta\xi}{\eta^2 + \xi^2}. \quad (1.43f)$$

Coefficient Q contains the density-driven convection term. The cross product was evaluated by first expressing $\hat{\mathbf{g}}$ in its $(\hat{\mathbf{e}}_\eta, \hat{\mathbf{e}}_\xi)$ components via the transformation matrix described in Appendix 1.C. Boundary conditions are derived and explained in Appendix 1.B.3. These are

$$\frac{\partial\omega}{\partial\xi}(\eta, 0) = \frac{\tilde{h}u_n}{Sc\Delta\tau_v}, \quad \frac{\partial\omega}{\partial\eta}(\eta, 1) = \frac{4a'\eta}{a(\eta^2 + 1)} + \frac{2}{a}u_\eta(\eta, 1), \quad (1.44a, b)$$

$$\omega(0, \xi) = 0, \quad \frac{\partial\omega}{\partial\eta}(\infty, \xi) = 0. \quad (1.44c, d)$$

Here, $\Delta\tau_v$ is the computational time step for the viscous transport of momentum. We shall report its meaning in §1.4.5.

1.4.4 Formulation for the mass transfer problem

In dimensionless form, the advection–diffusion equation (1.2) becomes

$$\frac{\partial c}{\partial\tau} + \mathbf{u} \cdot \hat{\nabla} c = \hat{\nabla}^2 c, \quad (1.45)$$

or equivalently,

$$\frac{\partial c}{\partial\tau} = F \frac{\partial c}{\partial\eta} + G \frac{\partial c}{\partial\xi} + H \left(\frac{\partial^2 c}{\partial\eta^2} + \frac{\partial^2 c}{\partial\xi^2} \right), \quad (1.46a)$$

with

$$F = -\frac{\eta^2 - \xi^2}{2a\tilde{h}\eta} - \frac{a'\eta}{a} - \frac{u_\eta}{\tilde{h}}, \quad G = -\frac{\xi}{a\tilde{h}} - \frac{a'\xi}{a} - \frac{u_\xi}{\tilde{h}}, \quad H = \frac{1}{\tilde{h}^2}. \quad (1.46b-d)$$

The velocity field components $u_\eta(\eta, \xi, \tau)$ and $u_\xi(\eta, \xi, \tau)$ must of course be computed beforehand as detailed in section 1.4.3. Boundary conditions for the concentration are

$$\frac{\partial c}{\partial\xi}(\eta, 0) = 0, \quad c(\eta, 1) = c_i, \quad \frac{\partial c}{\partial\eta}(0, \xi) = 0, \quad \frac{\partial c}{\partial\eta}(\infty, \xi) = 0. \quad (1.47a-d)$$

The interfacial concentration $c_i(\tau)$, appealing to Henry's law, is given by

$$c_i = \left(p + \frac{\sigma}{a} \right) - \Upsilon. \quad (1.48)$$

The dimensionless molar flow rate μ' across the interface may be computed non-dimensionalising (1.6), resulting in

$$\mu' = -3\Lambda a \int_0^\infty \frac{\eta}{1+\eta^2} \frac{\partial c}{\partial \xi} \Big|_{\xi=1} d\eta. \quad (1.49)$$

Finally, the last equation remaining is the dimensionless ideal gas law,

$$\left(p + \frac{\sigma}{a}\right) a^3 = \mu. \quad (1.50)$$

1.4.5 Numerical procedure

The experiments were simulated by numerically solving the governing equations presented in the previous section. To do so, we used a second-order finite-difference discretisation in space and an implicit Euler method in time. The latter was chosen in search for unconditional stability, bearing in mind that the grid spacing becomes infinitesimally small as $\eta \rightarrow \infty$.

We have seen in §1.3.4 that this problem involves multiple scales. The governing equations have been non-dimensionalised in time with the time scale $t_m = R_i^2/D_m$ for mass diffusion, $\tau = t/t_m$. The mass transport equation will therefore require a time step $\Delta\tau_m$ that suitably advances within t_m . However, the momentum transport equation requires a much smaller time scale t_v and consequently, $\Delta\tau_v \sim \Delta\tau_m/Sc$. Stability of the scheme requires to advance in $\Delta\tau_v$. Doing so, however, the overall number of time iterations and computational cost required to span the whole duration of the experiments would be exceedingly high.

This issue could be solved making use of the quasi-steady advection approximation, validated in 1.3.4. Essentially, this approximation allows to advance the simulation in $\Delta\tau_m$ rather than in $\Delta\tau_v$. After time step $\Delta\tau_m$, time advances from τ_n to τ_{n+1} , where subscript n refers to the n -th time iteration. Given the actual concentration field c_n , suppose mass transfer across the bubble interface results in a change of radius from a_n to a_{n+1} with corresponding rate a' . What is the vorticity field ω_{n+1} for this new configuration? We first make the initial guess: $\omega_{n+1} = \omega_n$. The vorticity field is then allowed to independently evolve through the vorticity transport equation, advancing with time step $\Delta\tau_v$. By virtue of the quasi-steady advection approximation, the concentration field, bubble radius and velocity are treated as invariants. After k iterations, the vorticity converges to the steady-state solution. We used the following criterion for convergence:

$$\varepsilon_{max}^2 = \max \left\{ \frac{(\omega_{k+1} - \omega_k)^2}{\max(\omega_k^2)} \right\} < 10^{-6}. \quad (1.51)$$

The resulting vorticity and velocities are then used to solve the advection–diffusion equation to find c_{n+1} . The process is then repeated for the following time step. This way, the overall number of iterations and computational time are greatly reduced.

The numerical procedure followed at every time iteration n consists of the following steps:

1. Update time τ_n and primary variables: vorticity ω_n , concentration c_n and mole number μ_n . Define the time step $\Delta\tau_m$.
2. Obtain value of the externally applied pressures p_n and p_{n+1} through linear interpolation of the experimental pressure data.
3. (1.50) yields a cubic equation, $p_n a_n^3 + \sigma a_n^2 - \mu_n = 0$. Solve to obtain the radius a_n .
4. Compute μ'_n from (1.49) and integrate over $\Delta\tau_m$ to obtain μ_{n+1} .
5. Obtain the radius a_{n+1} in the same way as in step (iii) and then compute a' .
6. Compute ω_{n+1} and velocity components u_ξ and u_η with the streamfunction–vorticity method. First set $\omega_{k=0} = \omega_n$. Define the secondary time step $\Delta\tau_v$.
 - (a) Update ω_k .
 - (b) Compute ψ from (1.39) using ω_k .
 - (c) Compute u_ξ and u_η from (1.41).
 - (d) Compute ω_{k+1} from (1.43).
 - (e) Check for convergence of ω_{k+1} . If tolerance in (1.51) is met, $\omega_{n+1} = \omega_{k+1}$; otherwise, update k and return to step (a).
7. Compute c_{n+1} from (1.46).
8. Update n and return to step (i).

1.5 Simulation results and discussion

The simulation predictions for the bubble size history are compared with the experiments in figure 1.11. The simulation input parameters consist of the physical properties for CO₂ gas and water, together with specific reference parameters for each experiment. These are listed in table 1.1. The saturation

Physical properties	Exp.	R_i mm	P_0 bar	T_∞ °C	Υ	Λ	$\sigma \times 10^3$	Gr_0
$k_H = 3.36 \times 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$	1	0.226	5.92	21.6	1.0	0.823	1.05	0.218
$D_m = 1.92 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	2	0.226	6.48	21.8	1.001	0.824	0.96	0.240
$\gamma_{lg} = 7.0 \times 10^{-2} \text{ N m}^{-1}$	3	0.205	6.42	22.6	1.004	0.826	1.06	0.177
$\lambda = 9.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$	4	0.233	5.45	21.9	1.0	0.824	1.10	0.221
$\nu = 1.004 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$								

Table 1.1: Values of the parameters used in the simulations, corresponding to the experiments discussed in §1.2. For completeness, the Schmidt number is $Sc = \nu/D_m = 523$.

1. The history effect on bubble growth and dissolution

Figure 1.11: Time evolution of the dimensionless bubble radius, $a(\tau)$. Simulation (black curves) is compared to experimental data (markers) for experiments (a) 1, (b) 2, (c) 3 and (d) 4. The time evolution of the dimensionless ambient pressure, $p(\tau)$, is also included (grey curve). The different simulation curves correspond to (i, iv) the full solution, (ii) solution where density-induced convection is neglected, (iii) solution for pure diffusion (both density-induced convection and boundary-induced advection are neglected). Moreover, case (iv) is only used to model experiment 4 as seen in (d), corresponding to the full solution coupled with the CO_2 stratification model, with $\Upsilon_{wall} = 1.25$.

level of the far field, $\Upsilon = C_\infty/k_H P_0$, was accurately determined from the initial evolution of the radius time history of each experiment before the first jump in pressure, as described in §1.2.

Case (i) in figure 1.11 corresponds to the full solution. For cases (ii) and (iii), density-induced convection is neglected: $\lambda = 0$, thus $Gr_0 = 0$. This translates to setting $Q = 0$ in the vorticity transport equation (1.43). Additionally (iii) is the solution for pure diffusion, i.e. without any velocity. This implies setting $u_\eta = u_\xi = a' = 0$ in the mass transport equation (1.46). Consequently, solution (iii) does not make use of the streamfunction–vorticity formulation and the mass transfer problem can be solved independently. Examination of panels (a), (b) and (c) (corresponding to experiments 1–3) reveals that taking into account the interface-induced advection is essential in order to reproduce the experimental results beyond the first growth stage. Note that this holds although the Péclet numbers here are small, in fact of the order of the dimensionless pressure jumps, i.e. approximately 0.1–0.2. It can be concluded that, although the instantaneous rate of mass transfer may only be

slightly affected by advection, its effect accumulates over time and becomes important to describe the evolution of the bubble when subjected to successive expansion–compression cycles. In fact, neglecting advection will always yield smaller bubble sizes: during growth, advection squeezes the concentration boundary layer around the bubble, thus increasing the concentration gradient and therefore the mass transfer rate of gas into the bubble. Analogously, during shrinkage, advection stretches the boundary layer and smoothens up the gradient, which results in a dissolution slower than that predicted for pure diffusion. In consequence, advection effects accumulate during both growth and dissolution, which makes them noticeable over long times. Contrarily, our numerical results show that taking into account convection barely modifies the calculated radius time evolution. We will get back to the effect of convection below.

Experiment 4, whose results are shown in figure 1.11(d), deserves special attention. The simulation predicts a complete dissolution of the bubble after the first jump in pressure. Interestingly, the experimental dissolution rate is much slower. We hypothesise that there exists a thin stably stratified layer of thickness $\lesssim R_i$ above the substrate oversaturated with CO_2 . This high density layer can easily form during the compression–expansion cycles used to stabilise the bubble size described in §1.2.1. Indeed, we have observed in laser-induced fluorescence experiments reported elsewhere [46] that such a layer can form in a matter of seconds during bubble shrinkage. Notice that the accumulation of CO_2 near the substrate becomes more effective at inhibiting bubble dissolution as the bubble becomes smaller. Contrarily, for the case of bubble growth, such a layer would affect the mass flux in a region that corresponds to the ‘dead zone’ proposed by [34] (see discussion below), which would explain why its existence barely affects experiments 1–3. Thus, for experiment 4, the far-field concentration can no longer be taken as uniform. In fact, we may speculate that this layer is characterised by a vertical concentration gradient bounded by C_{wall} at the wall and C_∞ at the unstratified, bulk fluid.

Our streamfunction–vorticity method has the limitation that the simulation domain covers a small region in the vicinity of the bubble. Imposing a stratified concentration field as the initial condition is ineffective, since the surplus of dissolved CO_2 in this small liquid volume is promptly engulfed by the bubble and a uniform concentration field is quickly established.

We may bypass this limitation by modelling the effect of stratification essentially through just an effective increase (decrease) of mass transfer towards (from) the bubble. It consists in imposing a reduction on $\Delta C = C_i - C_\infty$ as the bubble becomes sufficiently small. This is done by replacing C_∞ by an ‘effective’ far-field concentration, $C_{\infty,eff}(R) \geq C_\infty$, that depends on the current

Figure 1.12: Sketch of the “effective” far-field concentration as a function of the instantaneous bubble radius as a means to model the effect of stratification on the mass transfer rate across the bubble interface

size of the bubble. As the bubble shrinks, the effective far-field concentration increases and so $\Delta C_{eff} = C_i - C_{\infty,eff}$ gets positively closer to zero (slower dissolution) or becomes more negative (faster growth). We propose a concentration profile for the dimensionless ‘effective’ far-field concentration of the form

$$\Upsilon_{eff} = \begin{cases} \Upsilon_{wall} + (\Upsilon - \Upsilon_{wall}) a^{1/2}, & \text{for } a < 1 \\ \Upsilon, & \text{for } a \geq 1 \end{cases} \quad (1.52)$$

where $\Upsilon_{eff} = C_{\infty,eff}/k_H P_0$ and the free parameter $\Upsilon_{wall} = C_{wall}/k_H P_0$ is the extrapolated saturation level at the wall. It is sketched in figure 1.12. Note that the ‘effective’ concentration profile proposed does not, by any means, represent the actual stratification profile that one would observe experimentally. The exponent of $1/2$ on a is chosen arbitrarily, on the grounds that the effect of stratification becomes stronger closer to the wall. For our purposes, a linear relation (exponent of 1 on a) would nonetheless yield similar results.

The replacement of ΔC by ΔC_{eff} can be easily implemented in the mass transfer problem equations through the concentration boundary condition at the bubble interface (1.47b). The dimensionless interfacial concentration defined in (1.48) now becomes

$$c_{i,eff} = c_i - (\Upsilon_{eff} - \Upsilon) = p + \sigma/a - \Upsilon_{eff}. \quad (1.53)$$

For the simulation corresponding to experiment 4, Υ_{eff} was found to vary within a maximum of 10% when taking $\Upsilon = 1.0$ and $\Upsilon_{wall} = 1.25$. Nevertheless, it has a remarkable effect on the mass transfer rates across the bubble in our simulations, as the bubble shrinks to a size comparable to the hypothesised thickness of the layer. We stress that this artificial approach nonetheless portrays the physical significance that a slightly oversaturated layer close the substrate can have a big impact on the bubble dissolution rate.

Figure 1.13: Dimensionless concentration field contours for experiment 2 according to simulation at the instant of time when the bubble radius is $a = 1.05$ during the (a) first growth stage and (b) second growth stage. The darker concentration contours (from pink to green to dark blue) indicate positively increasing values.

We focus now on the history effect. As explained in the introduction, this effect is a manifestation of the influence in the instantaneous concentration field of the previous growth or dissolution stages that the bubble has been subjected to. To illustrate the occurrence of this effect in the current configuration, figure 1.13 shows a comparison of the concentration field for experiment 2 (cf. figure 1.5 and later figure 1.11(b)) obtained at the (a) first and (b) second growth stage at the instant when the bubble radius is of the same size: $a = 1.05$. The history effect on the growth rate is evident: the concentration contours in (b) are noticeably closer together than those in (a). This thinner shell translates to steeper gradients and increased mass transfer, which explains the faster growth rates observed in the second cycle in figures 1.4(c), 1.5(c) and 1.6(c).

The results of our simulations can also be used to validate the hypothesis made by [34] about the existence of a “dead zone” near the contact point where mass transfer is almost zero. As these authors show, the growth rate of a bubble attached to a plate can be computed by considering that the mass flux is uniform along the bubble surface, as given by the spherically symmetric

Figure 1.14: Dimensionless mass-flux across the bubble interface as a function of the angle θ for different times during the first growth stage of experiment 2. The step-like markers indicate the angle θ^* delimiting the effective bubble area available for mass transfer, where $\cos(\theta^*) = -a/(a + \sqrt{\pi\tau})$ according to [34].

solution, except in a region close to the contact point between the bubble and the plate, where it is nearly zero. The boundary of this region is given by the intersection of the plate with a sphere of radius $R + \sqrt{\pi D_m t}$, which approximately corresponds to the outer limit of the concentration boundary layer around the bubble. Therefore, the overall mass flux across the bubble interface can be modelled as if the mass exchange occurred only across an effective area that excludes this zone. In figure 1.14 we plot the local mass flux distribution along the bubble surface for different time instants during the first growth cycle of experiment 2. The step-like markers indicate the start of the dead zone computed using the model by [34]. It can be seen that the effective area predicted by this model agrees fairly well with the region where the mass transfer is nearly uniform, especially at short times.

Finally, we come back to the role of natural convection. Figure 1.15 portrays the structure of the flow and concentration field around a growing bubble assuming there is no natural convection. The boundary layer at the wall due to the no-slip condition is highly distinguishable, as is the vorticity generation at the bubble boundary. It follows that the structure of the flow field is identical for growth and dissolution, except that the direction of the flow velocities are reversed. On the other hand, density-induced natural convection greatly modifies the structure of the flow, as one may observe from figure 1.16. Natural convection breaks down the symmetry of the flow structure when comparing

Figure 1.15: Simulation snapshots for solution (ii) of experiment 1, in which natural convection has been neglected. The snapshots are taken at $\tau = 3.5$, corresponding to the first growth stage (see figure 1.11(a)). These show (a) the velocity field (arrows) and streamlines, (b) the vorticity field contours and (c) the concentration field contours. The darker vorticity and concentration contours (from pink to green to dark blue) indicate positively increasing values.

growth against dissolution. In dissolution, a low velocity recirculation region surrounding the bubble is observed. As a result, the concentration field is stretched upwards in growth and compressed downwards in dissolution. However, despite the changes that convection induces in the velocity field, its effect on the concentration boundary layer near the bubble is minute, as is revealed by the comparison between figures 1.15(c) and 1.16(c). Consequently, under the conditions investigated here, its effect on the bubble radius is barely noticeable. It should be pointed out that, would the growth stage last for longer times, the relatively large value of the Rayleigh number of these experiments ($Ra \sim 20$) suggests that convection should contribute significantly to the growth rate of the bubble, based on recent results by [47]. Indeed, in figure 8 of that paper, it can be appreciated how for a Rayleigh number of approximately 20, the Sherwood number exhibits a noticeable difference with respect to the value for very small Rayleigh numbers. Although the configuration that they explore, a sessile droplet of a liquid heavier than the environment, is different, it is reasonable to conclude that a similar influence might be expected here if the bubble was left to grow indefinitely.

1.6 Conclusions

We have experimentally and numerically explored the influence of the past history of the ambient pressure experienced by a bubble on its instantaneous rate of mass transfer—the so-called history effect. This effect is caused by a history-induced pre-existing concentration boundary layer of dissolved gas

Figure 1.16: Simulation snapshots for solution (i) of experiment 1, which takes into account natural convection. The snapshots of (a) the velocity field and streamlines, (b) the vorticity field contours and (c) the concentration field contours are taken at $\tau = 3.5$, corresponding to the first growth stage (see figure 1.11(a)). Snapshots (d)–(f) show the same fields as (a)–(c) above, but are taken at $\tau = 9.5$, corresponding to the first shrinkage stage. The darker vorticity and concentration contours (from pink to green to dark blue) indicate positively increasing values. The thick black contourlines in (b) and (e) mark the zero-vorticity contour. Despite the significant changes that natural convection induces in the velocity field, its influence on the concentration field in the vicinity of the bubble is minute, as is revealed by the comparison of the iso-concentration lines with and without convection (panel (c) vs. figure 1.15(c)).

that surrounds the bubble at the beginning of a given growth or dissolution stage.

To illustrate the existence of the history effect in practical situations, we report here several experimental results. Firstly, we show that the mass of the bubble, represented by the ambient radius R_0 , can experience transient growths even when the (varying) pressure is kept above saturation at all times. We would naively expect that such a situation would lead to a monotonic dissolution, since the liquid is undersaturated during the whole process.

Secondly, by subjecting the bubble to two consecutive identical expansion–compression cycles, we are able to observe how the history effect becomes manifest in a higher growth rate at the beginning of the second cycle. Thirdly, we report an additional experiment in which the order of the expansion–compression stages has been swapped, obtaining analogous results.

Subsequently, a vorticity–streamfunction formulation has been developed to accurately describe the experimental results reported in the paper, and can be applied to other situations of practical interest in areas such as microfluidics or carbon sequestration.

By performing order of magnitude analyses, we show that our experiments belong to a regime dominated by mass and viscous diffusion. Moreover, the flow around a growing/dissolving bubble in presence of natural convection can be considered quasi-steady, since the viscous time scale is much faster than the time scale of mass transfer. Thus, the momentum equation can be decoupled from the mass transfer problem. The simulations performed with this strategy are able to describe accurately the experimental results in most cases.

One of the most important lessons learnt from these simulations is that boundary-induced advection needs to be taken into account if the bubble radius is to be described accurately. The reason for this is that advection enhances growth and diminishes dissolution, thus its effects accumulate to yield larger bubble sizes. Regarding natural convection, we have seen that it greatly modifies the overall structure of the flow around the bubble, albeit its influence on the concentration boundary layer near the bubble surface—where mass transfer takes place—is only subtle under the conditions explored here, i.e. a bubble subjected to successive growth–dissolution periods rather than one that is left to growth for long times.

Finally, we must point out that our simulation strategy does not describe well the case of a bubble that first dissolves and then grows. An explanation is proposed to fix this problem, which consists in assuming the existence of a stably stratified, CO_2 -rich fluid layer that accumulates on top of the plate. This way, as the bubble size becomes of the order of the layer thickness, the apparent bulk concentration that the bubble sees is higher. Therefore, it dis-

solves more slowly than theory predicts. Our estimations suggest that even slight excesses in the apparent bulk concentration may have a strong effect in the dissolution rate of the bubble.

1.A On the density change with concentration

For dilute solutions far from the solvent's critical point, the partial molar volume of the solvent can be taken as its molar volume in the pure state, and the solute partial molar volumes are independent of concentration [40]. In addition, the concentration of the solute is then approximately proportional to its mole fraction x_g , where $x_g \ll 1$ ($x_g = 0.003$ for a CO_2 -water solution saturated at 5 bar).

Let us then consider a binary solution at pressure P_0 consisting of a single solute CO_2 and solvent (pure water). At the experimental conditions, the ionisation of $\text{CO}_{2(\text{aq})}$ into HCO_3^- and H^+ ions may be neglected since ionic concentrations are low. In fact, we may prove this by defining a molar dissociation ratio (where we first make the dilute solution approximation that molality is proportional to molarity) as

$$\frac{x_{\text{HCO}_3^-}}{x_{\text{CO}_2}} = \frac{x_{\text{H}^+}}{x_{\text{CO}_2}} \approx \sqrt{\frac{K}{x_{\text{CO}_2}}} = \sqrt{\frac{K}{k_H V_l P_0}}, \quad (1.54)$$

where K is the equilibrium constant ($K = 4.17 \cdot 10^{-7}$ at 20°C), k_H is Henry's solubility constant and V_l is the partial molar volume of pure water. We see that the dissociation ratio decreases with pressure or total CO_2 concentration. For pressures from 1 to 8 bars, the ionised form only accounts for around 2.5% down to 1% of the total CO_2 in solution, respectively.

Considering thus a non-ionic binary liquid-gas solution, Henry's law relates the molar concentration and the mole fraction of the solute to its partial pressure P_0 by

$$C = k_H P_0, \quad x_g = k_H V_l P_0, \quad (1.55a, b)$$

where V_l denotes the partial volume of the solvent. The solution density may be obtained from

$$\rho = \rho_l + \Delta\rho = \frac{x_l M_l + x_g M_g}{x_l V_l + x_g \bar{V}_g^\infty}, \quad \text{with} \quad x_g + x_l = 1. \quad (1.56)$$

Here M_l and M_g denote the molar masses of solvent and solute, while $\bar{V}_g^\infty(T)$ is the partial molar volume of the gas at infinite dilution. For dilute solutions,

i.e. in the limit $x_g \rightarrow 0$, the density will change with concentration according to

$$\frac{\partial \rho}{\partial C} \approx \lim_{x_g \rightarrow 0} V_l \frac{\partial \rho}{\partial x_g} = \lim_{x_g \rightarrow 0} V_l \frac{V_l M_g - M_l \bar{V}_g^\infty}{[V_l + (\bar{V}_g^\infty - V_l)x_g]^2} = M_g - \frac{M_l \bar{V}_g^\infty}{V_l}. \quad (1.57)$$

The expression in (1.8) for the concentration expansion coefficient immediately follows.

1.B Boundary conditions

1.B.1 Boundary conditions for velocity

The velocity field at the moving bubble boundary must satisfy both the kinematic and dynamic boundary conditions. The kinematic boundary condition refers to the continuity of the velocity component normal to the interface. We recall that the bubble boundary is described by $\xi = 1$ at all times. The interface normal velocity is thus $u_\xi(\eta, 1)$ and it must be exactly equal to $-u_{rel,\xi}(\eta, 1)$ as derived in §1.4.2. Therefore,

$$u_\xi(\eta, 1) = -\tilde{h}\xi'. \quad (1.58)$$

The dynamic boundary condition refers to the continuity of tangential stress across the interface. Neglecting the viscosity of the gas, this condition reads

$$\frac{\partial}{\partial \eta} \left(\frac{u_\xi}{\tilde{h}} \right) + \frac{\partial}{\partial \xi} \left(\frac{u_\eta}{\tilde{h}} \right) = 0 \quad \text{on} \quad \xi = 1. \quad (1.59)$$

The remaining set of boundary conditions for the dimensionless velocity field are no-slip at wall, zero flow velocity at the contact point and symmetry conditions along the vertical (z) axis:

$$u_\eta(\eta, 0) = 0, \quad u_\xi(\eta, 0) = 0, \quad u_\eta(\infty, \xi) = 0, \quad u_\xi(\infty, \xi) = 0 \quad (1.60a-d)$$

$$u_\eta(0, \xi) = 0, \quad \frac{\partial u_\xi}{\partial \eta}(0, \xi) = 0. \quad (1.60e,f)$$

These boundary conditions are used to determine those for the streamfunction ψ and vorticity scalar ω . It will be seen that the kinetic boundary condition (1.58), the zero normal velocity at the wall (1.60b) and contact point (1.60c), in addition to the zero-normal velocity across the z -axis (1.60e), shall be implicitly enforced by the boundary conditions for ψ . Moreover, the zero-stress boundary condition (1.59), together with the no-slip (zero-tangential velocity) at the wall (1.60a) and symmetry condition at the z -axis (1.60f) are enforced by the boundary conditions for ω . The vorticity boundary condition at the contact point is derived following a special treatment.

1.B.2 Boundary conditions for the streamfunction

From (1.41b), boundary condition (1.60b) implies that $\partial\psi/\partial\eta = 0$. Hence, ψ is constant along the wall. The streamline value along the wall may be arbitrarily set to zero, i.e. $\psi(\eta, 0) = 0$. Following the same argument, (1.60c) implies that the streamfunction value at the contact point is also zero: $\psi(\infty, \xi) = 0$.

From (1.41a) and (1.58), the streamfunction at the bubble boundary must satisfy

$$\frac{\partial\psi}{\partial\eta} = \tilde{h}^2 \tilde{h}_\phi \xi' \quad \text{on} \quad \xi = 1. \quad (1.61)$$

Making use of the definitions for $\tilde{h}$, $\tilde{h}_\phi$ and ξ' provided in (1.34) and (1.37b), analytical integration of (1.61) results in

$$\psi(\eta, 1) = -\frac{2a^2 a'}{\eta^2 + 1} + f(\xi = 1), \quad (1.62)$$

where $f(\xi)$ accounts for the unknown function in ξ that would be obtained had we been able to integrate $\partial\psi/\partial\xi$. Nevertheless, we can easily determine the value of the constant $f(\xi = 1)$ from the boundary condition $\psi(\infty, 1) = 0$. This, of course, yields $f(\xi = 1) = 0$.

Finally, (1.60e) implies that $\partial\psi/\partial\xi = 0$ and therefore $\psi(0, \xi)$ must be constant. Its value is found simply by evaluating (1.62) on $\eta = 0$.

1.B.3 Boundary conditions for vorticity

From (1.13), the velocity components are related to the vorticity ω through

$$\omega = \frac{1}{\tilde{h}^2} \left[\frac{\partial}{\partial\eta} (\tilde{h} u_\xi) - \frac{\partial}{\partial\xi} (\tilde{h} u_\eta) \right]. \quad (1.63)$$

The boundary condition for the vorticity generated at a free surface may be conveniently expressed in terms of the tangential and normal velocity components $u_\eta(\eta, \xi, \tau)$ and $u_\xi(\eta, \xi, \tau)$ [48]. Entering the zero-stress boundary condition (1.59) into (1.63) leads to the following expression for the vorticity at the interface:

$$\omega = \frac{2}{\tilde{h}} \frac{\partial u_\xi}{\partial\eta} + \frac{2}{a} u_\eta \quad \text{on} \quad \xi = 1. \quad (1.64)$$

An analytical expression of the first term may alternatively be obtained directly through (1.58). This results in (1.44b). At the wall, the Dirichlet-type vorticity boundary condition for no-slip

$$\omega = -\frac{1}{\tilde{h}^2 \tilde{h}_\phi} \frac{\partial^2 \psi}{\partial \xi^2} = -\frac{1}{\tilde{h}} \frac{\partial u_\eta}{\partial \xi} \quad \text{on} \quad \xi = 0 \quad (1.65)$$

is usually used. The term $\partial^2\psi/\partial\xi^2$ can be easily expressed in discretised form appealing to Thom's formula [49] or any of its variants [50]. However, we must bear in mind that $\tilde{h}^2\tilde{h}_\phi \rightarrow 0$ as $\eta \rightarrow \infty$, i.e. our coordinate system is singular as it approaches the contact point. As a result, a Dirichlet-type boundary condition at the wall was found to be highly unstable.

[38] employed the zero-vorticity gradient condition $\partial\omega/\partial\xi = 0$. The zero-vorticity gradient assumes a zero-pressure gradient along the wall and consequently there is no vorticity generation at the wall [51]. In other words, the no-slip condition (1.60a) is not enforced.

The no-slip boundary condition may be alternatively imposed by Lighthill's dynamic description of vorticity. The idea is that the spurious non-zero slip velocity at the wall, i.e. $u_\eta(\eta, 0) \neq 0$, obtained by numerically differentiating ψ , should be counteracted by artificially creating vorticity on the wall. [52] derived a Neumann-type vorticity boundary condition for no slip,

$$\nu \left. \frac{\partial\Omega}{\partial n} \right|_{\text{wall}} = -\frac{U_t}{\Delta t}, \quad (1.66)$$

where $\partial/\partial n = \hat{\mathbf{n}} \cdot \nabla$ denotes the directional derivative in the direction normal to the wall, U_t is the spurious velocity tangential to the wall, and Δt denotes a small interval of time (computational time step) in the viscous time scale t_v (cf. §1.3.4) in which the vorticity flux is assumed constant. In our dimensionless variables, this vorticity boundary condition becomes

$$\frac{\partial\omega}{\partial\xi} = \frac{\tilde{h}u_\eta}{Sc\Delta\tau_v} \quad \text{on} \quad \xi = 0, \quad (1.67)$$

where $\Delta\tau_v$ is the viscous computational time step (see §1.4.5).

The geometry of the bubble very close to the contact line can be approximated by a two-dimensional wedge with contact angle θ and polar coordinates (r, φ) . In viscous corner flow, inertial effects may be neglected and Stokes momentum equation is described by the biharmonic equation $\nabla^4\psi = 0$.

An approximate yet acceptable boundary condition for vorticity at the contact point ($\eta = \infty$) may be determined from the flow solution to the contact line pinning (CR mode) scenario. The bubble surface is then taken as a hinged plane on $\varphi = \theta$ which rotates around the origin with angular velocity θ' on which the zero-shear stress condition applies. The horizontal plane ($\varphi = 0$) is a solid wall at rest which is impermeable and allows no slip. Dimensional analysis gives a solution of the form [53, 54]

$$\psi = \theta' r^2 f(\varphi), \quad (1.68)$$

where $f(\varphi)$ is a suitable function. Hence, the vorticity close to the contact line must be independent of r , i.e. $\omega = \omega(\varphi)$. As $\eta \rightarrow \infty$, it may be shown that

$\varphi \rightarrow \theta\xi$, which leads to the zero-vorticity gradient condition $\partial\omega/\partial\eta = 0$ across the contact line.

Finally, referring to (1.60e) and (1.60f) to evaluate (1.63) on $\eta = 0$ results in a zero-vorticity boundary condition (consistent with symmetry) on the z -axis.

1.C Transformation matrix

Any vector expressed in Cartesian coordinates, $\mathbf{v}_{\{x,y,z\}} = v_x \hat{\mathbf{e}}_x + v_y \hat{\mathbf{e}}_y + v_z \hat{\mathbf{e}}_z$, may be mapped to tangent-sphere coordinates $\mathbf{v}_{\{\eta,\xi,\phi\}} = v_\eta \hat{\mathbf{e}}_\eta + v_\xi \hat{\mathbf{e}}_\xi + v_\phi \hat{\mathbf{e}}_\phi$ by

$$\mathbf{v}_{\{x,y,z\}} = \mathbf{J} \mathbf{v}_{\{\eta,\xi,\phi\}}, \quad (1.69)$$

with

$$\mathbf{J} = \begin{bmatrix} -\frac{\eta^2 - \xi^2}{\nu^2 + \xi^2} \cos \phi & -\frac{2\eta\xi}{\nu^2 + \xi^2} \cos \phi & -\sin \phi \\ -\frac{\eta^2 - \xi^2}{\nu^2 + \xi^2} \sin \phi & -\frac{2\eta\xi}{\nu^2 + \xi^2} \sin \phi & \cos \phi \\ -\frac{2\eta\xi}{\nu^2 + \xi^2} & \frac{\eta^2 - \xi^2}{\nu^2 + \xi^2} & 0 \end{bmatrix}. \quad (1.70)$$

Since $\mathbf{J}$ is orthogonal, then $\mathbf{v}_{\{\eta,\xi,\phi\}} = \mathbf{J}^T \mathbf{v}_{\{x,y,z\}}$ gives the opposite transformation. This is useful for plotting purposes, since the Cartesian velocity components in the x - z plane ($\phi = 0$) may be easily obtained from u_η and u_ξ as follows:

$$u_x = -\frac{(\eta^2 - \xi^2)u_\eta + 2\eta\xi u_\xi}{\nu^2 + \xi^2}, \quad u_z = \frac{(\eta^2 - \xi^2)u_\xi - 2\eta\xi u_\eta}{\nu^2 + \xi^2}. \quad (1.71a, b)$$

2

Gas depletion through single gas bubble diffusive growth *

When a gas bubble grows by diffusion in a gas-liquid solution, it affects the distribution of gas in its surroundings. If the density of the solution is sensitive to the local amount of dissolved gas, there is the potential for the onset of natural convection, which will affect the bubble growth rate. The experimental study of the successive quasi-static growth of many bubbles from the same nucleation site described in this paper illustrates some consequences of this effect. The enhanced growth due to convection causes a local depletion of dissolved gas in the neighbourhood of each bubble beyond that due to pure diffusion. The quantitative data of sequential bubble growth provided in the paper show that the radius-versus-time curves of subsequent bubbles differ from each other due to this phenomenon. A simplified model accounting for the local depletion is able to collapse the experimental curves and to predict the progressively increasing bubble detachment times.

2.1 Introduction

Diffusive processes leading to bubble formation are present in many different situations, such as gas-driven volcanic eruptions [2], bubble growth in porous

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media [55] affecting, among others, oil production [4], bubbles emerging in carbonated beverages [7, 56, 57] such as beer [6] and the recently discovered nanobubbles [15]. Several different physical processes affect bubble nucleation and growth in all these situations: diffusion, history effects (as in [Ch.1, 27, 32]), electrolysis [11, 12], catalysis [14], ultrasound [58] and others. In view of these and many other occurrences, the study of bubble diffusive growth has been actively pursued for a long time, starting with the seminal works by Epstein & Plesset [25], Scriven [42] and others. More recently, due to new developments in experimental techniques [see e.g. 34] and new applications, such as energy generation by chemical reactions [13], the topic has been the object of renewed attention.

In most previous studies, the long-term effects due to the gas depletion of the volume surrounding a bubble nucleation site have not been studied in detail. Although this depletion has limited effects on electrolytic bubble growth [11, 12], where gas is continuously generated, it has very marked consequences in the situation in which the overall initial dissolved gas concentration in the liquid is fixed. In this article, we qualitatively and quantitatively deal with gas depletion effects when successive bubbles quasi-statically grow by diffusion on a silicon chip. We follow the growth of several tens of bubbles from the same nucleation site. Due to the small mass diffusivity of gases in liquids, this process is very slow and each bubble takes many minutes to grow to its final radius before detaching due to buoyancy. We will however find that also convective effects, which less surprisingly appear in strongly supersaturated gas-liquid solutions [59, 60], also play a very subtle but dominant role towards the end of the bubble growth for a weak supersaturation level.

From a modelling point of view, the pure diffusion-driven growth of a spherical gas bubble in an infinite supersaturated liquid is a well-known problem whose dynamical equation has the following form [25]:

$$\frac{dR}{dt} = D \frac{c_s}{\rho_g} \left(\frac{1}{R} + \frac{1}{(\pi D t)^{\frac{1}{2}}} \right) \zeta, \quad (2.1)$$

where D is the diffusion coefficient, c_s is the dissolved gas concentration by mass at the bubble surface, ρ_g is the gas density in the bubble and ζ is the supersaturation level, defined as

$$\zeta = \frac{c_0 - c_s}{c_s}, \quad (2.2)$$

with c_0 being the ambient dissolved gas concentration in the liquid. This

2. Gas depletion through single gas bubble diffusive growth

equation can be readily solved by defining two dimensionless variables, namely

$$\epsilon \equiv \frac{R}{R_0}, \quad x \equiv \sqrt{\left(\frac{2D\zeta c_s}{\rho_g R_0^2}\right)} t, \quad (2.3)$$

where R_0 is a reference radius which [25] identify with the initial bubble radius. The simplified solution can be written as

$$\epsilon \approx \left(\gamma + (1 + \gamma^2)^{\frac{1}{2}}\right) x \equiv Sx, \quad (2.4)$$

where $\gamma = \sqrt{\zeta c_s / 2\pi \rho_g}$. As mentioned before, this solution is valid for a bubble growing in an unbounded domain, or in other words, an infinite bulk. The dynamical equation (2.1) needs to be modified when the bubble grows on a solid surface, which changes the boundary conditions to be applied to the solution of the diffusion equation [58]. [34] approximated the effect of the solid surface by introducing the concept of an effective area through which gas diffuses into the bubble. In their experiment, the bubble grew out of a pit of radius R_p on the solid surface. They set $R_0 = R_p$ in equation (2.3) and found:

$$\epsilon \approx \left(\gamma + \left(\frac{1}{2} + \gamma^2\right)^{\frac{1}{2}}\right) x \equiv S^* x. \quad (2.5)$$

Since the parameter S^* is evidently smaller than S , the bubble is predicted to grow on a solid surface at a smaller rate in comparison to a bubble in an unbounded liquid.

2.2 Experimental set-up

To grow bubbles in a controlled way, we use the set-up documented in [37]. The system mainly consists of two containers which are used, one to prepare the gas-liquid solution, and the other to perform the experiments. Pressure and temperature are controlled throughout the whole experiment. The bubbles grow out of a pit etched on a silicon chip, which ensures a growth on a designated spot. The pit is coated with black silicon, an extremely hydrophobic material.

Our procedure starts with the preparation of a saturated solution of carbon dioxide and ultra-pure degassed water at a certain pressure and temperature. The concentration c of CO_2 in the solution depends on temperature and pressure, according to Henry's law (originally documented in [26], see also e.g. [61]):

$$c(T, P) = k_H(T)P, \quad (2.6)$$

Figure 2.1: (a) Schematic of the experimental set-up. The gas-liquid solution is introduced into the tank through the valve V1. By lowering the pressure by means of the controller, the solution becomes supersaturated and bubbles grow on the designed location on the chip. The images are recorded through the lateral glass window. (b) Bubble cycle: nucleation, growth and detachment. The sequence corresponds to the first bubble growing on the substrate after the pressure decrease. It can be appreciated that the bubble gains an almost perfect spherical shape from the very early stages after nucleation. The last snapshot in the sequence corresponds to the moment prior to detachment.

where k_H is a decreasing function of temperature and P is the pressure. This relation shows that, after reaching thermodynamic equilibrium, a solution can become supersaturated either by increasing the temperature or decreasing the pressure. Experimentally, the easier option is the latter one, which we adopt in this study. After preparing a saturated solution in the high pressure tank, we transfer it to the other container, in which the chip has been previously introduced and all other gases have been removed by flushing with CO_2 . The diameter of the experimental vessel (12 cm) is much larger than any bubble radius at detachment ($\sim 300 \mu\text{m}$), therefore any wall effect can be neglected. After lowering the pressure in the latter, according to equation (2.6), the liquid becomes supersaturated and bubbles start to grow on the desired spot. We record the succession of bubbles through a lateral window on the walls of the experimental tank, see figure 2.1.

In the performed experiments, the temperature was measured to be 20.7°C for all the cases. We created the saturated condition at a pressure of 914 kPa (9.14 bars). Under this condition, the water contains around 15.5 kg/m^3 of dissolved CO_2 . Decreasing its value to 810 kPa (8.01 bars), we obtain a gas excess of approximately 2 kg/m^3 , which needs to be released in the form of bubbles. Thus, we achieve a supersaturation level $\zeta = 0.14$ which is small enough to assume a quasi-static diffusion-driven evolution [see e.g. 34]. For most of the bubble growth time, we can therefore neglect convective effects, except for the middle-late stages of the bubble growth, in which natural convection becomes important (see below). Accordingly, advective effects caused by concentration difference are also neglected. The diffusivity has a value of $D = 1.78 \cdot 10^{-9} \text{ m}^2/\text{s}$ at saturation [62–64], whereas the surface tension is $\sigma = 0.059 \text{ N/m}$ ([65], lower than the value for pure water due to the high pressure level and the large amount of dissolved gas, as can be found in [66]), the mixture density is $\rho_m = 1016.7 \text{ kg/m}^3$ [67, 68] and the gas density is $\rho_g = 14.53 \text{ kg/m}^3$ [69]. These parameters are necessary for computing the dimensionless values ϵ , x and γ , and the value of the bubble detachment radius (defined in the next section). Under these conditions, the temperature change due to cooling by evaporation has been calculated to be of the order of $\Delta T \approx 1 \mu\text{K}$. Therefore, this effect can be disregarded throughout the whole experiment.

2.3 Analysis of experiments

We analyse a long succession of bubbles nucleating, growing and detaching from the same pit over many hours, as depicted in figure 2.2, focusing on the differences between the first and latest bubbles. It can be clearly detected that, as time goes by and many bubbles have been growing and detaching,

Figure 2.2: The radius of successive bubbles as function of time (solid line). The vertical portions represent the detachment of each bubble, followed by the nucleation of the subsequent one. Dots indicate the detachment radius. The dotted line at the top is the radius given by Fritz's formula (2.7). The dashed line shows the corrected value considering the effective pinch-off radius, see figure 2.3(a) and equation (2.8). The detachment frequency progressively decreases, as later bubbles grow more slowly due to the depletion effect studied in this paper.

2. Gas depletion through single gas bubble diffusive growth

the growth rate decreases significantly. In addition, figure 2.2 represents the bubble detachment radius over time. The maximum value of the detachment radius is given by Fritz's formula, which is derived by balancing the buoyancy force for a perfect sphere, $F_b = (4/3)\pi R^3(\rho_m - \rho_g)g$, with the capillary force for a bubble attached to the pit of radius $R_p = 10 \mu\text{m}$ at the point where the buoyancy exceeds the maximum force that surface tension can exert, $F_c = 2\pi\sigma R_p$ [70, 71]:

$$R_{det} = \left(\frac{3\sigma R_p}{2(\rho_m - \rho_g)g} \right)^{\frac{1}{3}}, \quad (2.7)$$

where g is the gravity acceleration. In our case, bubbles are attached to the inside of the pit, forming a neck between the trapped gas and the actual bubble growing outside, see figure 2.3. The neck radius is effectively smaller than the pit radius. We can thus correct equation (2.7), accounting for the smaller neck radius, i.e. the effective pit radius R_{eff} , $F_c = 2\pi R_{eff}\sigma$. In that case, the following expression for the detachment radius is obtained:

$$R_{det} = \left(\frac{3\sigma R_{eff}}{2(\rho_m - \rho_g)g} \right)^{\frac{1}{3}}. \quad (2.8)$$

From figure 2.3(b), the neck radius can be measured to be $4 \mu\text{m}$, evidently smaller than the nominal pit radius. The correction accounting for this effective smaller radius is represented in figure 2.2 by the dashed line, presenting excellent agreement. From the same figure, it can be appreciated that the detachment radius barely changes in the succession. Therefore, we conclude that depletion does not affect the equilibrium of forces which determine the detachment radius, but it does play a role in the detachment time and the way bubbles grow.

To study the effect of successively growing bubbles, we need to understand how gas diffuses through the concentration boundary layer formed around the bubble while it grows. The thickness of the diffusion layer increases according to $\delta \sim \sqrt{\pi D t}$. However, once a bubble detaches, part of this layer, together with the absorbed gas, is taken away by the bubble, also breaking the approximately spherical symmetry of the diffusion layer as the bubble escapes rapidly from the chip. To study how gas depletion will affect future bubbles, we need to analyse the growth rates after successive bubbles have been growing, see figures 2.4(a) and (b). The oscillations in the latter figure are due to the numerical differentiation of the data in the former one.

In addition, since the bubbles in our experiment have typical detachment radius $R_{det} \approx 0.3 \text{ mm}$, their (terminal) rise velocity in water is of the order of $U_r \sim 5 \text{ cm/s}$. This terminal velocity can be regarded as an upper limit to our

Figure 2.3: (a) Sketch of a bubble attached to the hydrophobic pit (not to scale). The bubble detaches from a neck smaller than the pit radius. The detached gas volume is estimated as that of a perfect sphere. The error by assuming perfect sphericity and by neglecting the gas contained in the pit has been calculated to be smaller than 0.3%. (b) Detail of the bubble just before detachment. The circle indicates the opening of the pit, which is larger than the stem from which the bubble detaches (curved lines). (c) Scanning electron microscopy (SEM) image of the hydrophobic pit. The black silicon coating the bottom of the pit provides the preferential spot for bubble nucleation and growth.

case scenario. This leads to a Reynolds number $Re \sim 15$, and consequently both viscous and inertial effects may be important. Bubbles then rise to the free surface, which is typically ~ 5 cm above the substrate, in approximately one second. Assuming dominance of the Stokeslet term and a characteristic length corresponding to the bubble radius at detachment (due to the presence of the chip, the distance to the closest boundary is the appropriate length scale), the magnitude of the velocity near the chip during the rise of the bubble will be set by $u(t) \sim UR_{det}/(R_{det} + U_r t)$, where U is a characteristic bubble velocity at the chip surface. So the velocity will decay approximately as R_{det}/t during most of this rising process. Any possibly present residual inertial fluid motion near the substrate will damp out due to the presence of the chip. The time in which this happens is set by the speed at which the chip momentum boundary layer grows (approximately $\delta_m \sim \sqrt{\nu t} \sim R_{det}$), such that this time can be estimated as $t \sim R_{det}^2/\nu$, where $\nu = 9.58 \cdot 10^{-7} \text{ m}^2/\text{s}$ is the kinematic viscosity of water [39, 64]. This time is calculated to be of the order of tenths of a second. One could argue that one should multiply this time with a rather large number because in most of the momentum boundary layer the velocity would be closer to that in the bulk rather than that at the substrate, but it will still be of the order of seconds at most. Therefore, both rising and damping time are very small compared to the bubble growth time

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Figure 2.4: (a) Evolution of the bubble radius normalised by the pit radius R_p as a function of the dimensionless parameter $x \propto \sqrt{t}$ defined in equation (2.3) for several bubbles from the sequence in figure 2.2. The line marked Epstein & Plesset represents the simplified expression in (2.4) and the line marked Enríquez *et al.* its modification (2.5) correcting for the presence of the chip. (b) Dimensionless growth rate $(1/S^*) (d/dx)(R/R_p)$ vs. dimensionless time x for the same bubbles plotted in (a). The line marked Epstein & Plesset (with asymptote S/S^*) shows the exact solution given by these authors; the Enríquez *et al.* line accounting for the presence of the chip asymptotes to 1.

(several minutes) and even to the time it takes for a bubble to renucleate after the previous one has detached, which in our experiments is typically of the order of ten seconds or longer. This implies that every new bubble starts to grow in liquid that is essentially quiescent and convective flows remaining from the rise of the previous bubble play no significant role.

The initial bubbles follow the tendency of the simplified Epstein & Plesset solution (2.4) corrected for the presence of the chip, equation (2.5). From the middle stages of the bubble growth until its detachment, there is a final faster volume increase which results from the onset of density-driven convection, as found in [34]. As subsequent bubbles grow and detach, the experimental data no longer approach the theoretically predicted behaviour. This is the first indication of depletion, which appears in figure 2.4(a) from the fifth bubble on. In figure 2.4(b), there are two main events occurring for later bubbles in the sequence: the plateau indicating the diffusive regime reaches a decreasingly lower value than the predicted one and the upward slope starting at $x \approx 20$ (which is attributed to the onset of convection) becomes more and more horizontal, i.e. the change from diffusion to convection at these late stages becomes less pronounced. To quantify these effects, we plot in figure 2.5(a) the value of the saturation plateau for each bubble in the sequence, whereas in figure 2.5(b) we represent the slope values corresponding to the convective regime

Figure 2.5: (a) Saturation plateau in the intermediate stage of bubble growth ($5 \leq x \leq 20$ in figure 2.4(b)) and (b) convective slope gradient in the final stages of the growth ($20 \leq x$, see text). The decreasing tendency in (a) suggest that diffusive growth suffers from gas depletion caused by the growth of earlier bubbles. The decrease in (b) shows that the convective contribution to mass transfer progressively decreases for the same reason.

in the final stages of the growth. To generate these values, we use the last 30 data points of each bubble to fit the slope and the previous ones to generate the plateau (ignoring the first 10 points). We repeated the process varying the number of points between 25 and 35, finding very similar results.

For further analysis, it is convenient to introduce two dimensionless numbers, namely the Sherwood and Rayleigh numbers. The Sherwood number is the dimensionless mass transfer rate into the bubble,

$$Sh = \frac{2\rho_g R \dot{R}}{D(c_0 - c_s)}, \quad (2.9)$$

where $\dot{R}$ is the growth rate. The Rayleigh number represents the ratio of buoyancy to viscous forces and diffusive effects:

$$Ra = \frac{g\lambda_c(c_0 - c_s)(2R)^3}{\nu D}, \quad (2.10)$$

where λ_c is the concentration expansion coefficient, defined by

$$\lambda_c = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial c} \right)_{P,T} \approx \frac{1}{\rho_{m,0}} \frac{\rho_{m,s} - \rho_{m,0}}{c_s - c_0}, \quad (2.11)$$

where subindices 0 and s refer to the states at saturated and supersaturated conditions, respectively. For our specific case, λ_c has a value of $6.5 \cdot 10^{-4}$

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m^3/kg . Often, λ_c is approximated by $\lambda_c = (M_g/\rho_l) - \bar{V}_g$ [39], where M_g is the molecular mass of the gas, ρ_l is the liquid density and $\bar{V}_g$ is the partial volume of the gas in the mixture. However, this partial volume cannot be measured with the desired precision by the means we have access to; therefore, we have used the original definition as in (2.11).

In case of steady-state density-driven convection around a sphere in an infinite medium, Sh depends on Ra as [see e.g. 72, 73]:

$$Sh = 2 + K Ra^{\frac{1}{4}}, \quad (2.12)$$

where 2 is the Sherwood number corresponding to pure diffusion (which occurs when $Ra \ll 1$) and K is a fitting constant which is found to be 0.569 according to [74] and 0.535 as reported by [75]. As documented in [34], plotting the experimental results for Sh vs. Ra , the change from diffusion to convection can be detected, since during the early stages of growth ($Ra < 10$), we experimentally find that Sh remains approximately constant irrespectively of the value of Ra , whereas above $Ra \approx 10^2$, the experimental curves start increasing proportionally to $Ra^{1/4}$ as in (2.12). Note that the relation (2.12) also holds for the case of a dissolving droplet with lower density as that of the surrounding solvent, as documented in [47].

Rewriting Sh and Ra with the dimensionless parameters defined in (2.3), we obtain the following expressions:

$$Sh = 2 \frac{\epsilon}{x} \frac{d\epsilon}{dx}, \quad (2.13a)$$

$$Ra = \frac{8g\lambda_c(c_0 - c_s)R_p^3\epsilon^3}{\nu D}. \quad (2.13b)$$

The experimental results for these quantities are plotted in figure 2.6(a). For subsequent bubbles, the evolution differs from the first bubble, which grows in an homogeneous, non-perturbed environment: the horizontal portion of the curves, corresponding to purely diffusive behaviour, gradually decreases below the value $Sh = 2$, indicating depletion of the concentration field around the bubble.

2.4 Simplified model of gas depletion effects

To model the depletion occurring around the n -th bubble, let us assume that it grows in a locally depleted region where the concentration c_n is smaller than the concentration c_0 in the bulk far away from the nucleation site (see figure 2.7). We now define a depletion number,

$$\Upsilon_n = \frac{c_n - c_s}{c_0 - c_s}. \quad (2.14)$$

Figure 2.6: (a) The data of figure 2.4 replotted in the form of Sherwood number Sh vs. Rayleigh number Ra ; the continuous curve represents equation (2.12). (b) Sherwood number $\tilde{Sh}$ vs. Rayleigh number $\tilde{Ra}$ compensated for the local depletion of the solution as explained in the text.

For the first bubble, of course, $c_1 = c_0$ and therefore, $\Upsilon_1 = 1$. We can define the local Sherwood and Rayleigh numbers, $\tilde{Sh}_n$ and $\tilde{Ra}_n$:

$$\tilde{Sh}_n = \frac{2\rho_g R \dot{R}}{D(c_n - c_s)} = \frac{Sh}{\Upsilon_n} \quad (2.15a)$$

$$\tilde{Ra}_n = \frac{g\lambda_c(c_n - c_s)(2R)^3}{\nu D} = \Upsilon_n Ra, \quad (2.15b)$$

A test of this simple conceptual model can be carried out by trying to collapse all the data of figure 2.6(a) referring to the first bubble using Υ_n as a fitting parameter. Υ_n is thus adapted to achieve a universal curve $\tilde{Sh}_n(\tilde{Ra}_n)$. The results for this curve are shown in figure 2.6(b). The various values of Υ_n turn out to decrease for successive bubbles, i.e. the gas concentration surrounding the bubble is reduced from cycle to cycle, see figure 2.8(a). Equation (2.12) can be similarly adjusted to fit the experimental data rewriting it in terms of $\tilde{Sh}_n$ and $\tilde{Ra}_n$.

By the definition (2.15b) and the results in figure 2.6(b), we find that the maximum local Rayleigh number $\tilde{Ra}_n$ attained before detachment decreases for successive bubbles, which is an indicator that convection diminishes, which agrees with the decrease of mass transfer as subsequent bubbles keep growing and detaching, together with the diminishing slope represented in figure 2.5(b).

Before providing a theoretical estimate of the depletion number Υ_n , we now first discuss the origin of the depletion effect in a more qualitatively manner. If the bubble could be modelled as a time-independent mass sink and if diffusion

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Figure 2.7: (a) Schematic of the gas depleted volume around a growing bubble after the growth and detachment of several previous ones. The bubble depicted is surrounded by a depleted solution with a concentration c_n smaller than the initial one c_0 , which still prevails at further distances. Because of the convective contribution to mass transfer, which is faster than can be replenished by diffusion, each bubble leaves behind a depleted volume of liquid as it detaches. This effect is expressed in the image by a less intense colour around the bubble. (b) The upper boundary of each colour band depicts the gas concentration for pure diffusion. The lower boundary is the gas concentration as modified by the effect of convection. The area bounded by the two lines thus illustrates the gas depletion caused by convection. The dashed lines on the right are the edge of the diffusion layer generated by each bubble (not to scale). The vertical dotted lines show the effective extent of the volume from which each bubble receives gas; α is a fitting parameter introduced in equation (2.18).

alone were to be considered, a steady state would be rapidly reached in which the mass transfer towards the bubble will be exactly equilibrated by the gas diffusion from the bulk to the bubble surroundings. The concentration in a purely diffusive problem decays proportionally to $1/r$ (as seen in many text books, such as [72]), where r refers to the radial distance measured from the point sink; thus, the gradient of concentration proportionally changes to $1/r^2$, which is constant at every defined r and independent of time. Therefore, if diffusion alone is set, then depletion does not occur, since the gradient of concentration will be exactly the same for all times, i.e. there would be an exact balance between the gas removed by the bubble and the gas diffusing from the bulk liquid. When, however, natural convection starts to occur, the mass flow into the bubble is enhanced and therefore, more gas will be locally transported into the bubble than is supplied by the steady state diffusion profile, leading to a local depletion in the region that surrounds the bubble. This depletion occurs at least as long as the convective transfer is not strong enough to transport gas-depleted liquid outside the immediate surroundings of the bubble.

Additionally, there are two other effects that need to be taken into account. The first is that a bubble growing in a homogeneously supersaturated liquid according to the diffusive Epstein & Plesset law, equation (2.5), is never in a steady state. It can be easily verified from the approximate law $R(t) \propto \sqrt{t}$ that the mass flow rate into the bubble is not constant but proportional to $\sqrt{t}$ as well. Moreover, it can be shown that also the diffusive boundary layer grows as $\sqrt{t}$. If one would consider a series of bubbles diffusively growing from the same spot and if each bubble would detach as soon as it reaches its detachment radius, equation (2.8), then after a couple of bubbles a diffusive steady state would be reached similar to the one discussed in the previous paragraph, and natural convection would be needed to create a sustained depletion effect as was observed in our experiments. Therefore, we conclude that more gas is absorbed by each bubble than would be supplied by diffusion alone: this excess gas is supplied by convection. As a result, each subsequent bubble grows in a new environment in which the local concentration is lower than for the previous one, with a correspondingly lower growth rate. The second additional effect is that there is a flow connected to the detachment of the bubble. As each bubble rises, it advects a volume of liquid of the order of half the bubble volume away from the region where the bubble grows. As a result of the need to refill the space that is left by the rising bubble and the liquid advected with it, the liquid in the bubble growth region will get mixed with liquid that is less gas depleted coming from somewhat farther away. From the Stokeslet term, we can estimate the typical distance d_f travelled by a fluid particle during this

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event by integrating the velocity near the chip $u(t)$ over the rising time, which gives $d_f \sim \log(t_r/t_0)$, where $t_0 = R_{det}/U_r \approx 0.3 \cdot 10^{-3}/5 \cdot 10^{-2} = 15$ ms and the rising time $t_r \approx 1$ s. So $d_f \approx 2R_{det} \approx 0.6$ mm. This implies that the fluid that is mixed during the detachment event typically comes from within the diffusive boundary layer around the bubble.

Of course, all the above contributions to the depletion effect are difficult to model. For a quantitative estimate of the successive values of the depletion number Υ_n , we therefore assume that, at the start of the growth of the n -th bubble, the concentration of dissolved gas in the surrounding liquid is smaller than if the preceding bubble had grown by pure diffusion. A quantitative measure of this effect can be based on the before-mentioned solution of the diffusion equation in the presence of a point sink (derived in Appendix 2.A):

$$c = c_n - \frac{\dot{m}_n}{4\pi Dr} \operatorname{erfc}\left(\frac{r}{2\sqrt{Dt}}\right), \quad (2.16)$$

where erfc is the complementary error function and $\dot{m}_n$ is the average mass loss rate value approximated from the gas content of the detached bubble as

$$\dot{m}_n = \frac{4\pi\rho_g R_{det}^3}{3t_{det,n}}, \quad (2.17)$$

with $t_{det,n}$ the experimentally measured detachment time of the n -th bubble and R_{det} the detachment radius, common for all the bubbles. This defined mass loss rate is larger than the one which would be found in the case of pure diffusion. The solution (2.16) only describes the concentration field up to a distance of the order of $\sqrt{\pi Dt_{det,n}}$ from the bubble. As a justification for the use of the point sink approximation, we may note that the ratio $\sqrt{\pi Dt_{det,n}}/R_{det}$ increases from approximately 4 for the first few bubbles to nearly 30 for the later ones: the depletion eats deeply into the gas reservoir. Further out, the concentration tends to the bulk value c_0 , see figure 2.7(b). We now identify the concentration c as given by (2.16) with $r = R_{det} + \alpha\sqrt{\pi Dt_{det,n}}$ (with α a fitting parameter which characterises the distance within the diffusive boundary layer in which the depleted concentration for the subsequent bubble in the succession will be defined) as c_{n+1} , the ambient concentration in which the next bubble will grow. With this identification, we find:

$$\Upsilon_{n+1} = \Upsilon_n - \frac{\dot{m}_n}{4\pi D(c_0 - c_s)(R_{det} + \alpha\sqrt{\pi Dt_{det,n}})} \operatorname{erfc}\left(\frac{R_{det} + \alpha\sqrt{\pi Dt_{det,n}}}{2\sqrt{Dt_{det,n}}}\right). \quad (2.18)$$

This equation is solved by an iterative process in which the depletion number depends on the corresponding depletion number of the previous bubble

Figure 2.8: (a) The depletion number Υ_n , defined in (2.14) for successive bubbles. The decrease of this number from 1 gives an indication of the progressive depletion of the solution surrounding each bubble. The dots are the experimental points and the line is the theoretical prediction according to equation (2.18), which is linearised in time in order to join the calculated discrete points. (b) The detachment time of successive bubbles: comparison between experiments (dots) and the approximate prediction of equation (2.19) (line).

growing in succession. We compare both the experimental data and the predicted theoretical behaviour, with best fitting constant $\alpha = 0.72$, in figure 2.8(a). This value of α is reasonable as one would expect c to tend to c_n at the edge of the diffusion layer corresponding to the n -th bubble, for which $\alpha \sim 1$. The agreement of this somewhat crude model is gratifying. As an explanation of this somewhat surprising result, it may be noted that, in spite of its foundation on pure diffusion, the effect of convection is implicitly included in the use of the experimentally determined value of $\dot{m}_n$, as given by (2.17). Thus, (2.16) represents the equivalent concentration field that would produce the mass rate $\dot{m}_n$ if diffusion were the only process in play. The so-defined model does not directly face the onset of convection and mixing, but accounts for their effect in an indirect way.

The detachment time for successive bubbles can be estimated using the depletion number and combining equations (2.5) and (2.8), yielding

$$t_{det,n} = \frac{\rho_g R_{det}^2}{2\tilde{S}_n^*{}^2 D \tilde{\zeta}_n c_0}. \quad (2.19)$$

This detachment time only considers diffusion-driven processes, as it is derived from a pure diffusion equation. The change due to the depletion of the bubble

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surroundings needs to be accounted for in the parameters $\tilde{\zeta}_n$ and $\tilde{S}_n^*$, namely

$$\tilde{\zeta}_n = \zeta \Upsilon_n, \quad \tilde{S}_n^* = \sqrt{\frac{\tilde{\zeta}_n c_0}{2\pi\rho_g}} + \left(\frac{1}{2} + \frac{\tilde{\zeta}_n c_0}{2\pi\rho_g} \right)^{\frac{1}{2}}. \quad (2.20)$$

The results for the corrected detachment time accounting for depletion effects are presented in figure 2.8(b), where they are seen to be compatible with the data, displaying qualitative agreement between experiments and theory. It is good to note that the comparatively large difference between model and experiment in figure 2.8(b) originates from the fact that equation (2.19) is based on pure diffusion and does not at all account for the enhanced growth caused by the onset of natural convection during the bubble growth. Nevertheless, the estimation (2.19) gives a good approximation for the increase in detachment time as bubbles keep growing in succession.

2.5 Conclusions

The origin of depletion effects in the successive diffusive growth of gas bubbles from the same nucleation site has been experimentally studied. A simplify theory has been described which is able to account for the basic features of the data. The depletion effect is caused by the contribution of natural convection to the bubble growth beyond the purely diffusive process. Thus, depletion occurs because diffusion is unable to replace the extra gas supplied by convection and removed by the detaching bubbles. The progressively increasing depletion reduces the mass transfer towards the bubbles and, therefore, their growth rate. The radius-versus-time curves of successive bubbles are different from each other, but can be collapsed through the introduction of a dimensionless depletion number Υ_n , which can quantitatively account for the decrease of the local gas concentration around the bubble due to depletion. As a result, every bubble evolution curve can be adjusted to a universal evolution curve which accounts for diffusion when the Rayleigh number Ra is small and changes afterwards to density-driven convection as Ra becomes larger and larger. A first estimation of the detachment time can be also calculated from this depletion number, qualitatively accounting for the increase in the time bubbles take to grow and detach. Because of the depletion effect, the analytical solution given by [25] and adapted by [34] is found to be valid only for the growth of the first few bubbles.

2.A Solution for the point sink diffusion-driven mass transfer equation

For the derivation of equation (2.16), we start from the diffusive mass transfer equation in spherical coordinates, assuming that each bubble n grows in an infinite domain in which the starting concentration corresponds to the depleted concentration c_n left after the previous bubble growth:

$$\frac{\partial \Delta c}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Delta c}{\partial r} \right), \quad (2.21)$$

where $\Delta c = c - c_n$ is the concentration change with respect to a starting concentration level c_n . Since the mass transfer partial differential equation (PDE) (2.21) depends on two variables, one of them being involved in a second partial derivative, three boundary conditions are needed to complete the final solution. As opposed to the Epstein & Plesset [25] solution, equation (2.4), in which the conditions were given close to the bubble limit, we take a farther approach, namely, bubbles will be considered as a gas sink, studying the evolution of the surroundings of that point, which is extracting gas from the environment. Therefore, the boundary conditions can be written as:

$$\Delta c(r, t = 0) = 0, \quad (2.22a)$$

$$\Delta c(r \rightarrow \infty, t) = 0, \quad (2.22b)$$

$$\lim_{\xi \rightarrow 0} \left(4\pi \xi^2 D \frac{\partial \Delta c}{\partial r} \bigg|_{r=\xi} \right) = \dot{m}_n, \quad (2.22c)$$

where $\dot{m}_n$ is the mass loss rate. To solve the partial differential equation (2.21) with the boundary conditions (2.22a – c), we assume self-similarity and non-dimensionalise in the usual way,

$$\Delta \tilde{c} = D \frac{r \Delta c}{\dot{m}_n}, \quad (2.23a)$$

$$\tilde{r} = \frac{r}{\sqrt{Dt}}. \quad (2.23b)$$

We can thus reduce the partial differential equation (2.21) to an ordinary differential equation,

$$-\frac{1}{2} \tilde{r} \frac{d\Delta \tilde{c}}{d\tilde{r}} = \frac{d^2 \Delta \tilde{c}}{d\tilde{r}^2}. \quad (2.24)$$

The three boundary conditions (A 2a – c) for the PDE can be transformed into two for the similarity ordinary differential equation (ODE) (2.24), namely

$$\Delta \tilde{c}(\tilde{r} \rightarrow 0) = 0, \quad (2.25a)$$

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$$\lim_{\tilde{r} \rightarrow 0} \left(\tilde{r} \frac{d\Delta\tilde{c}}{d\tilde{r}} - \Delta\tilde{c} \right) = \frac{1}{4\pi}, \quad (2.25b)$$

with which equation (2.24) can be straightforwardly solved to give $\Delta\tilde{c} = -\text{erfc}(\tilde{r}/2)/(4\pi)$, or in dimensional variables

$$\Delta c = -\frac{\dot{m}_n}{4\pi Dr} \text{erfc} \left(\frac{r}{2\sqrt{Dt}} \right), \quad (2.26)$$

which is equivalent to equation (2.16).

Transition to convection in single bubble diffusive growth *

We investigate the growth of gas bubbles in a water solution at rest with a supersaturation level that is generally associated with diffusive mass transfer. For CO_2 bubbles, it has been previously observed that, after some time of growing in a diffusive regime, a density-driven convective flow enhances the mass transfer rate into the bubble. This is due to the lower density of the gas-depleted liquid which surrounds the bubble. In this work, we report on experiments with different supersaturation values, measuring the time t_{conv} it takes for convection to dominate over the diffusion-driven growth. We demonstrate that by considering buoyancy and drag forces on the depleted liquid around the bubble, we can satisfactorily predict the transition time. In fact, our analysis shows that this onset does not only depend on the supersaturation, but also on the absolute pressure, which we corroborate in experiments. Subsequently, we study how the depletion caused by the growth of successive single bubbles influences the onset of convection. Finally, we study the convection onset around diffusively growing nitrogen N_2 bubbles. As N_2 is much less soluble in water, the growth takes much longer. However, after waiting long enough and consistent with our theory, convection still occurs as for any gas-liquid combination, provided that the density of the solution sufficiently changes with the gas concentration.

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3.1 Introduction

The physics of bubble growth in mildly supersaturated solutions is potentially relevant to several processes associated with energy production and consumption, e.g. increased production rate in oil generation [4, 76]. Alternative energy generation methods such as syngas [77], photo-electrochemical hydrolysis to obtain hydrogen [78–80] and catalytic reactions [14] must deal with multi-phase systems which are often affected by bubble formation. As one last example, CO₂ bubble formation is an undesired event in carbon sequestration, where CO₂ is injected at high pressures into reservoirs of saline water trapped in porous rocks at depth [81–83]. It appears sensible to assume that in liquids at rest such slow bubble growth (or dissolution) takes place exclusively by diffusion, as in the seminal theoretical analysis by Epstein & Plesset [25], which predicts that the bubble radius R evolves in a pure diffusive regime as

$$R(t) \approx \left(\sqrt{\frac{c_0 - c_s}{2\pi\rho_g}} + \sqrt{1 + \frac{c_0 - c_s}{2\pi\rho_g}} \right) \sqrt{\frac{2D(c_0 - c_s)}{\rho_g} t}. \quad (3.1)$$

Here, c_0 is the concentration in the bulk liquid at the initial saturation pressure P_0 , c_s the supersaturated concentration at the ambient pressure P_s during the experiments, ρ_g the gas density and D the diffusion coefficient of the dissolved gas in the liquid. Such time evolution of the bubble radius has been confirmed in several experimental works, with supersaturations $\zeta = (c_0 - c_s)/c_s$ comparable to that of carbonated beverages ($\zeta \sim 1 - 3$) [56, 84–86].

However, in previous experimental studies of single CO₂ bubbles growing on a silicon substrate in a very mildly supersaturated solution with $\zeta \sim 0.1 - 0.3$ [Ch.2, 34], significant differences were observed with respect to purely diffusive growth. The most notable discrepancy consists of an enhanced mass transfer rate towards the later stages of the bubble growth, which exceeds the predicted diffusive growth rate and corresponds to a time evolution of the bubble radius different from $R \propto \sqrt{t}$. This behaviour originates from the development of buoyancy-driven convection induced by the decreased density of the CO₂-depleted liquid around the bubble. It has been shown that buoyancy-driven convection is also the cause of higher dissolution rates of sessile droplets in a less dense liquid [47] and during droplet evaporation [87]. Both situations are physically analogous to growing bubbles and customarily treated as purely diffusion-driven phenomena [15, 88, 89], neglecting convective effects.

In this article, we further delve into the development of natural convection around a single growing bubble. We focus in particular on the time that it takes for convection to set in as an appreciable mass transfer mechanism and what external conditions, such as the concentration in the bulk liquid c_0 and

the supersaturation level ζ , have more influence on its transition. We present a simple theoretical criterion to predict the time t_{conv} at which convection becomes important and find a good agreement with experimental measurements using CO_2 bubbles. Afterwards, the long term effects of depletion in a single bubble succession are investigated, showing a significant influence on t_{conv} and the strength with which convection sets in. Finally, two different gases in solution (CO_2 and N_2) are contrasted, revealing a unique behavioural change in the mass transfer rate at the predicted time t_{conv} due to the different gas properties.

3.2 Experimental set-up and theoretical approach

Our experiments start with an equilibrated solution of either CO_2 or N_2 in ultra-pure degassed water at a starting saturation pressure P_0 . The initial dissolved gas concentration c_0 is given by Henry's law, i.e. $c_0 = k_H P_0$, where k_H depends on the gas-liquid couple and the temperature T . We then drop the pressure isothermally ($T \approx 20^\circ\text{C}$) to P_s in order to induce a supersaturation

$$\zeta = \frac{c_0 - c_s}{c_s} = \frac{P_0 - P_s}{P_s}. \quad (3.2)$$

The pressure controller induces some oscillations after the pressure drop, which can be slightly detected in the figures shown later. Due to the pressure drop, a bubble grows out of a hydrophobized micro-pit of radius $R_p = 10 \mu\text{m}$ or $50 \mu\text{m}$ which is covered with black silicon [90] and acts as an artificial bubble nucleation site [91]. The size of the pit, etched on a silicon substrate, determines the minimum supersaturation for which a bubble grows [92] as well as its maximum detachment radius, which is defined by the equilibrium of capillary and buoyancy forces, also known as Fritz radius [70]:

$$R_{\text{det}} = \left(\frac{3R_p\sigma}{2(\rho_m - \rho_g)g} \right)^{1/3}, \quad (3.3)$$

where σ is the surface tension coefficient, ρ_m is the solution density and g is the gravitational acceleration. The pit is located so that the bubble growing atop is far from the holding device, where several bubbles usually grow, and also far enough from the edges of the substrates, where parasitic bubbles might grow on the micro-roughness caused by the dicing process through which an original silicon wafer is cut into the shape of the experimental chips. Unless otherwise indicated, the bubbles always grow on top of the substrate and all experiments are done in the range $0.1 < \zeta < 0.5$; higher supersaturations result in too many bubbles on the walls of the tank and on the edges of the silicon

Figure 3.1: Sketches of (a) the experimental set-up and (b) the growing bubble. (a) A saturated water- CO_2 solution is prepared in the reservoir tank at a pressure P_0 . After transferring part of the mix to the observation tank, the pressure is dropped to P_s in order to produce a small supersaturation. A bubble grows from a nucleation site defined by a single hydrophobic cavity etched in a silicon substrate. We record the process using a long distance microscope objective through a lateral window of the tank. (b) As the bubble radius R grows, it develops a concentration c and density ρ_m profile of thickness $\delta(t)$.

substrate and, consequently, it can no longer be ensured that the liquid is at rest. Figure 3.1(a) shows a sketch of the experimental set-up. A detailed description can be found in [37].

Figure 3.1(b) shows a sketch of a growing bubble. The Laplace pressure due to the surface tension is in our case very small compared to P_s and can be safely neglected. Hence, the gas concentration at the interface can be considered constant and equal to c_s and, therefore, the bubble grows due to the diffusive gas flow driven by the concentration difference $c_s\zeta$ and the gas diffusivity D . The idealised initial condition is that the bubble grows from a radius R_p with concentration c_s at the interface and c_0 everywhere else. The asymptotic solution for the growth of a bubble in an infinite medium with the aforementioned initial conditions (3.1) [25] needs to be adapted to account for the presence of the silicon substrate below the bubble interface [34], which obstructs the mass transfer towards the bubble. The corrected asymptotic solution thus reads:

$$\epsilon \approx \left(\sqrt{\frac{c_s\zeta}{2\pi\rho_g}} + \sqrt{\frac{1}{2} + \frac{c_s\zeta}{2\pi\rho_g}} \right) x \equiv S^*x, \quad (3.4)$$

where $\epsilon = R/R_p$ is the dimensionless bubble radius and $x = \sqrt{(2Dc_s\zeta t)/(\rho_g R_p^2)}$. Note that R_p works in (3.4) as a reference value and does not directly affect the growth rate [85].

3. Transition to convection in single bubble diffusive growth

	CO ₂	N ₂
D (m ² /s) [94]	1.79×10^{-9}	1.88×10^{-9}
k_H (kg/(m ³ Pa)) [95]	1.67×10^{-5}	1.78×10^{-7}
λ_c (m ³ /kg) (Equation (3.5) and [96])	9.90×10^{-4}	-2.32×10^{-4}
ρ_g (kg/m ³) [69, 97]	9.97	6.29

Table 3.1: Properties of CO₂ and N₂ when dissolved in water at $P = 0.55$ MPa and $T = 21^\circ\text{C}$. The large difference in the values of Henry’s constant k_H accounts for the two orders of magnitude change in solubility.

As the bubble grows, it depletes its surroundings of gas [Ch.2], developing a diffusively-growing concentration profile that extends a distance $\delta = \sqrt{\pi Dt}$ into the liquid solution (figure 3.1(b)). Variations in concentration imply changes in the solution density, determined by the concentration expansion coefficient λ_c , which for a dilute solution of gas in water can be approximated as [Ch.1, Ch.2, 93]:

$$\lambda_c = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial c} \right)_{P,T} \approx \frac{1}{\rho_{m,0}} \frac{\rho_{m,0} - \rho_{m,s}}{c_0 - c_s}, \quad (3.5)$$

Hence, a positive λ_c means that the density of the solution increases with the gas concentration. If the density of the saturated solution is $\rho_{m,0}$, the density value at the bubble surface is given by $\rho_{m,s} = \rho_{m,0}(1 - \lambda_c c_s \zeta)$. The different gas properties of CO₂ and N₂ are listed in table 3.1. Combining λ_c with $c_s \zeta \approx 2$ kg/m³ (for the CO₂ experiments; $c_s \zeta$ is much smaller for the N₂ case) implies that $|\lambda_c c_s \zeta| \ll 1$ and makes it tempting to neglect the changes in density, which has been routinely done in most earlier works on bubble growth in supersaturated solutions. However, the long growth times of the bubbles require that we do take long term density changes into consideration.

As it will be thoroughly explained in the following section, after an initial diffusive growth, a transition to density-driven natural convection occurs. In order to experimentally measure the time in which this transition takes place, two methods are used and compared. An analytical model comparing buoyant and viscous forces will be defined to theoretically approximate this transition time, which only depends on the properties of the solution and the supersaturation level ζ at which bubbles grow. Whereas for a purely diffusively growing bubble (3.4) the ratio between the bubble radius and its diffusive concentration boundary layer $R/\delta = S^* \sqrt{2c_s \zeta / \pi \rho_g}$ remains constant through time, the transition to convection enhances the bubble growth rate but does not influence δ . Thus, the ratio R/δ increases as compared to a purely-diffusive case. Higher supersaturation levels ζ and P_0 (which directly relates to c_s) also make this ratio increase. However, within this relatively smaller concentra-

Figure 3.2: Dimensionless bubble growth rate (or, equivalently, the dimensionless change in the bubble surface over time) divided by S^* as a function of $x \propto \sqrt{t}$. The leftmost rising part and horizontal plateau of the curves are expected from a diffusion-driven growth; the right-hand slope suggests the influence of convection. The horizontal dashed line represents the purely diffusive evolution according to (3.4). (a) Experiments at $P_0 = 0.35$ MPa and a pit of $R_p = 50$ μm with various supersaturation levels ζ . In all cases, the bubble grows on top of the silicon chip. The vertical solid lines in corresponding colours indicate the experimentally-measured dimensionless square root of the transition time x_c for each ζ . The two reference lines used on its calculation are shown as dotted lines for $\zeta = 0.10$. (b) Experiments at $P_0 = 0.65$ MPa, a pit of $R_p = 10$ μm and $\zeta \approx 0.2$ with the bubble growing in different geometrical configurations, indicated by the sketches next to the corresponding curves.

tion layer, higher concentration gradients are reached, which results in higher and intensified onset to natural convection, as we will analyse in the following section.

3.3 The case of CO_2 bubbles

The typical bubble growth from our experiments is best appreciated by plotting the derivative $d\epsilon/dx$, which represents the dimensionless rate of change of the bubble area. Following equation (3.4) this should be constant and approximately equal to S^* . Figure 3.2(a) shows $d\epsilon/dx$ divided by S^* for some experiments with CO_2 solutions at $P_0 = 0.35$ MPa and different ζ . After the initial transient, there is indeed a plateau around $(1/S^*)(d\epsilon/dx) \approx 1$, which indicates a diffusion-driven growth. The plateau reaches larger values with increasing ζ . This originates from the stronger bubble growth rate at larger supersaturation levels ζ , which the asymptotic model (3.4) cannot follow any

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Figure 3.3: a) Sherwood number Sh as a function of Rayleigh number Ra in double logarithmic scale from the same data presented in figure 3.2(a). The dashed line represents a $1/4$ power law, which indicates that in the advanced stages, growth is driven by natural convection [Ch.2, 34]. The dotted horizontal line stands for a purely diffusive growth and its intersection with the power law indicates the transition to convection. The vertical solid lines in corresponding colours indicate the measured Ra_c for each curve. (b) Rayleigh number Ra_c at the crossover to convection-driven growth as a function of the supersaturation ζ . Blue circles correspond to experiments with $P_0 = 0.35$ MPa and $R_p = 50$ μm and red diamonds to $P_0 = 0.65$ MPa and $R_p = 10$ μm .

longer. Nevertheless, for the experimental range studied, the expected plateau corresponding to a diffusive process is always found. Afterwards, the curves start to rise as a result of the enhancement of mass-transfer caused by natural convection. To properly associate this effect with a transition to natural convection, following [34], we introduce the Sherwood number Sh and the mass Rayleigh number Ra , respectively defined as:

$$Sh = \frac{2R\dot{R}\rho_g}{Dc_s\zeta}, \quad Ra = \frac{g\lambda_c c_s \zeta (2R)^3}{\nu D}, \quad (3.6)$$

where $\dot{R}$ is the (dimensional) bubble growth rate and ν is the kinematic viscosity of water. Defined this way, Sh stands for the dimensionless mass transfer rate towards the bubble and Ra for the dimensionless buoyancy force due to the concentration difference in the liquid. When Sh is plotted against Ra (figure 3.3(a)), the rising part of the curve follows a power law $Sh \propto Ra^{1/4}$, which is the expected relation between Sh and Ra for natural convection around a sphere [see e.g. 72, 98]. Further experimental confirmation of the presence and influence of natural convection is obtained by comparing the bubble growth in different geometrical configurations, such as the situation where the bubble grows underneath the substrate and where it grows between two horizontal parallel plates with a vertical separation of 1 mm (a distance approximately

2.5 times larger than the bubble detachment radius), figure 3.2(b). In the first case, an increase of the growth rate is still observed, but at a slower pace, which is to be expected because of the geometrical inversion of the problem where the buoyant depleted liquid needs to move sideways due to the presence of the substrate. In the second case, the growth rate starts to rise but decreases again as the bubble surface approaches the other wall, which inhibits the possibility for convection to develop further.

3.3.1 The transition to convection-driven growth

To characterize the crossover to convection-driven growth in experiments, we fit a horizontal line to the plateau region of the Sh vs. Ra curves (figure 3.3(a)) and a $1/4$ -power law to their rising part and assume that the transition takes place at the intersection of those two lines. The crossing Ra_c can be directly associated with a bubble radius R and thus directly translated to a transition time t_{conv} . Equivalently, we also fit a horizontal line to the plateau in the derivative curves in figure 3.2(a) and a best-fit ascending straight line on their slope, measuring their intersection. From there, we obtain x_c , which by its definition is easily converted to t_{conv} . The fitting of the plateau was sometimes troublesome due to its short duration and the proximity to the initial transient; for this reason, the determination of the transition Ra_c (or x_c) cannot be made very precisely, which explains the scatter in the data. The crossover Ra_c values increase with increasing ζ (see figure 3.3(b)). The origin of this behaviour will be explained later in the text.

The gas-depleted region that develops around the bubble is subjected to an upward buoyant force due to its lower density compared to the fluid bulk. In order to estimate the force magnitude, we calculate the volume V_b of the buoyant region determined by the spherical segment (of horizontal diameter $2R+2\delta$ and height $2R+\delta$) denoted by the dotted line in figure 3.1(b) minus the volume of the bubble. With the bubble radius and buoyant region growing as $R \approx S^* \sqrt{2Dc_s \zeta t / \rho_g}$ and $\delta \approx \sqrt{\pi D t}$, respectively, the buoyant volume is given by

$$V_b = \frac{1}{3}(\pi D t)^{3/2} \left(24S^{*2} \frac{c_s \zeta}{\rho_g} + 9S^* \sqrt{\frac{2\pi c_s \zeta}{\rho_g}} + 2\pi \right) \equiv f_V t^{3/2} \quad (3.7)$$

where f_V stands for a volumetric buoyant factor. We stress that f_V is a dimensional constant that depends on the liquid-gas properties and, most importantly, on the supersaturation ζ .

We then estimate the terminal rising velocity u_b of the buoyant region by recognising that the only relevant forces acting upon it are buoyancy F_b and the viscous drag F_d , which for definiteness we estimate from the Stokes' flow.

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This last assumption is reasonable since the Reynolds number Re is small at all times, as we will see later. The small density difference and ‘quasi-static’ (extremely slow) growth of V_b in the small supersaturated regime result in a negligible acceleration, and therefore, negligible added mass force on V_b . Hence, we define:

$$F_b = c_s \zeta \lambda_c \rho_{m,0} g V_b, \quad F_d = 6\pi u_b (R + \delta) \mu, \quad (3.8)$$

which once equated lead to

$$u_b = \frac{c_s \zeta \lambda_c g V_b}{6\pi \nu (R + \delta)} = \frac{c_s \zeta \lambda_c g f_V}{6\pi \nu (R + \delta)} t^{3/2}. \quad (3.9)$$

Note that, in the end, the final scaling is $u_b \propto t$ and that the expression presented above has been written as $u_b \propto t^{3/2}/(R + \delta)$ for convenience.

The lighter liquid around the bubble will thus rise with the velocity u_b which sets up a flow of similar magnitude over the substrate to which the bubble is attached. This will lead to a viscous boundary layer that is described by a Reynolds number

$$Re = \frac{u_b (R + \delta)}{\nu} = \frac{c_s \zeta \lambda_c g V_b}{6\pi \nu^2} = \frac{c_s \zeta \lambda_c g f_V}{6\pi \nu^2} t^{3/2}, \quad (3.10)$$

Only if the buoyant velocity u_b is large enough to overcome the viscous velocity $\nu/(R + \delta)$ in a boundary layer over the substrate of similar size as the buoyant volume, the liquid will start to rise and convective mass transport will start to set in. This implies that $Re > 1$, and that the threshold value, i.e., $Re \approx 1$, marks the moment in time t_{conv} at which convection sets in,

$$t_{\text{conv}} \approx \left(\frac{6\pi \nu^2}{c_s \zeta \lambda_c g f_V} \right)^{2/3}. \quad (3.11)$$

Incidentally, the Reynolds number defined in (3.10) can be easily interpreted as a Grashof number based on the length scale $(V_b/6\pi)^{1/3}$. By the definition in (3.10), the higher the buoyant velocity u_b , the earlier and more intensified the onset of convection occurs and the more the mass transfer is enhanced.

In figure 3.4(a), we see that the crossover time prediction agrees well with experimental measurements. We also show, for reference, the experimental detachment times t_{det} and the theoretical ones if the bubbles would grow only by diffusion (3.4) to a radius of 500 μm , i.e. the approximate detachment size (3.3) from a pit of $R_p = 10 \mu\text{m}$. Furthermore, we include the detachment times of experiments by other authors [56, 84] who reported no influence of natural convection during bubble growth. Those times are only slightly larger

Figure 3.4: (a) Experimental and theoretical convection transition times t_{conv} (solid symbols and solid lines, respectively) as function of the supersaturation level ζ for $P_0 = 0.35$ MPa (blue circles) and $P_0 = 0.65$ MPa (red diamonds). Open symbols show the experimental detachment times t_{det} , whereas the dashed line represents the theoretical one for a bubble growing until R_{det} (3.3) following the growth law (3.4). Inset: detachment times of bubbles in the experiments by [56] (diamond) and [84] (square). They reported no influence of natural convection. (b) Theoretical crossover t_{conv} (solid) and detachment t_{det} (dashed) times as function of the supersaturation ζ for CO_2 (blue) and N_2 (red) bubbles. For thick solid lines, $P_0 = 0.65$ MPa, and for thin solid ones, $P_0 = 0.35$ MPa. The detachment curves are calculated considering pure diffusive growth until a radius $R_{\text{det}} = 500$ μm (3.3), corresponding to a pit radius of $R_p = 10$ μm .

than our prediction for t_{conv} , which suggests that in their experiments there was not enough time to observe this phenomenon. In addition, at higher supersaturation values (such as in those studies) the advective flow induced by the expanding bubble surface is no longer negligible and could possibly overwhelm the influence of natural convection.

To analyse the supersaturation range in which convection may become dominant, we compare the Sherwood number Sh (3.6) with the Péclet number $Pe = 2R\dot{R}/D$, i.e. we compare advective mass transport to the total mass transport:

$$\frac{Pe}{Sh} = \frac{c_s \zeta}{\rho_g} = \zeta k_H r_{\text{CO}_2} T, \quad (3.12)$$

where we have used both Henry's law and the ideal gas law. Here the specific gas constant for CO_2 equals $r_{\text{CO}_2} = 188.95 \text{ J/kg} \cdot \text{K}$. A necessary condition for natural convection to eventually become dominant is that $Pe/Sh < 1$, i.e. that advective transport is less relevant than the total mass transfer process including natural convection. Importantly, the threshold only depends on the specific gas, the supersaturation level ζ and the temperature T . In figure 3.5 we show the temperature dependence of the values of ζ corresponding to $Pe/Sh = 1$ and of k_H . At our experimental temperature ($T \approx 293 \text{ K}$), convection becomes dominant for supersaturation levels below $\zeta = 1.08$, including the entire range of our experiments. Therefore, we always observe a transition to density-driven convection during bubble growth. In contrast, the experiments from [56] and [84] had supersaturations of 1.78 and 1.07, with corresponding temperatures of 294 and 299 K. For these, $Pe/Sh = 1.65$ and 0.88 respectively, which puts them very close to the limit where -given enough time and experimental precision- convection might have been noticeable.

3.3.2 Effect of the initial saturation pressure P_0 on the onset of convection

As already indicated before, the gas concentration in a liquid c_0 depends on the properties of the gas-liquid couple, the temperature T and the saturation pressure P_0 . At constant T , c_s is directly proportional to P_s , and therefore the supersaturation level ζ can be easily controlled by pressure change. The time evolution of the radius in the diffusive regime is fixed by providing ζ [Ch.2, 25, 34]. This can be easily realized by noting that in equations (3.1) and (3.4), the factor $c_s \zeta / \rho_g = \zeta k_H r T$ depends on ζ . The situation is different in the case of buoyancy. Since the buoyant force is directly determined by the density difference $\Delta\rho = \rho_{m,0} \lambda_c c_s \zeta = \rho_{m,0} \lambda_c \zeta k_H P_s$, its effect is expected to depend on both the supersaturation ζ and the pressure P_s (or, alternatively, P_0). This implies that, when by fixing ζ the zeroth-order diffusive bubble growth is fixed,

Figure 3.5: Values of ζ for which $Pe/Sh = 1$ and (inset) Henry's constant k_H in water as function of temperature for CO_2 (solid blue lines) and N_2 (dashed red lines). In both cases, the region $Pe/Sh < 1$ is below the respective curve.

the time for convection to set in should still depend on the absolute pressure values.

To analyse this phenomenon, we performed experiments at a constant supersaturation level $\zeta = 0.15 \pm 0.02$ but initially saturating the solution at a different P_0 . Consequently, the pressure drop to $P_s = P_0/(\zeta + 1)$ is defined from (3.2). Figure 3.6(a) shows some representative curves of the derivatives of the dimensionless radius ϵ with respect to the dimensionless time x for three different initial saturation pressure P_0 . The influence of the onset of convection is evident: not only do we observe a shift in the onset time, but even more importantly, the plateau that represents diffusion reaching a higher value for higher P_0 , which indicates an intensified diffusive growth rate associated with larger concentration differences (but still of the same order of S^*). The slope of the convective portion of each curve also increases with P_0 , as can be determined by examining figure 3.6(b). In the latter, the data from figure 3.6(a) is replotted in its dimensionless form as Sh vs. Ra . Clearly, for the same Ra , Sh is larger at higher P_0 , indicating a stronger convection and an earlier onset. This intensification of the convective regime with increasing P_0 originates from the larger concentration change (and consequently, the larger solution density variation) to achieve a constant supersaturation level. Thus according to (3.9), the buoyant velocity u_b increases with P_0 , which results in a stronger convection and an earlier transition time t_{conv} .

Turning to the prediction (3.11), we observe that t_{conv} is inversely proportional to the gas concentration difference $c_s \zeta$. By applying Henry's law,

3. Transition to convection in single bubble diffusive growth

Figure 3.6: (a) Derivative of the dimensionless bubble radius ϵ against the dimensionless time x for experiments with different P_0 but same $\zeta \approx 0.15$ and $R_p = 50 \mu\text{m}$. The corresponding coloured dashed vertical lines stand for the theoretical t_{conv} , whereas the solid lines indicate the experimentally-measured one. The guidelines to calculate the latter are indicated as dotted lines for $P_0 = 0.8 \text{ MPa}$. The horizontal black dashed line indicates the theoretical behaviour for pure diffusion according to (3.4) [34]. Note that for purely diffusively growing bubbles, the experimental curves would be expected to coincide. (b) Sh vs. Ra for the first bubble after the pressure decrease at different P_0 and $\zeta = 0.15$ in logarithmic scale. The differences present in panel (a) are directly translated and better visualised in this representation, where for the same Ra , Sh , i.e. the dimensionless mass transfer, increases with higher P_0 . A 1/4 power law has been fitted to one of the experimental curves for comparison with the natural convective behaviour. The transition Ra_c is calculated as the intersection with the horizontal dotted line which represents a purely diffusive growth. The vertical solid lines in corresponding colour indicate the different Ra_c for each curve. The same colour palette in panel (a) applies to panel (b).

Figure 3.7: (a) t_{conv} for the different initial saturation pressure P_0 at $\zeta = 0.15$. Experiments are represented by error bars, whereas the theoretical estimation (3.13) is plotted as a solid blue line. Despite the imprecisions in the experimental measurements, specially for lower P_0 , theory agrees quantitatively with experiments, i.e. t_{conv} decreases with increasing P_0 . (b) Effect of depletion on the transitional time to convection $\tilde{t}_{\text{conv}}$. Blue circles correspond to $P_0 = 0.7$ MPa, whereas red diamonds refer to $P_0 = 0.3$ MPa. For both curves, $\zeta = 0.15$. Note that the numbers in the x -axis are presented in decreasing order. Even though theory (solid lines) indicates a gradual delay in $\tilde{t}_{\text{conv}}$, experiments show an intensified effect.

it can be rewritten as $c_s \zeta = k_H P_0 \zeta / (\zeta + 1)$. Thus, we may reformulate the approximate model (3.11) and obtain:

$$t_{\text{conv}} \approx \left(\frac{6\pi\nu^2}{k_H P_0 \left(\frac{\zeta}{\zeta+1} \right) \lambda_c g f_V} \right)^{2/3}. \quad (3.13)$$

Note that the volumetric buoyant factor f_V (3.7) also depends on P_0 as the product $c_s \zeta$ in its definition refers to a difference in concentration ($c_0 - c_s$), where c_0 is directly proportional to P_0 . The experimental results are plotted in figure 3.7(a). Despite the difficulties in measuring a proper t_{conv} , especially for the lower values of P_0 , in which there is not a clear transition towards convection, theory and experiments follow the same trend and qualitatively agree, i.e. t_{conv} decreases with increasing P_0 .

3.3.3 Long term effects on the convective transition during a single bubble succession

As single bubbles grow in succession, they will suffer the accumulated depletion which originates from the previous bubbles absorbing the gas from

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Figure 3.8: (a) Evolution of the depletion number Υ in time with different supersaturation level ζ and fixed $P_0 = 0.9$ MPa. An evident faster depletion occurs with larger ζ . The solid line stands for the theoretical behaviour in [Ch.2] with $\alpha = 0.42$ for the case $\zeta = 0.25$. (b) Evolution of Υ in time for different starting saturation pressure P_0 and $\zeta = 0.15$. The experimental results make it reasonable to suggest that P_0 , and therefore the intensity of the transition to convection, play a secondary role in the speed of depletion.

their surroundings. This cumulative depletion remarkably affects subsequent bubbles and significantly delays their growth rate and inhibits the transition to convection [Ch.2]. We account for the effect of depletion by defining the discrete depletion number Υ_n :

$$\Upsilon_n = \frac{\tilde{c}_n - c_s}{c_0 - c_s}, \quad (3.14)$$

where $\tilde{c}_n$ is the apparent bulk concentration that the n -th bubble in the succession observes. By definition, the first bubble in the succession, $n = 1$, grows in a non-depleted domain and therefore, $\Upsilon_1 = 1$. The subsequent values of Υ_n are calculated by collapsing the different curves Sh_n vs. Ra_n into one universal curve $\tilde{Sh} = f(\Upsilon_n, \tilde{Ra})$, where $\tilde{Sh} = Sh_n/\Upsilon_n$ and $\tilde{Ra} = Ra_n\Upsilon_n$, following the approach of [Ch.2], who also calculated a simplified analytical expression for Υ_n . By obtaining the different values of Υ_n , figure 3.8, different responses can be identified. First of all, increasing the supersaturation level ζ at the same starting P_0 results in a faster depletion, and therefore, Υ decreases faster, as can be seen in figure 3.8(a). Secondly, saturating the solution at different P_0 does not play a significant role in the evolution of Υ , figure 3.8(b). In general, it is true that higher P_0 results in a slightly slower depletion, except for the case of $P_0 = 0.2$ MPa, in which depletion is much slower than in the others.

We identify this effect as originating from the difficulty in achieving a specific value of ζ , which becomes more challenging at lower P_0 .

Depletion also affects the time at which convection sets in. By assuming that the effective concentration difference $c_s\zeta$ which affects the transition to convection is governed by the apparent bulk concentration $\tilde{c}$, (3.11) can be redefined as

$$\tilde{t}_{\text{conv}} \approx \left(\frac{6\pi\nu^2}{(\tilde{c} - c_s)\lambda_c g f_V} \right)^{2/3} = \left(\frac{6\pi\nu^2}{\Upsilon c_s \zeta \lambda_c g f_V} \right)^{2/3}. \quad (3.15)$$

This equation relates the delay in the transition to convection as depletion intensifies. We plot some experimental results and compare them to this theoretical expression in figure 3.7(b). Despite the toughness in calculating $\tilde{t}_{\text{conv}}$, which becomes even more difficult as depletion increases and there is no longer a defined transition from plateau to slope in the curves $d\epsilon/dx(x)$ nor $Sh(Ra)$ [Ch.2], experimental results indicate a significant delay in the transitional time to convection, which is in accordance with (3.15).

3.4 The case of N₂ bubbles

CO₂ is a gas with a very high solubility in water, indicated by Henry's constant k_H , whereas N₂ has a lower solubility (refer to table 3.1). The diffusivity D and the expansion coefficient λ_c in aqueous solutions are however of the same order of magnitude (in absolute terms) for both gases. That c_s is about one hundred times smaller for N₂ leads to a much smaller $c_s\zeta$ if the supersaturation ζ is the same as in the CO₂ experiments. Consequently, since the radius grows as $R(t) \propto \sqrt{2Dc_s\zeta t/\rho_g}$, N₂ bubbles grow more slowly and t_{conv} is expected to be much larger. Figure 3.4(b) compares the theoretical crossover t_{conv} and detachment t_{det} times for the two gases, showing the indeed much longer times to achieve convection and detachment for N₂. Our estimation of t_{conv} remains valid for negative λ_c , where in the final expression (3.11), λ_c needs to be replaced with its absolute value $|\lambda_c|$. Some experimental $d\epsilon/dx$ curves are shown in figure 3.9 along with a reference curve for CO₂. Note that, although the time scales are very different in experiments with each gas, x is similar for N₂ and CO₂. The early stages look very similar; in fact, the slow growth of N₂ bubbles allows for a smoother plateau region, avoiding the slight oscillations of the CO₂ curve caused by the pressure controller after the pressure drop. At the predicted t_{conv} there is a clear change in behaviour for the N₂ bubbles, but very different from that of the CO₂ case. In this case, λ_c is negative and therefore, the stratified density profile is stable: the solution is then denser close to the bubble than in the bulk liquid, i.e. the depleted volume may

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	t_{conv} (s)	$R(t_{\text{conv}})$ (mm)	$\delta(t_{\text{conv}})$ (mm)
CO ₂ , $\zeta = 0.381$	60	0.300	0.610
N ₂ , $\zeta = 0.304$	3280	0.210	4.400
N ₂ , $\zeta = 0.457$	2620	0.230	4.000

Table 3.2: Comparison of crossover time t_{conv} , bubble radius at crossover time $R(t_{\text{conv}})$ and boundary layer thickness at crossover time $\delta(t_{\text{conv}})$ for CO₂ and N₂ bubbles.

Figure 3.9: Derivative of the dimensionless bubble radius ϵ vs. the dimensionless time x for one CO₂ (yellow squares) and two N₂ (blue and red circles) bubbles. The vertical dashed lines in corresponding colours indicate the predicted convection crossover times x_{conv} for each case (refer to figure 3.4(b)). The horizontal dashed line stands for equation (3.4).

stay on the substrate and sink. The subsequent convective stream flows in the opposite direction as that generated in the CO₂ case. Still, the transition to natural convection occurs since additional gas is brought from the bulk to the bubble interface. However, the behaviour is totally different from that of CO₂ bubbles: now the growth rate oscillates around the solution for purely-diffusive growth. The different transition times for CO₂ and N₂ are listed in table 3.2. As one can see from the data in the table, the crossover radius $R(t_{\text{conv}})$ is of the same order for both gases. However, the crossover time t_{conv} and consequently the boundary layer thickness $\delta(t_{\text{conv}})$ are much larger for N₂.

As we previously mentioned in section 3.2, it is not uncommon that some bubbles grow on the edges of the silicon substrate during the experiments, which are at least 4 mm away from the target bubble. For CO₂ bubbles this is not a problem, since that distance is much larger than the boundary layer

thickness at the time convection sets in, $\delta(t_{\text{conv}})$, and hence beyond the range in which they might interact [99, chapter 5]. However for N_2 , this distance allows for considerable overlap of buoyant regions, which may cause that the mixing due to natural convection brings liquid that is already depleted of gas to the bubble surface. This is consistent with the irregular growth rates and the lack of reproducibility that we observe in all our N_2 experiments after t_{conv} even though the initial growth is reproducible and similar to CO_2 bubbles in dimensionless units, figure 3.9. In addition, the mixing process itself might be significantly altered in the case of N_2 bubbles where, despite the similar magnitude of the buoyant force (in absolute terms), the buoyant depleted volume is much larger than for CO_2 bubbles. Finally, and regarding the supersaturation range where diffusion effects should prevail over convection in the case of N_2 , we can see in figure 3.5 that the small solubility of this gas in principle sets a very high supersaturation limit to this phenomenon, which again is indicated by the threshold $Pe/Sh = 1$. The transition to convection is therefore most likely to occur in the majority of applications involving N_2 bubbles.

3.5 Conclusions

We have shown that diffusive bubble growth driven by a small gas supersaturation in a liquid solution can lead to natural convection and, thereby, enhance the bubble growth rate (figures 3.2 and 3.3(a)). This transition to natural convection or density-driven convection originates from the change in density experienced by the solution surrounding the bubble as it absorbs the dissolved gas and the liquid becomes depleted. For experiments with CO_2 , the prediction for the crossover time t_{conv} agrees with measurements, despite the difficulty in precisely determining t_{conv} (figures 3.4(a) and 3.7(a)). The analytical prediction of t_{conv} suggests that, in principle, density-driven convection around a growing bubble can occur at any value of supersaturation ζ as long as the detachment radius is large enough (figure 3.4). However, the balance between the expansive motion of the bubble surface and the convection due to concentration differences establishes a supersaturation threshold for which convection is expected to become relevant (figure 3.5). The initial saturation pressure P_0 at which the solution is prepared significantly affects results as well. At constant supersaturation ζ , a higher P_0 implies a larger pressure drop, and consequently, a larger concentration and density change. As a result, convection sets in at earlier t_{conv} and with intensified effects, indicated by the different convective slopes in the derivative analysis (figure 3.6(a)).

Single bubbles growing in a succession are also extremely affected by the

3. Transition to convection in single bubble diffusive growth

transition to convection. The study of the depletion number Υ yields that depletion is highly dependent on the supersaturation level, whereas the initial starting pressure P_0 has a secondary role and barely influences the results. This sheds some more light in the possible origin of depletion: even though the transition to convection may be relatively important, the major cause of depletion emerges from the evident fact that bubbles absorb gas as they grow (gas that cannot be fully replaced by the diffusive transport through the bulk) and from the way bubbles alter their surroundings while detaching. Besides, depletion causes a significant delay in the transition to convection, which becomes less relevant as subsequent bubbles keep growing and detaching.

For N_2 bubbles, there is a clear transition occurring at t_{conv} , consistent with the presence of natural convection, but different from the CO_2 case. This originates from the different solubilities and the different way in which the solution density changes with the gas concentration, which is reflected in an opposite sign of λ_c as that for the CO_2 bubbles. The convective plumes flow in a different direction and consequently, the bubble evolution during the convective regime and the time needed for it to set in behaves differently, as depicted in both tables 3.1 and 3.2 and figures 3.4(b), 3.5 and 3.9. Nevertheless, that we observe such transition with a gas one hundred times less soluble suggests that this can happen for any gas-liquid solution as long as its density changes with the gas concentration.

4

Diffusive growth of successive bubbles in confinement *

4

We analyse how a succession of single bubbles extracts dissolved gas from a liquid solution while they grow and detach in spatial confinement. Like bubbles growing on a liquid-immersed free surface, these bubbles absorb the dissolved gas in the liquid around them and hence deplete their surroundings. The supersaturation level ζ stands out as the main parameter which determines the diffusive bubble dynamics, both in the confined and unconfined scenarios. For slightly supersaturated solutions, the bubble evolution is rather similar for the two cases. In the confined case, however, higher supersaturation levels imply a significantly different long-term behaviour, which originates from the hindrance to fully develop a buoyant depleted boundary layer within the confinement walls and the inhibition of the refreshing mechanism of the depleted liquid with non-depleted solution from the bulk. On the other hand, convective and advective effects resulting from bubble detachment and the subsequent rising enhance mixing within the confinement, which partially counteracts the effect of depletion. We propose a modified depletion model which accounts for this geometrical configuration and its effect on the effective area through which gas diffuses into the bubble. The model can accurately describe the experimental results and sheds more light on the origin of the depletion effect due to successive bubble growth.

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4.1 Introduction

Bubbles have been studied from many different points of view since their behaviour is crucial to a wide variety of applications. They play a critical role in chemical reacting processes, such as electrolysis [11, 12] and catalysis [13, 14]. Their generation is extremely important in the confinement of nano- and micro-channels [100–102] since bubbles are known to (partially) block them and impede their proper use. Bubbles in a flow travelling through a conduit are formed either of dissolved gas which accumulates in cracks along the walls, or liquid vapour originating from boiling or chemical processes occurring along the channel [103–105]. When a bubble partially blocks a conduit, the flow needs to circumvent the bubble surface and consequently the flow rate decreases since the cross section is reduced. Hence, the mass transfer towards the bubble is altered and the bubble shape is modified [102, 105]. Ultimately, bubbles can grow up to a point that they fully block the channel [106], impeding mass transport and causing clogging. In these cases, heat [100, 107] and mass transfer considerations are essential to understand bubble growth [108]. When the growth of the bubble is governed by diffusion, in principle the Epstein & Plesset [25] theory still applies; nonetheless, several modifications need to be adopted to account for the inertial terms corresponding to the flow running through the channels [109].

In this article, we deal with a geometrical configuration similar to the confinement induced in the previously mentioned nano-/micro-channels: a series of single bubbles grow in succession in a domain constrained by lateral walls, an intermediate step between bubbles growing on a liquid-immersed free surface and full confinement. In the latter case, bubbles grow in a volume which cannot be deformed and therefore their growth implies the compression of the liquid surrounding it [110]. In this case, the system can be approximated as a harmonic oscillator and the original theory of [25] needs to be adapted accordingly. As for bubbles growing on a free surface, the recent work in [Ch.2] showed that such bubbles deplete their surroundings as they diffusively grow and absorb the dissolved gas in the liquid solution. The local decrease of gas concentration results in a decrease in the solution density, which promotes the onset of (natural) density-driven convection from the middle stages of the bubble growth, therefore enhancing the mass transfer [Ch.3]. As a consequence, bubbles absorb more gas than diffusion through the bulk alone can supply. The subsequent bubbles grow in a region which has less available gas in dissolution, hence their growth rate is significantly slowed down.

A deeper understanding of how bubbles behave in confined domains with no external forced flows involved is necessary to understand the fundamentals of bubble growth in nano- and micro-channels. With the presence of confinement

around a succession of bubbles growing on a surface we pretend to shed more light on the origin of depletion and gain a better understanding of the way in which bubbles absorb the gas from their surroundings. Our system remains in a quasi-static configuration and, thus, the bubbles grow mainly by diffusion [25].

Along this article, we first introduce the experimental set-up (§4.2) and summarise earlier results regarding the analysis of the bubble growth dynamics (§4.3). Afterwards, we focus particularly on two independent scenarios: in the first, we study the different bubble growth evolution in confinement for different supersaturation levels ζ (§4.4); in the second, we compare the successive growth of bubbles in confinement with that of bubbles on a free surface (§4.5). Finally, §4.6 contains the concluding remarks.

4.2 Experimental set-up and procedure

The experiments were performed in a pressure-controlled set-up. For details concerning the fabrication and use of the equipment, the reader is referred to [37]. To summarise, a mixing tank contained a mixture of liquid (ultra-pure water) and gas (CO_2) saturated at a certain pressure P_0 and $T \approx 20^\circ\text{C}$. The water was degassed prior to experiments to ensure that there were no other spurious gases in solution. The other (measurement) tank contained a silicon substrate which was held by a lateral clip. A preferential spot for bubbles to nucleate and grow was etched on its surface and was composed of black silicon [20, 21, 91], a superhydrophobic material. Around this site (a pit of radius $R_p = 50 \mu\text{m}$), a glass cylinder of radius $R_c = 2.5 \text{ mm}$ and height $H = 10 \text{ mm}$ was glued to the substrate by means of curing a hydrophilic resin with ultraviolet light. A schematic of the set-up can be seen in figure 4.1, together with an experimental snapshot.

At the beginning of the experiment, the measurement tank was pressurised with CO_2 gas at the same saturation pressure P_0 as the mixing tank. Then, by means of different valves, the solution was brought from the main tank to partially fill the experimental one. To generate bubbles, we decreased the pressure inside the latter to a value $P_s < P_0$, and therefore, the solution became supersaturated and bubbles began to grow from the hydrophobic pit. Once a bubble had detached, a new subsequent bubble formed and the succession continued. The time in-between two successive bubbles was larger than 10 s, such that no advective effects related to the previous bubble departure were expected to affect the growth of the subsequent one [Ch.2].

We performed different sets of experiments starting from the same saturation pressure $P_0 \approx 9 \text{ bars}$. The supersaturation level $\zeta = (c_0 - c_s)/c_s$ (where

Figure 4.1: (a) Schematic (not to scale) of the experimental geometry with the substrate holding the cylindrical confinement of radius $R_c = 2.5$ mm and height $H = 10$ mm around the growing bubble. The single bubble grows from the superhydrophobic pit of radius $R_p = 50$ μm according to the imposed supersaturation level ζ . Once the bubble detaches, a subsequent one nucleates and the succession continues. (b) Snapshot of one of the experiments. The contour of the cylinder base surrounding the bubble can be appreciated. The position of the superhydrophobic pit from which the bubble nucleates and grows is also indicated. One clearly detects the neck joining the entrapped gas in the pit and the bubble growing outside [Ch.2].

c_0 and c_s are the gas concentrations at the initial saturation pressure and at supersaturated conditions) can be written in terms of pressure by using Henry's law, $c = k_H(T)P$, where in general $k_H(T)$ is a decreasing function of temperature dependent on the gas/liquid couple. By decreasing the pressure to different values of P_s and keeping the temperature constant at all times, we achieved different values of $\zeta = (P_0 - P_s)/P_s \approx 0.15, 0.25$ and 0.47 .

The walls surrounding the bubble nucleation spot hinder the gas diffusion in the perpendicular direction [111, 112], similar to the case of trapped gases in porous media or zeolites [113, 114]. The effect is the higher the closer the walls are to the bubble surface. In that case, diffusivity is sometimes interpreted as a multicomponent vector whose components indicate the different apparent diffusivities in the three spatial directions [115, 116]. In our case, the maximum radius of the bubbles at detachment was approximately $R_{det} \approx 0.8$ mm, which is 3 times smaller than the cylinder radius. In this configuration, diffusivity can be safely assumed constant in the three spatial directions and characterised by only one diffusion coefficient D .

The cylinder curvature may affect the acquisition of images since the light illuminating the experiments is refracted while crossing the cylinder surface. We have made use of a ray-tracer [117] to confirm that the refraction resulting

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from the light crossing the cylinder walls was inconsequential, and hence, no correction to the images needed to be applied.

As bubbles approached their detachment radius, due to the effect of buoyancy their shape started to become elongated approaching that of a balloon. In order to calculate a precise bubble radius, we have compared three different techniques: in the first, we fit a circle to the bubble contour; in the second, the radius was obtained by equating the measured projected area of the full bubble to that of a perfect circle; in the third, we computed the volume of the revolution body generated by rotating the bubble profile around its vertical symmetry axis. We found that, within measurement error, the three methods produced identical outcomes except for the very last moments close to bubble detachment. The variability was however less than 1%, thus we could safely assume that the bubbles behaved as perfect spheres at all times.

4.3 Analysis of the growth dynamics: theoretical framework

Bubble growth in mildly supersaturated solutions is standardly associated with diffusion-driven mass transfer phenomena. In this section, we summarise results from [34], Ch.2 and Ch.3, where the behaviour of single bubbles growing on a substrate immersed in a mildly supersaturated solution is described in depth. To study the behaviour of bubbles in such a configuration, two dimensionless quantities are defined:

$$\epsilon = \frac{R}{R_0}, \quad x = \sqrt{\left(\frac{2D\zeta c_s}{\rho_g R_0^2}\right)} t, \quad (4.1)$$

where R is the bubble radius, R_0 is a reference radius which we associate with the radius of the pit R_p , and ρ_g is the gas density. Here, ϵ represents a dimensionless bubble radius and x a dimensionless square root of time. The diffusive bubble growth is then characterised by the Epstein & Plesset [25] equation slightly modified to account for the presence of the substrate below the bubble. The approximate solution becomes then

$$\epsilon \approx \left(\sqrt{\frac{\zeta c_s}{2\pi\rho_g}} + \left(\frac{1}{2} + \frac{\zeta c_s}{2\pi\rho_g} \right)^{\frac{1}{2}} \right) x \equiv S^* x. \quad (4.2)$$

As one can extrapolate from this equation, the bubble growth is strongly dependent on the supersaturation level ζ , which will be our control parameter in the experiments provided below.

From the middle stages of the bubble growth, an onset to density-driven convection takes place and enhances the mass transfer towards the bubble. Two characteristic dimensionless numbers, namely Sherwood number Sh and Rayleigh number Ra , relate the mass transfer towards the bubble to the ratio of buoyant, viscous and diffusive effects. These two numbers can be written as [see e.g. 72, 73]:

$$Sh = \frac{2\rho_g R \dot{R}}{D(c_0 - c_s)}, \quad Ra = \frac{g\lambda_c(c_0 - c_s)(2R)^3}{\nu D}, \quad (4.3)$$

where λ_c is the concentration expansion coefficient and ν the kinematic viscosity. The onset of convection originates from the density decrease in the solution around the bubble as it absorbs the dissolved gas and depletes the liquid. Therefore, the parameter λ_c becomes very relevant since it relates the way in which a solution changes in density with the concentration of dissolved gas. In the case of CO_2 , a growing bubble may then cause a relevant decrease in the density of the surrounding liquid, which originates the formation of a buoyant depleted boundary layer and a significant enhancement of mass transfer. For the case of a sphere with fixed radius in steady-state (natural) convection in an infinite medium, Sh and Ra can be related as [see e.g. 72]

$$Sh = 2 + K Ra^{\frac{1}{4}}, \quad (4.4)$$

where 2 is the value of Sh in the pure diffusive case and $K \approx 0.569$ is a fitting constant [74, 75].

For the study of the long term depletion as the bubble succession continues within the cylinder, the depletion number is defined as

$$\Upsilon_n = \frac{\tilde{c}_n - c_s}{c_0 - c_s}, \quad (4.5)$$

where n is the index indicating the bubble number within the succession and $\tilde{c}_n$ is the local apparent infinite concentration that the n -th bubble perceives due to the decreased gas concentration resulting from the previous bubble departure. By means of this description, we redefine (4.3) to consider the effects of depletion as

$$\widetilde{Sh} = \frac{2\rho_g R \dot{R}}{D(\tilde{c}_n - c_s)} = \frac{Sh_n}{\Upsilon_n}, \quad \widetilde{Ra} = \frac{g\lambda_c(\tilde{c}_n - c_s)(2R)^3}{\nu D} = Ra_n \Upsilon_n. \quad (4.6)$$

The curves Sh_n vs. Ra_n can then be collapsed onto one universal curve $\widetilde{Sh} = f(\widetilde{Ra})$ from which Υ_n is obtained. Υ_n can be analytically estimated by adapting the solution of a pure diffusive problem to account for the effect of convection caused by the density difference and by the detachment and

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subsequent rise of the bubble. As a bubble grows and absorbs gas from its surroundings, a concentration boundary layer develops following $\sim \sqrt{Dt}$. In the long term and under our geometrical configuration, this boundary layer occupies the full width of the cylinder and can only evolve in the vertical direction towards the aperture of the confinement. It is known that this layer reaches a length much longer than the bubble radius as the succession continues. In that scenario, the bubble can be approximated as a point sink which extracts gas from a certain bulk. In view of the above discussion, it is reasonable to assume that the problem becomes one-dimensional and therefore, the discrete depletion number reads (for a complete derivation, refer to Appendix 4.A):

$$\Upsilon_n = \Upsilon_{n-1} - \frac{\rho_g R_{det}}{3Dt_{det}(c_0 - c_s)} \left[2\sqrt{\frac{Dt_{det}}{\pi}} \exp\left(-\frac{(R_{det} + \alpha\sqrt{3.3Dt_{det}})^2}{4Dt_{det}}\right) - (R_{det} + \alpha\sqrt{3.3Dt_{det}}) \operatorname{erfc}\left(\frac{R_{det} + \alpha\sqrt{3.3Dt_{det}}}{2\sqrt{Dt_{det}}}\right) \right], \quad (4.7)$$

where R_{det} and t_{det} are the corresponding radius [70, 71] and time at detachment, and $\alpha \in [0, 1]$ is a fitting constant which accounts for the distance within the concentration boundary layer that defines the apparent bulk concentration for the subsequent bubble in the succession and, consequently, is a decreasing function of ζ , i.e. bubbles deplete their surroundings faster with increasing ζ [Ch.3]. Whereas R_{det} is a parameter which is determined by a force balance and remains constant throughout our experiments, the measurement of the detachment time t_{det} and α incorporates convective effects as the bubble grows. Note that equation (4.7) differs slightly from the expression provided in Ch.2, where a spherically-symmetric three-dimensional situation was modelled.

4.4 Effect of the supersaturation level ζ in confined bubble growth

In §4.3, we discussed that the supersaturation level ζ determines the speed at which bubbles grow, as one can see from the definition of x and S^* in (4.2). The higher its value, the faster it is expected that bubbles grow. We present the growth of different successive bubbles in confinement in figure 4.2(a). The bubble growth behaves as expected: higher supersaturation levels correspond to increased bubble growth rate. The cases of $\zeta = 0.15, 0.25$ are remarkably

Figure 4.2: (a) Dimensionless radius ϵ plotted against the dimensionless square root of time x for subsequent bubbles in confinement. The different colours represent different supersaturation levels ζ , namely, blue for 0.15, red for 0.25 and yellow for 0.47. The different symbols stand for the order of the bubble in the succession, namely circles for the 1st bubble and diamonds for the 5th, whereas equation (4.2) is plotted as solid lines in the corresponding colours. The inset shows the unscaled data for the time evolution of the bubble radius R prior to the non-dimensionalisation. (b) Derivative of the dimensionless radius vs. the dimensionless square root of time. The same colour-symbol coding as in panel (a) applies here. Equation (4.2) coincides for the three different ζ and is represented as a black solid line. Note that increasing ζ causes an earlier and intensified onset of convection.

similar. Nonetheless, since $x \propto \zeta^{1/2}$, the unscaled data for smaller ζ lie below those of larger ζ , as reflected in the inset of the same figure.

Depletion effects are expected to be strengthened by increasing the supersaturation level. The onset of density-driven convection and the advective effects caused by the detachment and subsequent rise of the bubbles permit them to absorb more gas than diffusion can supply from far away in the bulk liquid, and specifically for the geometrical configuration regarded in this article (figure 4.1), the cylinder walls also play a crucial role in inhibiting the refreshment with non-depleted bulk liquid. In figure 4.2(b), we show the derivatives of the curves in figure 4.2(a) with respect to the dimensionless square root of time x . As the supersaturation increases, we can perfectly appreciate that the onset occurs earlier and intensified, indicated by a higher transient peak and a shorter plateau before the slope. Figure 4.3(a) represents the diverse values of Sh plotted against Ra for the different curves in figure 4.2. By comparing the experimental data to the theoretical relation (4.4), we distinguish an early behaviour where $Sh \approx 2$ remains quasi-constant and indicates an early diffusive

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Figure 4.3: (a) Sherwood number Sh plotted against Rayleigh number Ra for the same bubbles in figure 4.2. Depletion can already be appreciated for the 5th bubble, which is clearly separated from the 1st curve. To compare, the theoretical relation for natural convection around bubbles in an infinite medium, equation (4.4), is shown. Note that the x axis is in logarithmic scale and the y axis in decimal scale for convenience. (b) The depletion number Υ decreases for increasing ζ , as expected for an enhanced bubble growth rate due to an intensified transition to convection. The solid lines represent the best theoretical approximation for each ζ according to equation (4.7).

regime, and a transition to convection from the middle stages of the bubble growth, which has been also confirmed for the analogous case of droplets [47].

Regarding the long term depletion effect, the different curves standing for the analytical solution (4.7) can be found in figure 4.3(b), together with the experimental results measured from collapsing the curves in figure 4.3(a). Similarly to the case of bubbles growing on a free surface [Ch.2], Υ_n decreases for every subsequent bubble in the succession and, for the different curves, an increase in ζ implies a stronger depletion, i.e. Υ decreases faster for higher ζ . The experiments are well described with the theoretical expression (4.7), with fitting constant $\alpha = 0.96, 0.90$ and 0.79 for $\zeta = 0.15, 0.25$ and 0.47 , respectively. The expected decreasing value of α with increasing ζ is also confirmed in the case of confinement. The slight deviation between experiments and the theoretical fit may be connected to the 1-D approximation.

To summarise this section, ζ has been proven to be the adequate control parameter which determines the speed at which bubbles grow, as well as an indicator of the speed and the intensity of depletion. The case is analogous to bubbles growing in a unbounded domain on a surface [Ch.2, Ch.3].

Figure 4.4: (a) Dimensionless radius ϵ plotted against the dimensionless square root of time x for experiments with $\zeta = 0.15$. In blue, the bubbles grow under confinement, whereas in red, the bubbles grow in an open medium. Different symbols are used to indicate the 1st (circle), 5th (diamond) and 10th (star) bubble in the succession. The curves within the same succession deviate from each other due to the effect of depletion. (b) Derivative of the dimensionless radius vs. the dimensionless square root of time. The effects of depletion are very noticeable in this data representation. The respective curves with and without confinement seem to run parallel, indicating a similar strength in the onset of convection. In both (a) and (b), the solid line corresponds to equation (4.2).

4.5 Comparison of confined and free bubble growth

In this section we focus on the actual effect of the confinement by comparing with experiments in which the bubbles grow on a surface in a (for practical purposes) infinite medium. We discuss two sets of ζ independently, since, contrary to expectations, we will see that depletion evolves in a qualitatively different manner for each case.

4.5.1 Supersaturation level $\zeta = 0.15$

The very low supersaturation level $\zeta = 0.15$ corresponds to an extremely slow growth rate, approximately 20 min for the first bubbles. Figure 4.4(a) shows the dimensionless bubble radius evolution in dimensionless square root of time in confinement compared to the same in the unconfined case. The beginning of the bubble growth in both scenarios is very similar: bubbles grow according to the theoretical curve (4.2). However, and contrary to expectations, the bubbles under confinement seem to grow slightly faster than the bubbles in the open medium. This fact can be better appreciated in figure 4.4(b), where the deriva-

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tives show that the curves corresponding to the bubbles under confinement lie somewhat above those for the open medium. The transition to convection occurs slightly earlier for confined bubbles and consequently bubbles grow to some degree faster than those on a free surface. This may originate from the local larger concentration gradients within the confined system, which would create a larger buoyant force on a smaller volume.

The depletion effects can be appreciated in figure 4.6(a), where Υ_n is plotted. For small supersaturation, depletion occurs faster in the confined case as a result of the rather enhanced bubble growth and the shielding effect of the walls for renewing the depleted liquid with fresh non-depleted solution once a bubble detaches. In figure 4.6(a) we plot the theoretical model (4.7) for the confined and the one in [Ch.2] for the unconfined case together with the corresponding experimental measurements, showing a good agreement for both models. Both the theoretical curves and the experiments show a very similar behaviour for the first few bubbles in the succession. This can be associated with the growth of the boundary layer, which for the confined case does not reach the walls of the cylinder until later in the succession. From that moment on, the curves start to diverge and hence, in the long term, depletion is slightly stronger in confinement than in the open system, as one would expect.

4.5.2 Supersaturation levels $\zeta = 0.25$ and 0.47

Once the supersaturation ζ increases, confinement starts playing a major and significant role on the way bubbles grow from the hydrophobic pit. Similarly to the previous subsection, figure 4.5(a) shows the dimensionless radius ϵ evolution for $\zeta = 0.47$ (for $\zeta = 0.25$, the bubble behaviour is qualitatively the same). Now this case shows a faster growth for the first bubbles in the unbounded case than for the confined case, contrary to what happened in the previous subsection with $\zeta = 0.15$. It is particularly interesting to notice that bubbles in confinement grow according to (4.2), whereas for the free case, the bubbles only match the analytical behaviour at the very early stages. This is due to the strong onset of convection which occurs at supersaturations $\zeta < 1 - 2$ achieved from a very high initial pressure P_0 [Ch.3]. The higher ζ , the faster and the stronger this onset occurs, as can be drawn from figure 4.5(b). This transition appears to be inhibited in the confined case, such that convection sets in later in time and without such a strength.

Consequently, figures 4.6(b) and 4.6(c) show that bubbles in an unbounded domain deplete much faster than bubbles in confinement, represented by a faster decreasing Υ_n . One would expect the opposite nonetheless, since the confinement impedes the dissolved gas in the bulk to diffuse towards the bubble and compensate for the absorbed gas, which indeed happens in the case

Figure 4.5: (a) Evolution of the dimensionless radius ϵ for $\zeta = 0.47$ and (b) corresponding derivative vs. the dimensionless square root of time x . The solid lines correspond to equation (4.2). There has been an inversion of some behaviour observed for $\zeta = 0.15$ (figure 4.4): now the first confined bubble grows slower than that in the unconfined case. However, due to a stronger depletion for the unbounded bubble, the subsequent bubbles in confinement grow faster.

of bubbles growing in an open medium. The explanation of this enhanced depletion in the open system resides in the mechanism from which it originates: a full buoyant depleted volume is formed as bubbles absorb gas from their surroundings, which induces the stronger and intensified transition to natural convection. That volume rises together with the bubble after detachment and partially replaces the depleted solution with liquid from the bulk [Ch.2]. In bounded domains, these phenomena occur differently, since the limiting walls firstly impede the formation of a buoyant depleted domain and, secondly, favour the gas mixing within the depleted area. These two effects combined result in a weaker long term depletion. However, confinement inhibits the refreshment of the depleted solution with non-depleted liquid, which can only come from the top aperture of the cylinder. For time scales beyond the duration of our experiments, we therefore anticipate that this impediment of solution refreshment due to the presence of the walls may start playing a dominant role and, therefore, the confined succession will start depleting faster as compared to the unbounded domain, as the crossover in extrapolating the curves in figures 4.6(b) and 4.6(c) appears to suggest.

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Figure 4.6: (a) The evolution of the depletion number Υ_n as a function of time for $\zeta = 0.15$ shows that for the first five bubbles in the succession, bubbles in the confined and open cases deplete their surroundings in very similar manner. In the long term, depletion is more affected by the minute stronger convective effect occurring in confinement. The solid lines in the corresponding colours represent the theoretical behaviour indicated by (4.7) for the confined domain (blue) and the model in [Ch.2] for the non-confinement (red). (b,c) The depletion number Υ_n for (b) $\zeta = 0.25$ and (c) $\zeta = 0.47$ strongly decreases for the unconfined scenario as compared to the bounded domain due to the full development of the buoyant depleted boundary layer. Increasing ζ provides the same qualitative behaviour.

4.5.3 The crossover between confined and unconfined bubble growth

In the previous subsection, it was concluded that a very small supersaturation results in very similar behaviour for the confined and unconfined bubble growth, whereas for larger values the unbounded succession of bubbles more strongly depletes the solution in which they grow. However, looking at figures 4.6(b) and 4.6(c), it is justified to assume that there will be a crossover time in which the impediment to refresh the solution within the confinement becomes more influential than the partial evolution of the buoyant depleted boundary layer and the enhanced mixing of the depleted solution.

By comparing the theoretical model (4.7) and the one in [Ch.2], we have estimated that there may exist a crossover time for the cases in which $\zeta \geq 0.17$. Lower values of the supersaturation level do not result in a crossover between the two theoretical depletion models. Therefore, for $\zeta < 0.17$, the confined bubble succession always depletes faster than the unbounded one, which corresponds to the results presented in §4.5.1 for $\zeta = 0.15$. For the higher supersaturations $\zeta = 0.25$ and $\zeta = 0.47$, we have predicted the crossover times by extrapolating the theoretical curves shown in the corresponding figures 4.6(b) and 4.6(c), obtaining values of approximately 133 and 208 min, respectively. This results qualitatively behave as expected: increasing ζ delays the crossover time since the bubbles in the open system undergo a much more intensified on-

set of density-driven convection and therefore deplete their surroundings much faster, whereas bubbles in confinement still suffer from the inhibiting effect of the walls on the evolution of the buoyant depleted boundary layer. We can therefore safely assume that for $\zeta > 0.17$ a crossover time may always exist, at least provided that ζ is not so large that advective effects due to massive expansion of the bubble interface would set in and finally become dominant.

4.6 Conclusions

Confinement around bubbles causes major effects on their growth and the way in which they absorb gas from the surrounding liquid, since the walls act as a shield which prevents the renewal of the liquid contained within the confinement with fresh non-depleted liquid from the bulk. The supersaturation level ζ determines the speed at which bubbles grow in this configuration and how fast the available gas is extracted from the saturated liquid. The higher the supersaturation is, the earlier and more intensified the onset of natural convection occurs, which results in a faster depletion, analogously to what occurs with bubbles growing on a free surface in an infinite bulk solution. For very low supersaturation levels, approximately $\zeta \approx 0.15$, confinement permits the bubble to grow slightly faster as compared to unbounded bubbles due to an enhanced onset of convection caused by the somewhat higher concentration gradients within the confined liquid. Therefore, the bubbles in confinement deplete slightly faster their surroundings. Nonetheless, the evolution of confined and unconfined bubbles under very small supersaturation level is rather comparable and similar. As the supersaturation is increased, the onset of natural convection plays a significant role from the early stages of the bubble growth. The origin of this convective onset plays a dominant role in the confined case, in which the cylinder walls impede the formation of the buoyant gas-depleted region around the bubble. Besides, the confinement now enhances the mixing of the depleted liquid within the cylinder walls. Depletion effects consequently become weaker as compared to bubbles growing on a free surface. Contrary to expectations, the lack of non-depleted liquid renewal from the bulk is counteracted by a better mixing within the confinement walls. On a much longer time scales, this compensating effect may actually be insufficient and the impediment to refresh the solution with non-depleted bulk liquid in the confined case will start causing a faster depletion at some point. The mathematical model (4.7) provides an excellent estimation of the long term depletion effects despite the many simplifications. We expect that also with higher supersaturation levels ζ , the model will still suffice as a first order approximation of results, but modifications will be necessary to account for many other side

effects which originate at large ζ , such as the appearance of parasitic bubbles which compete for the available gas and the much faster growth of the bubbles and their associated buoyant depleted boundary layer which is expected to result in the onset of strong advective effects.

4.A 1-D model for the depletion number Υ_n

Confinement has an extensive effect on how bubbles deplete their surroundings by means of absorbing the dissolved gas from the liquid. A buoyant depleted domain grows accordingly around the bubble and covers in the long term the full width of the cylinder. The only available expansion direction is therefore along the vertical axis z , which corresponds to the longitudinal axis of the cylinder. The concentration boundary layer is known to be significantly larger than the bubble radius [Ch.2], and it keeps growing as the succession continues.

To simplify matters, we model the succession of bubbles as a point sink extracting gas from a one-dimensional domain along the longitudinal axis z . That way, we write the diffusive mass transfer equation as

$$\frac{\partial \Delta c}{\partial t} = D \frac{\partial^2 \Delta c}{\partial z^2}, \quad (4.8)$$

where $\Delta c = c - c_0$. Two different boundary conditions and one initial condition are needed to obtain a unique solution for this equation:

$$\Delta c(z \rightarrow \infty, t) \rightarrow 0, \quad D \frac{\partial \Delta c(z, t)}{\partial z} \bigg|_{z=0} = \frac{\dot{m}}{A_b}, \quad \Delta c(z, 0) = 0. \quad (4.9)$$

Here, $\dot{m}$ is the mass transfer towards the bubble and A_b works as the bubble surface area. If we write this quotient in terms of the physical parameters used along this article, $\dot{m}/A_b = \rho_g R_{det}/3t_{det}$. As standard for heat transfer problems [see e.g. 72], this partial derivative equation is solved by means of Laplace transforms, in which we take the function $\Delta c(z, t)$ from a temporal domain t to a frequency domain s : $\mathcal{L}\{\Delta c(z, t)\}(s) = \mathcal{C}(z, s)$. We can then reformulate (4.8) and write

$$\frac{\partial^2 \mathcal{C}(z, s)}{\partial z^2} = \frac{1}{D} \mathcal{L} \left\{ \frac{\partial \Delta c(z, t)}{\partial t} \right\} (s) = \frac{1}{D} (s \mathcal{C}(z, s) - \Delta c(z, 0)). \quad (4.10)$$

By imposing the initial condition, it follows that

$$\frac{\partial^2 \mathcal{C}(z, s)}{\partial z^2} = \frac{s}{D} \mathcal{C}(z, s), \quad (4.11)$$

which can be directly integrated to obtain a solution of the type

$$\mathcal{C}(z, s) = A \exp\left(-\sqrt{\frac{s}{D}}z\right) + B \exp\left(\sqrt{\frac{s}{D}}z\right). \quad (4.12)$$

To determine the values of the integral constants, we need to impose the two spatial boundary conditions once transformed to the frequency domain s . By applying the first one,

$$\mathcal{L}\{\Delta c(z \rightarrow \infty, t)\}(s) = \mathcal{C}(\infty, s) = 0, \quad (4.13)$$

we directly obtain that $B = 0$. By the second one,

$$\mathcal{L}\left\{D \frac{\partial \Delta c(z, t)}{\partial z} \Big|_{z=0}\right\}(s) = D \frac{\partial \mathcal{C}(z, s)}{\partial z} \Big|_{z=0} = \mathcal{L}\left\{\frac{\dot{m}}{A_b}\right\}(s) = \frac{\dot{m}}{s A_b}, \quad (4.14)$$

we calculate A . The final solution in the frequency domain reads

$$\mathcal{C}(z, s) = -\frac{\dot{m}}{A_b D} \frac{1}{s} \sqrt{\frac{D}{s}} \exp\left(-\sqrt{\frac{s}{D}}z\right), \quad (4.15)$$

which transformed back to the temporal domain becomes

$$\Delta c(z, t) = -\frac{\dot{m}}{A_b D} \left(2\sqrt{\frac{Dt}{\pi}} \exp\left(-\frac{z^2}{4Dt}\right) - z \operatorname{erfc}\left(\frac{z}{2\sqrt{Dt}}\right)\right). \quad (4.16)$$

The change in the depletion number $\Delta \Upsilon_n = \Upsilon_n - \Upsilon_{n-1}$ is obtained by dividing Δc with $(c_0 - c_s)$. Considering that the 1-D length of the concentration boundary layer at detachment can be written as $R_{det} + \alpha\sqrt{3.3Dt_{det}}$, this leads to the final expression for the depletion parameter (4.7):

$$\begin{aligned} \Upsilon_n = \Upsilon_{n-1} - \frac{\rho_g R_{det}}{3Dt_{det}(c_0 - c_s)} & \left[2\sqrt{\frac{Dt_{det}}{\pi}} \exp\left(-\frac{(R_{det} + \alpha\sqrt{3.3Dt_{det}})^2}{4Dt_{det}}\right) \right. \\ & \left. - (R_{det} + \alpha\sqrt{3.3Dt_{det}}) \operatorname{erfc}\left(\frac{R_{det} + \alpha\sqrt{3.3Dt_{det}}}{2\sqrt{Dt_{det}}}\right) \right]. \end{aligned} \quad (4.17)$$

5

Coalescence of diffusively growing gas bubbles *

Under slightly supersaturated conditions, bubbles need many minutes to grow due to the low gas diffusivity in liquids. When coalescence occurs, the fact that the bubbles have diffusively grown on top of a surface allows for control with precision of the location and the timing at which the coalescence takes place. Numerous coalescences of two CO₂ microbubbles in water are recorded at a frame rate of ~65,000 fps. The evolution of the coalescing process is analysed in detail, differentiating among three phases: neck formation, wave propagation along the bubble surface and bubble detachment. First of all, the formation of the collapsing neck between both bubbles is compared to a capillary-inertial theoretical model. Afterwards, the propagating deformation along the surface is characterised measuring its evolution, velocity and dominant wave length. Once bubbles coalesce, the perturbing waves and the final shape of the new bubble breaks the equilibrium between buoyancy and capillary forces. Consequently, the coalesced bubble detaches and rises due to buoyancy, oscillating with its natural Minnaert frequency. In addition to the experiments, a boundary integral code has been used to obtain numerical results of the coalescence under similar conditions, showing excellent agreement with the experimental data.

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5.1 Introduction

For many years, scientists have focused on the study of drop coalescence, both experimentally [see e.g. 118, 119] and numerically [see e.g. 120], since this process is fundamental for many applications, such as inkjet printing and foam stability [121, 122]. The research on droplet coalescence driven by surface tension done by [123] showed that the coalescence mechanism of droplets is extraordinarily similar to that of bubbles. Indeed, the study of bubble coalescence has attained more interest as it affects mass transfer towards bubbles, i.e. bubble growth is highly affected by the presence of coalescence events [124]. Besides, bubble coalescence has a tremendous influence in the thinning and break up of liquid films [125, 126] and even alters the flavour of champagne [5]. The fact that bubbles emerge in many catalytic reactions with the purpose of energy conversion [see e.g. 14] and in many electrolytic processes [11] intrigues and motivates scientists to investigate how these bubbles behave in such conditions, and more concretely, how they interact with surrounding bubbles, including, of course, eventual coalescence and detachment processes, which in many applications is favoured, as attaching bubbles can hinder electrolytic and catalytic reactions.

In general, the coalescence of neighbouring growing bubbles is not always granted, as the presence of electrolytes [127, 128] and the viscosity of the surrounding liquid [129, 130] play a significant role, since the potentially coalescing bubbles need to push away the liquid layer in between them so that the coalescence event can occur [131]. [124] worked on the coalescence of 50–600- μm bubbles under a constant velocity flow, focusing on the oscillating frequency and damping time. [132] also worked on this subject, using bigger air bubbles in ethyl alcohol with an improved time resolution, allowing a more precise study of the early evolution and comparison of their results with their work about droplet coalescence [133]. On the other hand, [134] studied the growth of two cavitation bubbles and their coalescence in an inertia-dominated process. In our case, we focus on bubbles quasi-statically growing by diffusion, such that they take many minutes to grow and touch each other so that coalescence is dominated by capillarity. We precisely study the beginning of the coalescence and compare its results to previous research, improving both the experimental and the theoretical approach. We also study the capillary waves propagating along the surface of the coalescing bubbles, especially the velocity and dominant mode of the wave packet. The viscosity of the involved fluids is of relevance during this propagation, since the higher vibration modes are damped as the wave propagates along the bubble surface. To conclude, we comment on the detachment mechanism caused by energy liberation and buoyancy-driven upwards acceleration, as well as the bubble oscillation with

its Minnaert frequency during its rising.

5.2 Description of the experiments and computation of the boundary integral code

Bubble coalescence is challenging to record in a well-controlled way, e.g. when bubbles are chemically produced in a fast reaction, some instabilities in the bubble surroundings are created which hinder the record of their coalescence. The case of fast growing bubbles, in which the associated advective liquid flow may influence the coalescence process, or inertial bubbles hitting each other due to gravity, are also difficult to record. We use the set-up described in [37] to nucleate and grow bubbles. We can produce CO₂ bubbles quasi-statically growing in a diffusive regime and then study the coalescence with enough spatial and time accuracy. We use a small rectangular hydrophilic silicon chip with two hydrophobic pits, which are the bubble nucleation sites, as depicted in figure 5.1. We introduce the chip in a sealed tank filled with a CO₂-water saturated solution at pressure P_0 and temperature T . Afterwards, we decrease the pressure to $P_s < P_0$ by opening a control valve, turning the solution supersaturated according to Henry's law. Consequently, bubbles start growing until they touch and coalesce. The strong pinning conditions at the hydrophobic pits and the small ratio between the viscosities of the gas and the liquid [131] grant that the growing bubbles will push away the liquid layer in between them, guaranteeing coalescence. Finally, the coalesced bubble detaches from the substrate and a new couple of bubbles start growing. In every experiment, temperature and pressure are set to $T = 20.5 \pm 0.5^\circ\text{C}$, $P_0 = 9.2 \pm 0.05$ bar and $P_s = 7.75 \pm 0.05$ bar, thus achieving a supersaturation $\zeta = (c_0 - c_s)/c_s \approx 0.18$ (where c_0 indicates the gas concentration in the liquid at saturation and c_s at supersaturation), which is small enough to neglect advective effects influencing the bubble growth [as explained in e.g. 34].

For the coalescence process, we use a Photron SAX high speed camera to record images at 66,462 fps of 272×768 pixel resolution, which corresponds to $15.05 \mu\text{s}$ between two images and $5.5 \mu\text{m}$ per pixel. Figure 5.2 shows several snapshots of the coalescence of two $300 \mu\text{m}$ radius bubbles with a surface tension coefficient of $\sigma = 58.7 \text{ mN/m}$ [65], mixture density $\rho = 1014.5 \text{ kg/m}^3$ [67] and viscosity coefficient $\mu = 0.964 \text{ mN} \cdot \text{s/m}^2$ [64]. The radii of both bubbles at the moment of coalescence has been considered to be the same, even if they are slightly different due to small perturbations during their growth. However, the ratio of the two bubbles radii is always between 0.95 and 1.05.

To help analyse and compare the experimental results, we also simulate the bubble coalescence using an axisymmetric boundary integral (BI) code [see e.g.

Figure 5.1: (a) Sketch of two gas bubbles diffusively growing before coalescence. The attaching geometry is based on the study done in Ch.2. (b) Image recorded from experiments.

71, 135–137] under the assumption of zero viscosity. The simulation obtains information from the coalescence event in an easy way without the difficulties associated with performing experiments. Besides, higher-order waves can be studied in more detail. Aiming for simplification, some assumptions need to be made. We start the simulation when the bubbles are already connected through a thin neck at the symmetry axis (vertical line at a distance $d/2$ from each bubble, i.e. through the contact point at coalescence) to avoid the initial coalescence singularity [131, 138–141]. Different initial values of the connecting neck have been used, showing an extremely fast convergence to the actual initial experimentally measured neck radius [141]. Because we want to keep an axisymmetric configuration for simplicity, the wall is left out of the numerical configuration. Obviously, this is an oversimplification of the experimental situation. However, in this way, the simulation provides symmetric results along a horizontal axis which goes through the centre of the bubbles and along the symmetry axis. Results are thus accurate on the upper halves of the bubbles, since the presence of the pinning points in the experiments breaks the symmetry, as can be detected from image 5.2(d) on. Other codes, such as the free-surface Navier-Stokes code developed by [123] and the fully implicit arbitrary Lagrangian–Eulerian (ALE) method developed by [141], generated similar results.

Considering the gas–liquid properties, the liquid flow around the bubble is assumed to be irrotational, incompressible and inviscid. The gas inside the bubble behaves as an ideal gas with a polytropic exponent $n = 1.338$ [142] corresponding to the experimental conditions. The initial conditions in the simulation are matched to those in one of the experiments, i.e. distance between bubbles $d = 600 \mu\text{m}$, pressure at supersaturated conditions $P_s = 7.75$ bar, temperature $T = 20.5 \text{ }^\circ\text{C}$, surface tension coefficient $\sigma = 58.7 \text{ mN/m}$ and

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Figure 5.2: Snapshots of the coalescence of two $300\ \mu\text{m}$ radius bubbles pinned to $50\ \mu\text{m}$ radius pits. The images (a)-(o) are separated by $75\ \mu\text{s}$, images (o)-(t) by $150\ \mu\text{s}$ and images (t)-(y) by $300\ \mu\text{s}$. Three main stages can be identified: neck formation between the two bubbles, images (a)-(d); propagation of the capillary waves along the upper and lower half surface of the coalescing bubble and their final convergence at its side, images (e)-(j); and final detachment, upwards jumping, rising and oscillation with Minnaert frequency, images (k)-(y).

liquid (water) and gas (CO₂) densities $\rho_l = 1012.6 \text{ kg/m}^3$ and $\rho_g = 12.8 \text{ kg/m}^3$, respectively. The simulation has been run up to the point where the capillary waves propagating on the upper and lower half of the bubble converge at the opposite apex from the coalescence point, since we reach a singularity. Note that both outer (water) and inner (CO₂) fluid are independently modelled in the BI simulations [137]. A video which contains the one-to-one comparison between experiments and simulation can be found in the supplementary material.

5.3 Analysis of results

5.3.1 Diffusive bubble growth

We use several samples with different distances between the pits ($d = 300, 400, 500$ and $600 \text{ }\mu\text{m}$) and different pit radii ($10 \text{ }\mu\text{m}$ and $50 \text{ }\mu\text{m}$). We record the growth of successive bubble pairs with a LaVision camera at 2 fps, so that we can confirm their diffusion-driven growth. The theoretical evolution of the radius $R(t)$ of a single quasi-statically growing isolated bubble is given by the Epstein & Plesset equation [25]:

$$\dot{R} = D\zeta \frac{c_s}{\rho_g} \left(\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right) \quad (5.1)$$

where $D = 1.76 \cdot 10^{-9} \text{ m}^2/\text{s}$ [62–64, 143, 144] is the diffusivity of CO₂ in water. Equation (5.1) has been solved and the results agree with the experiments adding a term which accounts for the effect of the silicon chip on which the bubbles are growing [34]. The approximate solution for the dimensionless bubble radius $\epsilon = R/R_p$ reads:

$$\epsilon = \left(\sqrt{\frac{\zeta c_s}{2\pi\rho_g}} + \left(\frac{1}{2} + \frac{\zeta c_s}{2\pi\rho_g} \right)^{1/2} \right) x \equiv S^* x, \quad (5.2)$$

where R_p is the pit radius and $x = \sqrt{\left((2D\zeta c_s)/(\rho_g R_p^2) \right) t}$ the square root of the dimensionless time.

Because the two neighbouring growing bubbles compete for the dissolved gas, their growth is influenced by the distance d separating them [99]. However, the corresponding concentration boundary layers growing around each bubble as $\sqrt{\pi D t}$ merge in one concentration layer from which both bubbles absorb gas from the very early stages of the bubbles growth. Therefore, the influence of the distance d is negligible except for the very beginning of the process. In

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Figure 5.3: Temporal evolution of the dimensionless radius $\epsilon(t) = R(t)/R_p$ for two bubbles growing next to each other. The separation between the pits is indicated by the length d . Both bubbles show the same evolution and only one is represented for clarity. (a) Evolution of the dimensionless bubble radius ϵ before coalescence. The black line (corresponding to the same black curve in panel (b)) represents the theoretical Epstein & Plesset solution for a single bubble attached to a horizontal wall given by equation (5.2), based on [34]. (b) Evolution of the derivative of the bubble radius. The experimental points show a horizontal behaviour, corresponding to the expected competitive diffusive growth. The curve corresponding to $d = 600 \mu\text{m}$ differs from the others because the coalescence occurs in very early stages of the bubble growth, thus the mass transfer is settling to diffusion after the explosive initial growth right after nucleation.

figure 5.3, we represent the evolution of the bubble radii for different distances d between the pinning holes (which is equal to twice the coalescence radius, $d = 2R_{coal}$) and compare this to the theoretical radius evolution, equation (5.2). Indeed, the radius evolution is proportional to the square root of time as expected for a diffusive growth, figure 5.3(a). However, the nominal value of the slope $d\epsilon/dx$ is lower than the theoretical one [145] and independent of d [99], caused by the influence of each bubble growing next to a neighbouring one and the rapid merging of the two concentration boundary layers [146]. In figure 5.3(b), we plot the theoretical dimensionless radius derivative $(1/S^*)d\epsilon/dx = 1$ [following the representation depicted in 34] and compare it with the experimental derivative. The experimental data fall below the theoretically predicted diffusive growth for a single bubble growing on a substrate, which agrees with the expected behaviour for two neighbouring bubbles. Thus we confirm that the growth of both bubbles is driven by diffusion right before their coalescence. Note that long-time depletion effects [Ch.2] have not been observed during the diffusive growth of the bubble pairs, since the bubbles coalesce and detach before the onset of natural convection [34]. The area around the pits in which the new bubble pair will grow is also refreshed with new solution as the coalesced bubble detaches and rises. Whereas the damping time

Figure 5.4: Graphical definition of (a) the neck radius r_n and (b) the horizontal spacing between the two bubbles $\delta(r_n)$ measured in the equivalent configuration before coalescence.

of the originated flow is below one second [Ch.2], the new bubble pair needs approximately 10 s to renucleate afterwards and many minutes to grow until coalescence occurs, so the mass transfer enhancement caused by the refreshing flow plays no significant role on their growth.

5.3.2 Evolution of the neck between bubbles at the beginning of the coalescence

As seen in figure 5.2(a)-(d), the early coalescence is characterised by the neck formation between the bubbles. By integrating the axisymmetric Navier-Stokes equations from a quiescent point far away up to the neck radius, similar to the derivation of the Rayleigh–Plesset equation [147], we can model the evolution of the neck radius r_n , geometrically defined in figure 5.4(a), as:

$$\rho \left(\frac{dr_n}{dt} \right)^2 = \mu \frac{1}{r_n} \frac{dr_n}{dt} + r_n \Delta \rho g + \Delta P \quad (5.3)$$

where $\Delta \rho \approx \rho$ is the density difference between the liquid and the gas, g is the gravitational constant and ΔP is the Laplace pressure. We calculate the Reynolds $Re = \dot{r}_n d / 2\nu$ and Froude $Fr = \sqrt{2\dot{r}_n^2 / g d}$ numbers, comparing inertia with viscosity and gravity, respectively. We find that both Re and Fr are larger than 100, thus the inertial stress $\rho(dr_n/dt)^2$ is dominant in equation (5.3), such that we can neglect viscosity and gravity effects. Besides, surface tension dominates over viscosity, since the Ohnesorge number $Oh = \mu / \sqrt{\rho \sigma R_{coal}}$ is always of the order of $\sim 10^{-3}$. It is important to mention that up to 10 ns after the bubbles touch, the evolution of the neck is ruled by viscosity, crossing over to an inertia-dominated process, as demonstrated by [148]. The cross-over time is dependent on the viscosity of the liquids and gases involved in the coalescence, i.e. the higher the viscosity of the fluids involved, the later the cross-over will occur [149]. Our work focuses however on the capillary–inertia mechanics of the neck evolution.

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[133] suggested a Laplace pressure definition based on the neck radius r_n and the horizontal spacing between the two bubbles $\delta(r_n)$ measured in the equivalent non-deformable configuration according to the model in figure 5.4(b):

$$\Delta P = \sigma \left(\frac{1}{\delta(r_n)} - \frac{1}{r_n} \right). \quad (5.4)$$

Combining equation (5.3) and (5.4), and non-dimensionalising with the half-distance between pits $d/2$ and the capillary time $\tau = \sqrt{\rho(d/2)^3/\sigma}$, the ordinary differential equation (ODE) for the dimensionless neck radius $\tilde{r}_n = 2r_n/d$ becomes:

$$\frac{d\tilde{r}_n}{d\tilde{t}} = C \sqrt{\left(\frac{1}{\tilde{\delta}(\tilde{r}_n)} - \frac{1}{\tilde{r}_n} \right)}, \quad (5.5)$$

where C is a dimensionless fitting constant of order 1, $\tilde{\delta} = 2\delta/d$ and $\tilde{t} = t/\tau$. From geometry, we obtain $\tilde{\delta}(\tilde{r}_n) = 2 \left(1 - \sqrt{1 - \tilde{r}_n^2} \right)$ for the dimensionless horizontal spacing, which results in a differential equation for $\tilde{r}_n$ that can be numerically solved. Although [133] used δ as the length scale estimate in the Laplace pressure definition (5.4), we find a better agreement using the half-spacing between the two bubbles instead, which actually corresponds to an equivalent radius of curvature of the evolving neck in the axial direction. With this modification, the ODE for $\tilde{r}_n(t)$ becomes:

$$\frac{d\tilde{r}_n}{d\tilde{t}} = C \sqrt{\left(\frac{1}{1 - \sqrt{1 - \tilde{r}_n^2}} - \frac{1}{\tilde{r}_n} \right)} \quad (5.6)$$

Another approach with the square root of time is often proposed for the case of drops [119, 150]:

$$\frac{2r_n}{d} = B \sqrt{\frac{t}{\tau}}, \quad (5.7)$$

where B is a dimensionless fitting parameter. During the early coalescence, $\delta \ll r_n$ and $\delta \ll d/2$, conditions such that δ can be approximated as $\delta = 2r_n^2/d$, and therefore, $\Delta P = \sigma d/2r_n^2$. Introducing these new definitions into (5.3) after neglecting viscosity and gravity, we obtain

$$\frac{dr_n}{dt} = \sqrt{\frac{\sigma d}{2\rho r_n^2}}. \quad (5.8)$$

When solving this ODE, we recover equation (5.7), which is valid for the early coalescence and is only a particular case of the general equation (5.6). Indeed, [132] pointed out that this law is valid for $2r_n/d < 0.45$.

Figure 5.5: (a) Evolution of the dimensionless neck radius $r_n/(d/2)$ for different bubble radii at the moment of coalescence $R_{coal} = d/2$ and comparison with the Thoroddsen model (5.6) and Paulsen model (5.7), together with the results from the BI code. Time has been non-dimensionalised by the capillary time τ . Inset: same data as double logarithmic plot, for a better appreciation of the early coalescence. (b) Same evolution as in panel (a) but with the vertical axis compensated with the dimensionless time. Here we can appreciate with higher detail the discrepancies between experiments and the model with the square root of time, equation (5.7), which no longer agree after $t/\tau = 0.2$, whereas the model (5.6) is more realistic and precisely fits the experimental data even at high values of the neck radius. The BI results show excellent agreement with experiments, despite the initial coalescence singularity.

We measure the evolution of the neck radius for many coalescences with different values of the bubble radius. To compare the experimental results, we use the measured values for the upper part of the neck formed between the bubbles. Results for the lower neck are only considered for the very early coalescence, since the presence of the pits to which the bubbles attach breaks the symmetric neck evolution and impedes a free propagation of the deforming wave. The experimental results are compared to the theoretical models (5.6) and (5.7) in figure 5.5, as well as to the results obtained from the BI code. As expected, the square root scaling law (5.7) no longer accurately fits to the experimental data after $2r_n/d \approx 0.45$. Nevertheless, the capillary-inertial model, equation (5.6), precisely matches the experimental data at all times for a best fitting constant $C = 0.85$. In the literature, a fitting value of $C = 1.06$ in equation (5.5) for bubbles can be found [132], whereas a value $C = 0.80$ follows for the case of drops [133]. The difficulty in matching the experimental data to the theory originates from the choice of the initial time. Indeed, the first snapshot where we can see the bubble surface moving does not correspond to the exact beginning of the coalescence, which actually starts shortly before. To find time zero, we solved the ODE (5.6) with $\tilde{r}_n(\tilde{t} = 0) = 0$. Then, we shift the time of the experimental plot so that both theory and experiments agree.

Figure 5.6: (a) Evolution of the neck and its best-fit circle. The cross markers correspond to the contour of the top part of the coalescing bubble. Each contour from the bottom to the top of the figure is separated by $15 \mu\text{s}$ and the first contour on the bottom corresponds to the first recorded shape of the coalescing bubbles. The radius of the best-fit-circle corresponds to the neck curvature. (b) Time evolution of the top and bottom radii of curvature for $300 \mu\text{m}$ radius bubbles. The time when the two necks start growing differently corresponds approximately to image (c) on figure 5.2.

The results from the BI code precisely agree with the experimental data and with the theoretical model given by equation (5.6), which corroborates both of our modifications of the original model proposed by [133] and the results from our experiments.

In addition, we measure the time evolution of the neck radius of curvature in the axial direction $R_c(t)$, see figure 5.6. For the calculation of this radius of curvature, we fit a circle at the bridge formed between the bubbles at the position r_n , whose radius is by definition the neck curvature [132], as represented in figure 5.6(a). We investigate that the radius of curvature is also affected by the presence of the pinning points, figure 5.6(b). As expected, the early evolution is similar for both curves, but after $t \approx 0.1$ ms, the upper radius of curvature grows much faster than the bottom one due to the presence of the substrate and the pinning spots, which do not let the lower half-surface freely deform. As mentioned before, the same phenomenon occurs for the evolution of the neck radius.

Results concerning this radius of curvature are presented in figure 5.7. Figure 5.7(a) shows the time evolution of the radius of curvature. For the early coalescence, the curvature seems to follow a linear evolution if the radius of curvature is non-dimensionalised by the bubble radius at the start of the coalescence, accounting for any geometrical effect that may originate from the

Figure 5.7: (a) Time evolution of the dimensionless radius of curvature $R_c/(d/2)$ for different bubbles radii at coalescence R_{coal} . Inset: same data on a double logarithmic scale, for a better appreciation of the early coalescence. (b) Evolution of the radius of curvature $R_c(t)$ against that of the neck radius $r_n(t)$. It can be observed that the non-deformable model, in which any point on the bubble surface remains unaltered until it is reached by the perturbation, does not follow the experimental data. For both figures (a) and (b), the prediction given by the BI code accurately matches the experiments.

different $R_{coal} = d/2$ [151]. The radius of curvature also shows a linear dependence with the neck radius [132] during the early stages of the coalescence process, figure 5.7(b), increasing drastically as the neck radius approaches the value of the bubble radius. Both curves collapse into one universal behaviour, i.e. the capillary time τ is still relevant for the curvature evolution. Again, the BI code accurately matches the experimental results. The precision in the calculation of the radius of curvature is strongly affected by the bubble radius, with the last experimental values being extremely dependent on the selected points in the neck to which the curvature circle is fitted. Thus, the higher $2R_c/d$, the higher the inaccuracy in the calculation of the curvature radius.

If we assume that any point on the bubble surface remains unaltered until the perturbing wave reaches it, we can relate the radius of curvature to the neck radius as follows:

$$R_c = \frac{r_n^2}{d - \frac{r_n}{2}}. \quad (5.9)$$

However, the discrepancies between this limit and the experiments observed in figure 5.7(b) show that, indeed, the bubble surface at a certain point is deformed by the perturbing wave even before it reaches that spot. However, once more, the BI code provides an extremely good prediction of the radius of curvature related to the neck radius.

5.3.3 Propagation of the deformation wave

After the neck is formed between the two bubbles, the deformation travels along the bubble surface until the upper and lower waves converge at the opposite apex of the bubbles from the coalescence point, a shape with a reminiscence of a lemon, as shown in figure 5.2(g). We note that even though the lower deforming wave travels through the pits, figure 5.2(c)-(e), the coalescing bubble does not detach. Indeed, detachment occurs once the deformation moves backwards and goes through the pit position once more, figure 5.2(k)-(l). Despite surface tension dominating over viscosity during the wave propagation, $Oh \sim 10^{-3}$, a satellite pinch-off after the perturbing upper and lower waves meet at the side of the coalescing bubbles has not been observed, in contrast to the results documented by [152] and [140]. We associate the differences with the geometrical configuration of our system: the presence of the pits alters the perturbing wave propagation along the lower half-surface of the bubbles and breaks the axisymmetry of the process.

We focus on the surface deformation and how the collapsing waves travel along the bubble surface. Some results about capillary waves on a water–gas interface were discussed in [153] and [154], but with different geometries. Capillary waves have also been reported during the partial coalescence of droplets [155]. For a plane surface, the general dispersion relation for a single surface wave is (see e.g. [156] and [157, pp. 448-451]):

$$\omega^2 = \left(gk + \frac{\sigma}{\rho} k^3 \right) \quad (5.10)$$

with ω the angular frequency and k the wavenumber. Capillarity is dominant over gravity if $(\sigma/g\rho) \cdot k^2 \gg 1$, i.e. the wavelength $\lambda \ll 15.5$ mm for CO_2 bubbles in water. Our case fulfils this condition, since the wavelength we measure is smaller than 0.2 mm. We can thus neglect the gravity term in (5.10). Besides, for a spherical bubble, the angular wave vector has to be a natural number because of the periodic geometry. As shown in [157, pp. 468-469], the dispersion relation for the n mode of an air bubble in a liquid follows

$$\omega_n^2 = \frac{(n-1)(n+1)(n+2)}{\tau^2} \quad (5.11)$$

with capillary time $\tau = \sqrt{\rho(d/2)^3/\sigma}$, and the angular phase velocity

$$c_\theta = \frac{1}{\tau} \sqrt{\frac{(n-1)(n+1)(n+2)}{n^2}}. \quad (5.12)$$

The propagation of the surface deformation is a wave packet composed of many angular frequencies moving with different velocities, since the phase

Figure 5.8: Time difference Δt between the beginning of the coalescence and the convergence of the upper and lower waves at the opposite side of the coalescing bubbles (a) as function of the bubble radius at coalescence ($R_{coal} = d/2$) in logarithmic scale and (b) as function of the capillary time $\tau = \sqrt{\rho(d/2)^3/\sigma}$. The plots contain many different coalescence events. The red lines correspond to the best fit following (a) a power law and (b) a linear law.

velocity increases with n . To account for the wave packet main velocity, we measure the time Δt between the beginning of the coalescence and the moment in which the upper and lower waves meet each other at the sides of the bubble. Figure 5.8(a) shows the influence of the bubble radius at detachment R_{coal} on this time Δt for many different coalescence events. It is observed that the time the waves need to travel along the bubble surface and meet each other at the opposite apex from the coalescence point follows the power law $\Delta t \propto R_{coal}^{3/2}$. Therefore, it is straightforward to plot the measured time Δt against the capillary time τ . Clearly the plot in figure 5.8(b) reveals a linear dependency with a slope that corresponds to $\Delta t/\tau = 0.67$. Defining $c_\theta = \Delta\theta/\Delta t$, with $\Delta\theta$ being the angle θ (graphically defined in figure 5.9(a)) travelled by the wave packet during Δt , we can calculate a theoretical expression for the wave travelling time:

$$\Delta t = \tau \frac{n\Delta\theta}{\sqrt{(n-1)(n+1)(n+2)}} \quad (5.13)$$

The wave travels an angle $\Delta\theta = \pi$ when it reaches the opposite apex of the bubble from the coalescence point. Thus, assuming only one single mode n and knowing that $\Delta t/\tau = 0.67$, we find that the average mode $n = 20$ governs the wave propagation.

After having corroborated that the capillary time is the proper time scale, it is interesting to study the time evolution of the wave packet while it propagates

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Figure 5.9: (a) Definition of the angular position θ as calculated from experiments. (b) Angular position θ of the travelling deformation as function of the dimensionless time. It has been measured for 15 coalescing bubbles of different radii. The plot is on double logarithmic scale, showing convergence to a power law with exponent 1/2. The red line corresponds to the results given by the (axisymmetric) BI code, showing the very precise agreement between the experiments and the simulation.

along the bubble surface. More specifically, we analyse the evolution of the angular position of the deformation from the very beginning of the coalescence until the upper and lower waves reach the sides of the coalescing bubbles. After that, the coalescing bubble starts to fold inward, figure 5.2(h), and the measurement of the angular position using the centre of the initial bubbles no longer applies.

For a better understanding of the evolution of the wave packet as it moves along the coalescing bubble surface, we define an equivalent single wave with mode n at the angular position θ that will excite the same dominant mode of the wave packet at that same position. This dominant mode is obtained equalling the expression (5.12) to the corresponding definition of angular wave velocity $c_\theta = \theta/t$. Thus, assuming $n \gg 1$, we conclude that:

$$n = \left(\frac{\theta}{t} \right)^2. \quad (5.14)$$

An equivalent relation can be found for the case of partial coalescence [155]. Results are shown in figures 5.9(b) and 5.10, in which the results from different experiments with different R and d collapse when scaled with the capillary time [140]. We observe that the angular position does not change linearly with time because of the velocity dependence on n . The dominant mode is extremely high at the beginning of the coalescence, decreasing afterwards very rapidly to a value $n \approx 20$, as also appreciated by [152] and our results from equation (5.13). The logarithmic plots in figure 5.9(b) and 5.10(b) suggest

Figure 5.10: (a) Time evolution of the dominant mode of the wave packet during its propagation along the bubble surface, corresponding to the same experimental angular positions θ from figure 5.9. n is calculated for an equivalent single wave which would excite the same dominant mode as the wave packet, equation (5.14). (b) Logarithmic representation of the dominant mode, which suggests that its evolution follows a power law with an approximate exponent of -1 . For both figures (a) and (b), the red curve stands for the BI code results, which again accurately match the experiments. A small deviation can be detected when the waves propagating along the upper and lower half surface of the coalescing bubbles start approaching the opposite apex from the coalescence point. Even though the simulation results are within the spread of the experimental data, this deviation presumably originates from the simplifications employed in the BI code, i.e. the simulations neither account for viscous damping of the vibration modes (which becomes more relevant for the higher modes) nor for the presence of the pits which impede the free propagation of the lower wave. The small discrepancy can be better appreciated in figure 5.11.

Figure 5.11: Comparison between the experiments and the (axisymmetric) BI simulation (green line) for $300 \mu\text{m}$ radius bubbles. We notice the influence of the pits in the free propagation of the lower half wave, thus the code only provides accurate results for the upper half wave, which indeed freely propagates. Thus the final moments in which the two waves meet at the bubble sides cannot be codified with the desired precision. Besides, the wave packet contains more oscillation modes in the simulation, since viscosity damps the higher modes in experiments, which is not accounted for in the simulation.

Figure 5.12: Snapshots of the coalescing bubble (a) before the convergence of the upper and lower wave and (b) after. The red arrows point to the position of the peaks whose distance in-between corresponds to the wave length.

that the time evolution of the angular position and dominant mode follow a power law with an exponent of approximately $1/2$ and -1 , respectively, which is consistent with equation (5.14). The BI simulation precisely matches the experimental data except for the final points, where the deforming waves reach the bubble sides, figure 5.11. Besides, although viscosity can be neglected in the neck dynamics, it affects the highest vibration modes, damping the high frequencies in the wave packet. Indeed, the viscous time for an n mode is defined as:

$$\tau_\nu(n) = \frac{\lambda(n)^2}{\nu} = \frac{4\pi^2 R^2}{\nu} \frac{1}{n^2}, \quad (5.15)$$

where ν is the water kinematic viscosity. If we compare the capillary time τ with the viscous time τ_ν for $R_{coal} = 300 \mu\text{m}$ and $\nu = 9.64 \cdot 10^{-7} \text{ m}^2/\text{s}$ [64], we obtain $\tau_\nu(n = 500) = 0.02\tau$, $\tau_\nu(n = 100) = 0.54\tau$, $\tau_\nu(n = 50) = 2.2\tau$ and $\tau_\nu(n = 20) = 13.5\tau$. Figure 5.8(b) shows that the average time scale of the propagation is $\Delta t/\tau = 0.67$, therefore the higher modes are quickly damped during the propagation. This further explains the differences with the BI simulations, which do not take viscosity into account.

After the convergence of the waves at both bubble sides, we clearly see two peaks on the bubble surface instead of a single one, figure 5.12. We measure the velocity of those peaks and the distance between them, concluding that they remain quasi-constant with time. This suggests that the distance between the two peaks corresponds to the wavelength of the capillary wave, and therefore, it has now been reduced to a packet with a clearly dominant mode. Figure 5.13(a,b) shows the influence of the bubble radius after the coalescence, $R_b = \sqrt[3]{2}(d/2)$, on this wave length and phase velocity. As expected, the wavelength seems to be proportional to the final coalesced bubble radius R_b with a coefficient $a = 0.48$, figure 5.13(a). Since the wave length is equal to $2\pi R_b/n$, we find the value $n = 13$ for the dominant mode, which is smaller than the mode $n = 20$ governing the early propagation of the upper and lower

Figure 5.13: (a) Distance between the two peaks on the bubble surface for different bubble radii after the convergence of the upper and lower wave. We use the radius of the new bubble R_b , which is equal to $\sqrt[3]{2}(d/2)$ by conservation of volume. The dominant mode is thus directly proportional to the radius of the final coalesced bubble, as plotted in red. (b) Wave angular velocity after the top and bottom waves have met at the bubble side. The red curve corresponds to the theoretical phase velocity calculated using equation (5.12) and the fit in panel (a) for the distance between the experimental peaks, defined as the wave length.

5 wave towards the bubble sides. We surmise that viscosity continues to play a role, damping more and more the higher vibration modes of the bubble, as also occurred in [152]. Partial coalescence, as shown by [155], seems to follow the same mechanics regarding wave propagation.

5.3.4 Bubble detachment and rising

When the deforming wave passes again on its way back through the location of the pinning pits, the coalesced bubble typically detaches. Similarly to the case of droplets [158, 159], once the two bubbles coalesce, there is a liberation of surface energy $\Delta E_\sigma = 2\pi\sigma(d/2)^2 - \pi\sigma(d/\sqrt[3]{4})^2$ which is transformed into potential energy $\Delta P = \rho g \pi d^3 h/6$, where h is the height reached during the vertical jump that occurs as a result of this energy liberation. Energy conservation results in a jump of height $h = 6(1/2 - 1/\sqrt[3]{16})\sigma/\rho g d$. Afterwards, the bubble rises due to the effect of buoyancy. The equilibrium of forces on the bubble surface [160] can be expressed as follows:

$$(m_b + m_{add})\ddot{h} = (\rho - \rho_g)V_b g - F_d, \quad (5.16)$$

where $V_b = \pi d^3/3$ is the bubble volume after coalescence, $m_b = \rho_g V_b$ and $m_{add} = \rho V_b/2$ are the bubble and added masses and $F_d = 4\pi\mu(d/\sqrt[3]{4})\dot{h}$ is the drag force,

Figure 5.14: Rising position of the bubble after detachment vs. time. It can be appreciated that the actual rising of the bubble lays between the curves corresponding to the energy jump by the liberation of surface energy and the trajectory obtained by the equilibrium of forces on the bubble, equation (5.18). This implies that the coalesced bubble suffers from a small jump due to a partial energy liberation (which is much smaller than the calculated one) and is afterwards accelerated upwards by buoyancy.

which corresponds to the well-known Stokes' law on a clean bubble. This equation can be simplified considering that $\rho_g \ll \rho$, resulting in the following ODE:

$$\ddot{h} = 2g - \alpha \dot{h}. \quad (5.17)$$

This equation with $\alpha = 24\mu/\sqrt[3]{4\rho d^2}$ can be readily solved with initial conditions $h(0) = 0$ and $\dot{h}(0) = 0$ to obtain:

$$h(t) = \frac{2g}{\alpha}t + \frac{2g}{\alpha^2} \left(e^{-\alpha t} - 1 \right). \quad (5.18)$$

The jump height and the buoyancy-driven rising position of the bubble are plotted in figure 5.14 in comparison to the experimental data. It can be noticed that the energy jump is barely influential in this case, due to the high drag which the environmental liquid causes on the bubble and the energy loss due to the depinning from the substrate. However, experiments show that the actual bubble trajectory lies in between the region delimited by the energy conservation jump and the trajectory obtained by equilibrium of forces on the bubble. This fact implies that the bubble at detachment jumps instantaneously to a certain height by liberation of energy, being afterwards accelerated upwards by buoyancy with the corresponding resistance caused

by the Stokes' law term. Note again that Stokes's law is defined for a clean bubble, i.e. the slightest contamination will increase F_d and thus, α . We have varied the value of F_d up to a maximum of $F_d = 6\pi\mu(d/\sqrt[3]{4})\dot{h}$ corresponding to a small sphere, verifying that the theoretical curve (5.18) in figure 5.14 barely changes. This fact implies that the drag force caused by the liquid viscosity does not play a major role in the equilibrium of forces after bubble detachment, i.e. the upward rising is mainly dominated by buoyancy. Consequently, after the initial jump, the tendencies of both the experimental data and the theoretical curve (5.18) run quasi-parallel at all times.

After detachment, the new bubble surface oscillates, flattening first vertically and then horizontally, figure 5.2(p)-(y). This surface waving can be perfectly appreciated in the experimental data plotted in figure 5.14. The travelling waves are still deforming the surface even after detachment. The oscillation continues and is progressively damped while the bubble is rising, leaving its place for the next couple of bubbles to grow. In [157] and [161], it is shown that for a single oscillating bubble, the natural period of a given n mode can be written as

$$T_n = \tau \frac{2\pi}{\sqrt{(n-1)(n+1)(n+2)}}. \quad (5.19)$$

This expression is directly associated with the well-known Minnaert frequency [162]. Figure 5.15 shows the radial position of different points on the bubble surface during the oscillation after detachment. We notice that the oscillation amplitude is maximal at the angles $\theta = 0$ and $\theta = \pi$, and minimal at the angles $\theta = \pi/2$ and $\theta = -\pi/2$ (by symmetry). Figure 5.16 shows the radial position of the point $\theta = 0$ for different bubble radii. We directly conclude that the oscillation period is proportional to $\tau_b = \sqrt{\rho_l R_b^3 / \sigma}$, experimentally obtaining $T_{exp} / \tau_b = 1.88 \pm 0.25$, which corresponds to the mode $n = 2$ according to (5.19). Again, we see the effect of the energy loss at detachment and the viscosity in the damping of the higher modes of vibration.

5.4 Conclusions

Quasi-static, slow diffusive growth of two bubbles pinned to nearby pre-designed sites results in a well-controlled bubble coalescence without any instabilities caused by refreshing flows around the bubbles, spurious velocities, impact vibrations, chemical reactions or gas-feeding needles. Moreover, and contrary to drops, gravity and viscosity have no influence on the cause of the coalescence process in our current configuration, i.e. bubbles do not deform, reaching a perfect spherical shape, and coalescence is granted thanks to the low viscosity

5. Coalescence of diffusively growing gas bubbles

Figure 5.15: (a) Time evolution of the radial position of different points on the surface of the coalesced bubble after detachment. (b) Definition of the angles used for the curves in panel (a).

Figure 5.16: Evolution of the dimensionless radial length $r_{\theta=0}/R_b$ with the dimensionless time t/τ_b after bubble detachment, where τ_b is the capillary time using the reference radius R_b .

of the gas compared to that of the liquid and the presence of the pinning points on the substrate. The whole coalescence is only driven by capillary–inertia, with viscosity only playing a role in the damping of the vibration modes in the coalescing wave packet later in time. The capillary–inertial model (5.6) with the corrected term accounting for half of the horizontal spacing between bubbles accurately describes the evolution of the neck that bounds the two bubbles in the early coalescence. This evolution has been found to be universal, no matter which method triggers the coalescence, i.e. bubbles growing by diffusion have the same neck evolution while coalescing as bubbles in flows, bubbles coalescing by impact or bubbles generated by chemical reactions. On the other hand, the neck radius of curvature is hard to express in a theoretical way since it is very dependent on the deformation caused by the surface wave originated at the beginning of the coalescence. This deformation has been proven to be due to a pure capillary wave. The wave packet which propagates along the bubble surface can be approximately modelled by a single mode wave as the rest of the deformation spectrum (i.e. the vibration modes) is progressively damped, and therefore the propagating wave reaches in the end a constant velocity. The damping of the wave packet may be determinant for the potential detachment event to occur. Comparing the experimental data with the results of a BI code, we find an extremely similar coalescence evolution, except for the moment in which the capillary waves approach the opposite apex of the bubbles from the coalescence point, since the code does not account either for the presence of the two pinning spots or the role of viscosity in the damping of high modes in the wave packet. The deviations could be perfectly appreciated in figure 5.11. However, we proved that BI code and experiments can be compared one-to-one in the modelling of the upper half-bubble coalescence process, since this surface is not affected by the presence of the pits and can thus evolve freely. After detachment, the jump generated by surface energy liberation is barely influential compared to the buoyancy effect, equation (5.18), which makes the bubble rise rapidly. The fact that we achieved bubble detachment before the bubbles reach their theoretical detachment radius ($\approx 450 \mu\text{s}$ for a $R_p = 10 \mu\text{s}$ and $\approx 750 \mu\text{s}$ for a $R_p = 50 \mu\text{s}$) provides a good starting point for many applications which need to enhance bubble detachment for transporting gas away from a surface. While rising, the bubble keeps oscillating with a viscous-caused lower wave mode according to its Minnaert frequency. All the coalescence events occur in an extremely reproducible way, with no apparent influence of gas depletion caused by bubble detachment.

Figure 5.17: Snapshots of a coalescence event in which the final bubble is not detaching from the sample, with pit radii of $50\ \mu\text{m}$ and pits separation of $d = 150\ \mu\text{m}$. The first 8 images are separated by $75\ \mu\text{s}$ (including the interval between snapshots (8) and (9)), whereas the last 8 images are spaced by $600\ \mu\text{s}$. Note that the resulting bubble will continue growing diffusively on a much larger time scale until it reaches its detachment radius or coalesces with a new growing bubble from the other pit.

5.A Bubble coalescence without detachment

In one of our experimental designs, the distance d between the pits where the bubbles attach during their growth is chosen in such a way that the final bubble after coalescence does not reach the maximum volume which surface tension can exert [see e.g. Ch.2, 70, 71]. If the pit radii are $50\ \mu\text{m}$ and the distance between them is $150\ \mu\text{m}$, we observe that the coalesced bubble does not detach from the sample. Snapshots of this case are shown in figure 5.17. The early coalescence is similar to that in figure 5.2. However, in this case, since the touching bubbles do not have exactly the same radius, there is no symmetry in the wave propagation on the different bubbles. Whereas the smaller bubble detaches from the pit and merges into the bigger one due to its higher Laplace pressure, the bigger bubble stays on the substrate since the capillary force is strong enough to keep the coalesced bubble pinned to the

Figure 5.18: Snapshots of two different coalescence events when one bubble is much bigger than the other one. The images in the same row are separated by $75 \mu\text{s}$. This configuration is obtained by letting bubbles grow and coalesce without detaching. The bubble that remains pinned to the pit keeps growing while a new one grows from the other pit. After several coalescences have occurred, the difference in the radii of the bubble pair is more than noticeable.

surface. This event is followed by a new bubble growth from the pit where the now absorbed bubble was before, while the absorbing bubble keeps growing on the other pit until it reaches its detachment radius or coalesces with the much smaller new growing bubble. If the bubbles touched one more time, they would also collapse, but their radii would be significantly different, as shown in figure 5.18. The perturbation wave which is produced would also be considerably smaller than for the first coalescence, barely perturbing the absorbing bubble.

Ultrasound-mediated bubble removal from surfaces through rectified diffusion and microstreaming *

In mildly supersaturated solutions, gas bubbles generally grow by diffusion. However, in an ultrasound field, their growth rate is greatly increased once the resonant frequency of the bubbles is excited. In this article, we show and analyse the bubble behaviour under such an acoustic field, which results in a tremendous bubble growth enhancement induced by rectified diffusion and microstreaming. We show that the resonance curves corresponding to the bubble response increase in amplitude when the pressure amplitude of the ultrasound wave becomes higher. By anticipating the bubble response, we program different chirps of decreasing frequency which allow us to continuously enhance the mass transfer towards the bubble at different stages of its growth and consequently reach its detachment radius within a shorter time. Subsequently, we investigate the optimal configuration of a transducer to force bubble detachment from a surface within the acoustic parameter space. This configuration is potentially relevant to industrial applications where bubble accumulation becomes detrimental.

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6.1 Introduction

Bubble generation during chemical reactions is a problem which has concerned chemists, physicist and engineers for decades. Most electrolytic [11, 12] and catalytic [14, 163] processes involve the production of bubbles which, in the vast majority of cases, is detrimental due to overpotentials and decreasing reaction rates occurring as the bubbles block the reacting surfaces [13]. The problem becomes even more relevant in the recent era of modern fuels and energy conversion, where new techniques are being developed to increase the efficiency of the production of chemicals and, in particular, that of alternative fuels such as H_2 [Ch.7]. Innovative designs involve for example micropillars to artificially force bubble nucleation on designated locations [Ch.7, Ch.8]. Ultrasound applications present themselves as promising novel techniques to remove bubbles that are pinned to surfaces. In short, ultrasound refers to periodic pressure waves with a frequency in the range that may affect the behaviour of the bubbles. Ultrasound and bubbles are essential to many upcoming applications in the field of sonochemistry [58] and induce strong mechanical effects through cavitation [164, 165], which is especially the key phenomenon for surface rinsing [166] or local and controlled drug delivery in vivo [9, 167].

The size of a microbubble is the main parameter which governs its response to an ultrasound wave of a certain frequency, amplitude and number of cycles [161]. The most notable aspect of a microbubble reaction to ultrasound is the large volumetric oscillation at resonance. In turn, these volumetric oscillations initiate a number of secondary physical phenomena of which rectified diffusion is of principal importance. Rectified diffusion translates into an enhanced mass transfer towards the bubble [168–170], which originates from two main participations: the so-called area and shell effects [169, 170]. The former accounts for the combination of the change in gas pressure (proportional to the dissolved gas concentration at the bubble interface) during the expansion and compression cycles and the variation of the interfacial area allowing for gas exchange. The latter accounts for the influence of a change in the bubble volume on the boundary layer surrounding it, which is then forced to dilate or compress. These two effects combined result in a net mass flux towards the bubble [168], which may be affected by external conditions such as the presence of surfactants [171, 172].

The importance of rectified diffusion increases non-linearly with the bubble oscillation amplitude, and consequently, with the amplitude of the pressure wave [173]. Enhanced mass transfer by rectified diffusion is therefore significant when the bubble is driven at or near its resonance frequency, since only then the volumetric oscillations are sufficient to induce a substantial net gas flow towards the bubble [161]. Alternatively, the presence of a nearby surface

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generates non-spherical oscillations which, in turn, cause strong microstreaming with velocities of the order of 0.1 m/s and induce mixing over a length scale several times larger than the size of the bubble [174]. Microstreaming is known to occur hand-in-hand with rectified diffusion, although the relative effect of each has not often been quantified.

In the following, we introduce the experimental set-up (§6.2) and focus on two independent phenomena: the appearance and effect of rectified diffusion (§6.3) and the optimal setting for a transducer to achieve a successful bubble removal from a surface (§6.4). For the latter, two control parameters are selected: the amplitude of the pressure wave and the number of cycles. For the first, control over the ultrasound frequency also provides a means of exciting the resonant frequency of the bubble at different stages of its growth, and therefore, a mass transfer enhancement over a larger time span can be achieved. That way, the corresponding bubble detachment radius can be reached faster, freeing the surfaces from their detrimental presence.

6.2 Experimental set-up

The experiments were performed in a sealed tank which contains a pressurised solution of gas (CO_2) into a liquid (purified degassed water) [37], which is previously prepared in another independent pressurised tank. The initial pressure, $P_0 \approx 4$ bars, at which the solution is prepared determines the gas concentration in the bulk liquid by Henry's law. Several openings at the wall of the experimental tank allow for inserting the different control components. First of all, a holder maintains a silicon substrate horizontal at all times. On the surface of the substrate, a pit of radius $R_p = 10 \mu\text{m}$ is etched and covered with black silicon [21] such that it works as an artificial nucleation site for bubbles. Through another lateral opening, a transducer is directed towards the location of the pit. The transducer is connected to a power amplifier and a wave generator which allow for its configuration and control (refer to Appendix 6.A). On the opposite side of the tank, an ultrasound absorber collects the reflected waves to avoid the formation of standing waves within the tank. Light is shed through another lateral window and reflected by means of internal mirrors towards a long-distance microscope focused on the growing bubble. A schematic of the set-up is shown in figure 6.1.

In order to generate bubbles, the pressure is dropped to a certain lower value $P_s \approx 3.5$ bars to achieve a supersaturation level $\zeta = (P_0 - P_s)/P_s \approx 0.15$. Consequently, bubbles nucleate and grow on the preferential nucleation site on the substrate. When the ultrasound device is triggered, a pressure wave is sent towards the bubble. Its effect is recorded with a high-speed Photron SA-Z

Figure 6.1: Schematic of the experimental set-up from the camera perspective: a bubble grows from an artificial pit on a silicon substrate, an ultrasound wave is emitted from the transducer connected to a power amplifier and a wave generator, and the acoustic absorber collects the reflected waves to avoid the generation of standing waves within the tank.

camera at frame rates ranging from 1,000 to 200,000 fps. After bubble detachment, a new bubble subsequently grows and the process is repeated again. No sign of the depletion effects described in [Ch.2] has been observed. This may originate from the fact that the pressure waves act as effective solution mixers due to microstreaming, and parasitic bubbles at other locations within the tank may stimulate mixing such that the surroundings of the target bubble are refreshed at all times with non-depleted gas coming from the bulk liquid.

6.3 Mathematical and experimental analysis of rectified diffusion

The acoustically driven bubble obeys the well-known Rayleigh-Plesset equation [175–177],

$$\rho_m \left(R\ddot{R} + \frac{3}{2}\dot{R}^2 \right) = \left(P_0 + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3\kappa} \left(1 - \frac{3\kappa\dot{R}}{c} \right) - P_0 - \Delta P(t) - 4\mu \frac{\dot{R}}{R} - \frac{2\sigma}{R}, \quad (6.1)$$

where ρ_m is the solution density, σ the surface tension, $\kappa = 1.288$ the polytropic exponent of CO_2 in our experimental conditions [142], c the speed of sound in the solution, $\Delta P(t)$ the applied acoustic pressure and μ the dynamic viscosity. Finally, $R(t)$ is the bubble radius accounting for the oscillations around a

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reference radius R_0 , which is itself a slowly varying function of time due to (diffusive) processes that occur on a timescale much larger than the period of the ultrasound. This equation is readily linearised around R_0 to obtain the eigenfrequency f_{free} (also known as Minnaert's frequency) of the bubble as it oscillates in an infinite domain [162, 178]. Neglecting damping and excluding driving, we find:

$$f_{\text{free}} = \frac{1}{2\pi R_0} \sqrt{\frac{1}{\rho_m} \left[3\kappa \left(P_s + \frac{2\sigma}{R_0} \right) - \frac{2\sigma}{R_0} \right]}. \quad (6.2)$$

The presence of a substrate embedding the pit from which the bubble grows in our experiment is known to alter the response of bubbles to ultrasound. This problem can be treated with the image bubble method, in which the wall works as a secondary acoustic source generated by an image bubble. The equation describing the bubble dynamics attached to a wall then reads [179]

$$\rho_m \left(\frac{3}{2} R \ddot{R} + 2 \dot{R}^2 \right) = \left(P_0 + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3\kappa} \left(1 - \frac{3\kappa \dot{R}}{c} \right) - P_0 - \Delta P(t) - 4\mu \frac{\dot{R}}{R} - \frac{2\sigma}{R}, \quad (6.3)$$

which is an equation very similar to (6.1). In fact, the only changes are in the numerical prefactors on the left hand side, which change from $(1, 3/2)$ to $(3/2, 2)$.

To model the bubble response to the ultrasound wave, the system can be interpreted as a damped harmonic oscillator, and therefore, the corresponding resonance curve, i.e. the amplitude of the radial oscillation as a function of the driving frequency f , and the resonant frequency of the bubble f_{res} can be calculated by linearising (6.3) around R_0 (for the complete calculation, refer to Appendix 6.B). In our particular situation, the driving frequency f is fixed at all times whereas the bubble resonant frequency f_{res} decreases with increasing bubble radius R_0 . Therefore, we calculate the resonant curve as the amplitude of the radial oscillation as a function of the reference radius R_0 :

$$\Delta R = \frac{2\Delta P / 3\rho_m R_0}{\sqrt{\left(\frac{3\kappa \left(P_0 + \frac{2\sigma}{R_0} - \frac{2\sigma}{R_0} \right)}{\frac{3}{2}\rho_m R_0^2} - \omega^2 \right)^2 + \left(\omega \frac{\left(\frac{3\kappa R_0}{c} \left(P_0 + \frac{2\sigma}{R_0} \right) + 4\mu \right)}{\frac{3}{2}\rho_m R_0^2} \right)^2}}, \quad (6.4)$$

where $\omega = 2\pi f$. The second quadratic term within the square root contains

the damping coefficient δ :

$$\delta = \frac{\left(\frac{3\kappa R_0}{c} \left(P_0 + \frac{2\sigma}{R_0} \right) + 4\mu \right)}{\frac{3}{2}\rho_m R_0^2 \omega_{\text{wall}}}. \quad (6.5)$$

In this form, δ corresponds to the sum of the acoustic and viscous damping and $\omega_{\text{wall}} = 2\pi f_{\text{wall}}$, where f_{wall} equals the undamped eigenfrequency of the bubble, which is smaller than that for the free bubble case (6.2) [179] and reads

$$f_{\text{wall}} = \sqrt{2/3} f_{\text{free}}. \quad (6.6)$$

Including damping, the final resonant frequency of the bubble becomes

$$f_{\text{res}} = f_{\text{wall}} \sqrt{1 - \delta^2/2}. \quad (6.7)$$

From (6.4), we conclude that higher pressure amplitudes ΔP are followed by much more extensive bubble growth. The different resonance curves for a driving frequency $f = 50$ kHz are represented in figure 6.2 and compared to the experimental data. The theoretical curves agree qualitatively with the experiments when the viscous term of the damping coefficient δ is taken to be 3.5 times larger than the theoretically predicted one (6.5) at the corresponding conditions. This may originate from different side effects which could not be taken into account in the calculation of the resonant amplitude, such as the streaming caused by the bubble interface oscillations [174, 180, 181] and the increased vertical impedance due to the presence of the wall underneath [174]. It is also known that the system is additionally affected by thermal damping [169, 179, 182], which may have a rather strong contribution to the total damping coefficient. We have thus expanded the theoretical value of δ (6.5) to account for all these effects. For pressure waves of amplitude higher than $\Delta P = 12$ kPa, bubble detachment was achieved during resonance in the majority of cases, preventing the recording of full resonance curves.

Using (6.7), the $f = 50$ kHz driving frequency of the transducer directly results in an expected resonant radius $R_{\text{res}} = 95 \mu\text{m}$ (for other working frequencies, please refer to Appendix 6.C). Experimentally, a resonant radius $R_{\text{res}} = 91 \mu\text{m}$ is observed, which corresponds to the maximum of the experimental resonance curves represented in figure 6.2. The slight deviation may originate from the presence of spurious standing waves which cannot be fully cancelled by the acoustic absorber. In addition, in the same figure we show that the variation in the radius during rectified diffusion is proportional to the amplitude of the pressure wave ΔP , which is in agreement with (6.4).

As explained in §6.2, bubbles nucleate and grow from a pit of $R_p = 10 \mu\text{m}$ etched on a silicon substrate immersed in a mildly supersaturated solution of CO_2 in water. In this case, the bubble growth is mainly driven by

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Figure 6.2: Resonance curves of the bubble oscillation amplitude ΔR vs. the average radius R_0 for continuous ultrasound insonification at different pressure amplitudes ΔP at $f = 50$ kHz. Values higher than $\Delta P = 12$ kPa resulted in the majority of cases in bubble detachment much earlier than theory predicts, i.e. much below the Fritz radius, and therefore, the corresponding resonance curves could not be recorded beyond resonance. Clearly, increasing ΔP results in a larger ΔR . The experimental amplitude peak occurs at $R_{\text{res}} \approx 91 \mu\text{m}$, which coincides with the experiments in figure 6.3. The solid lines of corresponding colour represent the theoretical resonance curves (6.4), which agree qualitatively with experiments.

Figure 6.3: Bubble growth as a function of time under a continuous ultrasound pressure wave of $f = 50$ kHz. The dashed line corresponds to the theoretical prediction for pure diffusive growth on a substrate [Ch.2, 34]. Experiments up to the resonant radius show an excellent agreement with theory. Rectified diffusion occurs at a radius $R_{\text{res}} = 91 \mu\text{m}$ (horizontal solid line), which is slightly smaller than the theoretically predicted resonant radius. The corresponding jumps increase for higher ΔP . Note that after the sudden increase in radius has come to a stop, bubbles continue growing parallel to the theoretical diffusive curve.

diffusion [Ch.2, 25, 34]. The typical detachment radius is $R_{\text{det}} \approx 330 \mu\text{m}$, which corresponds to the so-called Fritz radius [70] with a correction due to necking between the gas trapped inside the pit and the bubble growing atop [Ch.2]. The resonant radius R_{res} is significantly smaller, such that no onset of density-driven convection described in earlier works [Ch.2, 34] is expected by the time rectified diffusion shall occur [Ch.3]. Figure 6.3 shows several radius versus time curves for a driving frequency of $f = 50$ kHz and different acoustic pressure amplitudes ΔP . It can be clearly seen that the bubbles first follow the theoretical predicted diffusive evolution $R \propto \sqrt{t}$ [Ch.2, 25, 34], but that the growth is suddenly and strongly enhanced when the bubble radius approaches its resonant value. Again, a resonant radius $R_{\text{res}} = 91 \mu\text{m}$ is reached, which accurately agrees with the maximum of the experimental resonance curves in figure 6.2. The enrichment in mass transfer takes place in the order of hundreds of milliseconds, and for a typical ultrasound pressure amplitude $\Delta P = 9.29$ kPa, the total radius jump corresponds to $\Delta R_0 = 20 \mu\text{m}$, which entails a volumetric increase of $(\Delta V)/V_0 = 80 \%$.

It is interesting to notice that after the bubble radius has suddenly jumped

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to a higher value, the bubble continues growing following the ordinary diffusive growth prediction. Therefore, rectified diffusion and streaming mainly occur in a very short time span around bubble resonance and fade drastically as soon as the bubble radius increases beyond R_{res} . Estimating the radius jump ΔR_0 as a function of the amplitude of the acoustic pressure wave ΔP is essential to achieve a controlled bubble growth. The resonance curve becomes therefore crucial at this point.

Further bubble growth enhancement can be achieved by replacing the fixed frequency excitation by a chirp excitation produced by linearly sweeping the ultrasound frequency from $f = 70$ kHz down to $f = 30$ kHz. During the frequency sweep, the microbubble will at some point attain resonance and undergo rapid growth. As a consequence, its resonant frequency will drop. As the chirp further decreases in frequency, the bubble will again enter resonance and will consequently rapidly grow once more. As a result, bubble growth may be sustained throughout the duration of the chirp, provided that the rate at which the bubble grows is faster than the frequency chirp rate. Figure 6.4 displays two sets of experiments in which we represent the bubble average radius R_0 and the associated resonant frequency (6.7) response to linear chirps with a duration of 20 and 2.5 seconds. At low ultrasound pressure amplitudes, the response follows the linear chirp up to a certain point where the bubble grows in a way that the ultrasound wave frequency cannot trigger any more resonance. For the highest amplitude, the chirp produces an instant increase of the bubble radius which generally ends up in detachment. In the case of the longer chirp, the bubble responds in steps to the ultrasound excitation, whereas the faster chirp permits the bubble to follow quasi-continuously the frequency evolution. In both scenarios, the bubbles reach an almost identical radius at the end of the chirp. If we focus on a typical $\Delta P = 9.29$ kPa, we obtain a total radius jump $\Delta R_0 = 70 \mu\text{m}$ for the two chirps, which results in a volume increase of 560 %, two orders of magnitude larger than for the case of a constant frequency ultrasound emission. As previously mentioned, the bubble growth induced by rectified diffusion is directly related to the oscillation amplitude ΔR [169, 177] and one would therefore naively expect the growth to exactly follow the chirp. The stepwise evolution of the bubble size suggests however that when the bubble hits resonance, it rapidly grows beyond its resonant size and overshoots the theoretically-calculated bubble jump ΔR_0 . We believe that this overshoot may be the result of microstreaming that locally replenishes the bubble surroundings with dissolved gas, such that the bubble may sustain its enhanced growth rate even beyond the resonant radius.

Figure 6.4: (a) Time evolution of the bubble radius R_0 and (inset) the corresponding resonant frequency f_{res} during the application of the frequency chirp. The correspondingly-coloured dotted lines stand for the moment in which the chirp was applied. The frequency changes linearly in time from $f = 70$ kHz to $f = 30$ kHz in a time span of 20 s. At low pressure amplitudes, the response follows the linear chirp until the ultrasound wave frequency cannot trigger any more resonance. For the highest amplitude, the chirp produces an instant burst of the bubble radius which ends up in detachment. (b) The chirp ranges here over 2.5 s, indicated in the inset as a black dotted line. The bubble frequency follows in a smoother way the rapid linear decrease of the transducer frequency. The highest amplitude in this case manages to retain the bubble on the substrate. However, the resulting aggressive oscillations impede that the bubble growth follows the chirp and, consequently, the expected prolonged enhancement cannot be properly achieved.

6.4 Bubble removal from surfaces

At higher ultrasound amplitudes, namely $\Delta P > 12$ kPa, the aggressive deformations suffered by the bubbles during resonance affect their pinning to the surface and, therefore, increase the probability of achieving an early detachment. Bubbles in an acoustic field experience two main forces [183]: one which derives from the bubble volume change in an oscillating pressure gradient and induces a displacement on the bubble that follows the pressure wave, known as primary Bjerknes force [178]; and a second which applies to acoustic scatter emitting secondary pressure fields and, consequently, makes bodies of the same type attract each other, known as secondary Bjerknes force [184]. In the present configuration, the secondary Bjerknes force contributes to the attraction of the bubble to its image materialised by the substrate, whereas the primary force promotes its movement along the substrate. The amplitude of the ultrasound pressure wave becomes therefore an essential ingredient to achieve a successful depinning of the bubble from the surface. In addition, the number of cycles plays a major role since, whereas short ultrasound bursts are expected to promote bubble detachment, long bursts will retain the bubbles attached to the substrate by the attractive action of the secondary Bjerknes force. The latter case may eventually end up in bubble repinning on a different location on the substrate. This competition results in an optimum, where detachment is achieved with the minimum amount of ultrasound energy density per area injected into the system. This energy density can be written as the product of the acoustic intensity $I_{\text{us}} = \Delta P^2 / 2Z$ (see e.g. [185]), where Z is the acoustic impedance, and the ultrasound working time t_{us} :

$$E_{\text{us}} = \frac{\Delta P^2}{2Z} t_{\text{us}} = \frac{\Delta P^2 N}{2Zf}, \quad (6.8)$$

where $N = t_{\text{us}}f$ is the number of cycles applied by the ultrasound. Figure 6.5 shows the results of a study performed at $f = 50$ kHz along two parameters: pressure amplitude ΔP and number of cycles N .

According to (6.8), high pressure amplitudes will in general end up in a successful outcome. However, extremely high amplitudes entail a much higher energy consumption and a more chaotic generation of bubbles by cavitation inside the experimental tank. Regarding the number of applied cycles, a low N translates into less energy applied by the transducer but results in an extremely low success percentage. The reason may not lie in the mechanism of detachment itself, but in the moment at which the ultrasound wave is emitted: a low number of cycles imply a wave of a few μs in working time, which makes it unlikely to hit the bubble when it is resonant, turning bubble removal into equally less likely. Consequently, the optimal configuration to achieve bubble

Figure 6.5: Study of the removal efficiency of a bubble under ultrasound of $f = 50$ kHz as a function of two control parameters: the pressure amplitude ΔP and number of cycles N . The ultrasound wave is emitted when the bubble is at resonance, i.e. $R_{\text{res}} = 91 \mu\text{m}$. Black circles stand for no bubble detachment, red squares for a 25 % removal efficiency, yellow diamonds for a 50 % efficiency, blue stars for 75 % efficiency and green hexagrams for complete success. For all the cases, downward-pointing triangles indicate that some bubbles were removed but pinned to the substrate in some other location.

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removal is a compromise between the lowest possible pressure amplitude and number of cycles. That way, we can optimise our transducer configuration to work at 5,000 cycles (which translates to $t_{\text{us}} = 0.1$ s at $f = 50$ kHz) and $\Delta P \approx 30$ kPa. Although figure 6.5 shows lower values of ΔP which also achieve successful bubble removal, we decided to opt for a higher ΔP for which the success in bubble removal appears to be consistent with the result distribution. The same applies to shorter working times t_{us} which could be considered as well: the required ΔP would need to be increased considerably. With the chosen optimal configuration ($N = 5,000$, $\Delta P \approx 30$ kPa), we managed to successfully remove all the bubbles whose size matched the frequency of the transducer.

As previously stated, using $\Delta P > 12$ kPa is followed by bubble detachment in the majority of cases, even for bubbles whose resonant frequency does not match the working frequency of the transducer. We varied the bubble size using the previous optimal configuration and achieved successful removal in an interval $R \in [45, 275]$ μm , which for a detachment radius $R_{\text{det}} \approx 330$ μm signifies that we are able to free the surfaces from the presence of bubbles whose radius lies in a range that covers 70 % of the bubble radii span.

6.5 Conclusions

Bubbles under the effect of an ultrasound field experience an enhanced mass transfer towards them, which results from the surface oscillations that occur when the resonant frequency of the bubble matches the frequency of the ultrasound wave. If an ultrasound wave of constant frequency is continuously emitted during diffusive bubble growth in a mildly supersaturated solution, enhanced diffusion occurs at resonance in the order of hundreds of milliseconds and its effect disappears as the bubble radius departs from the resonant radius and continues growing by ordinary diffusion. The magnitude of the oscillations and the jump in the bubble radius is determined by the amplitude of the ultrasound pressure wave ΔP , becoming larger as higher amplitudes are applied. The bubble dynamics and the streaming that originates from the bubble response to the ultrasound wave provide an excellent way of mixing the gas depleted liquid close to the bubble with fresh liquid from the bulk. In agreement with the above, no long term depletion effects are observed.

Knowing the bubble response to the different pressure amplitudes, chirps of decreasing frequency can be configured in a way that mass transfer is enhanced for a significantly longer time span as compared to the evolution under an ultrasound wave of constant frequency. The example given in the main text shows that for a typical $\Delta P = 9.29$ kPa, a constant ultrasound frequency entails a volumetric change of 80 %, whereas for the case of the frequency

chirp, we achieve a much larger variation (approximately 560 %). The use of frequency chirps to obtain longer and intensified growth rates is therefore remarkably viable.

As the pressure amplitude of the ultrasound wave is increased, bubbles suffer aggressive oscillations, which may end up in detachment at smaller radii than theory predicts. By means of controlling the pressure amplitude and the number of cycles, we conclude that the optimal configuration of our ultrasound set-up to remove resonant bubbles from the surface is at $\Delta P \approx 30$ kPa and $N = 5,000$ cycles (0.1 s at $f = 50$ kHz). Non-resonant bubbles in a wide range of radii may be successfully removed with these settings as well. This may originate from the intense resonance curve at these high driving pressures.

We conclude that ultrasound applications constitute a promising means to remove bubbles from surfaces to which they attach. Two possibilities may be regarded. One of them considers the enhancement of the bubble growth by the application of different chirps so that bubbles reach their detachment radius much faster. The second one consists in applying highly-energetic short pulses so that the bubble pinning points to the surface are broken and they can rise away by buoyancy. However, the question whether it is economically and energetically favourable to apply ultrasound waves in larger applications remains unanswered and open to discussion and further research. Nonetheless, these results constitute a first step towards new ultrasonic methods with the aim of releasing electrochemical surfaces from the detrimental effect that bubbles entail on them.

6.A Transducer calibration

The ultrasound wave is generated by a transducer (Benthowave BII-7501/50) connected to a power amplifier (AE TECHRON 2105) which receives a sinusoidal signal from a wave generator (Tabor Electronics 100 MS/s Arbitrary Waveform Generator 8026) activated by a trigger (BNC model 565 pulse/delay generator). Therefore we control the moment at which the ultrasound wave is emitted towards the bubble, its duration, its frequency and its amplitude.

The amplitude of the sinusoidal wave needs to be associated with a correspondent pressure amplitude ΔP which characterises the ultrasonic wave. The signal amplitude is fixed at the wave generator and amplified by the power amplifier before being transmitted to the transducer. The amplification curves of the power amplifier can be seen in figure 6.6. Throughout all the performed experiments, we work with a 100 % gain setting (the pertinent amplification is presented in figure 6.6(b)). At that configuration, the output voltage V_{out}

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Figure 6.6: (a) Output voltage V_{out} at different gain settings of the power amplifier when the sinusoidal wave is configured with an amplitude of 100 mV. (b) Output voltage V_{out} at 100 % gain for the different input voltage V_{in} from the wave generator.

behaves linearly with V_{in} and, therefore, the different signal amplitudes configured during experiments can be easily converted.

Once we determine the amplitude of the signal that the power amplifier is transmitting, we need to associate it to a pressure amplitude emitted by the transducer. For that purpose, we introduced the transducer into a pool of degassed water and activate it at typical working frequencies of $f = 50$ kHz and $f = 100$ kHz and a signal amplitude of 100 mV from the wave generator. By means of a hydrophone (Teledyne Marine TC4013-1), we measure the pressure field around the transducer and create a pressure map, figure 6.7, which we use to transform our signal amplitude from the wave generator to a pressure amplitude ΔP from the transducer. Note that the original location of the hydrophone is at 25 mm from the ultrasound surface and centred to its longitudinal axis. The different ΔP at other working signal amplitudes from the wave generator can be directly calculated due to the linear behaviour of the power amplifier.

As one can extract from figure 6.7(c), the transducer operates optimally at frequencies of $f = 57$ kHz and $f = 110$ kHz. During experiments, we decided to apply a lower frequency of $f = 50$ kHz, since the corresponding pressure amplitude ΔP permits us to better record the phenomena and to better control the bubble growth. From the pressure map in figure 6.7(a) and the position of the bubble on the substrate (0 mm lateral distance and 15 mm depth in the map -corresponding to an actual depth of 40 mm-) at 100 mV from the wave

Figure 6.7: (a,b) Pressure amplitude ΔP map at 100 mV from the wave generator at (a) $f = 50$ kHz and (b) $f = 110$ kHz. Note that the hydrophone original location is at 25 mm depth, so that 0 mm in the map actually corresponds to 25 mm in our experiments. (c) Pressure amplitude ΔP response for different frequencies of the transducer at 100 mV from the wave generator at the location of the bubble in the experiments. All the plots are measured at a 100 % gain from the power amplifier.

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generator, we obtain a $\Delta P = 9.285$ kPa. The outcome for different experiments at frequencies of $f = 110$ kHz are transformed to $\Delta P = 25.75$ kPa at 100 mV (see Appendix 6.C).

6.B Calculation of the resonance curve and resonant frequency of a bubble on a surface under the effect of ultrasound

To account for the influence of the wall on the bubble response to the ultrasound wave, the method of images is used, in which the presence of the wall is accounted for by an image bubble. The image bubble affects the dynamics of the original bubble in a way that the final dynamics equation can be written as (6.3) [179]:

$$\rho_m \left(\frac{3}{2} R \ddot{R} + 2 \dot{R}^2 \right) = \left(P_0 + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3\kappa} \left(1 - \frac{3\kappa \dot{R}}{c} \right) - P_0 - \Delta P(t) - 4\mu \frac{\dot{R}}{R} - \frac{2\sigma}{R}. \quad (6.9)$$

This equation can be solved by means of linearisation around the reference radius R_0 . In this case, the radius of the bubble at each moment R can be described as a small variation around an average radius R_0 , i.e. $R = R_0(1+x)$, where x represents a dimensionless oscillation around the reference value. By substituting in the previous equation and neglecting the non-linear terms with x , the following expression is obtained:

$$\frac{3}{2} \rho_m R_0^2 \ddot{x} + \dot{x} \left(\frac{3\kappa R_0}{c} \left(P_0 + \frac{2\sigma}{R_0} \right) + 4\mu \right) + x \left(3\kappa \left(P_0 + \frac{2\sigma}{R_0} \right) - \frac{2\sigma}{R_0} \right) = -\Delta P, \quad (6.10)$$

which can be directly associated with the standard equation for a harmonic oscillator of the form $\ddot{x} + \delta\omega_{\text{wall}}\dot{x} + \omega_{\text{wall}}^2 x = F(t)$, where $F(t) = F_0 \exp(i\omega t)$ is the acoustic forcing term. The small oscillations around the reference value can be then written as a harmonic response $x = x_0 \exp(i\omega t)$, where x_0 is the dimensionless oscillation amplitude. The corresponding first and second derivatives are therefore proportional to x , so that a final algebraic expression can be derived for x_0 :

$$x_0 = - \frac{\Delta P / \frac{3}{2} \rho_m R_0^2}{\frac{3\kappa \left(P_0 + \frac{2\sigma}{R_0} \right) - \frac{2\sigma}{R_0}}{\frac{3}{2} \rho_m R_0^2} - \omega^2 + i\omega \frac{\left(\frac{3\kappa R_0}{c} \left(P_0 + \frac{2\sigma}{R_0} \right) + 4\mu \right)}{\frac{3}{2} \rho_m R_0^2}}. \quad (6.11)$$

If we now compare this solution to the standard solution after linearising the equation for a harmonic oscillator, $x_0 = F_0 / (\omega_{\text{wall}}^2 - \omega^2 + i\delta\omega\omega_{\text{wall}})$, we

obtain that

$$\omega_{\text{wall}} = 2\pi f_{\text{wall}} = \frac{1}{R_0} \sqrt{\frac{2}{3\rho_m} \left[3\kappa \left(P_s + \frac{2\sigma}{R_0} \right) - \frac{2\sigma}{R_0} \right]}, \quad (6.12)$$

which equals (6.6). To obtain the resonant frequency, the maximum of (6.11) needs to be found with respect to ω by solving $dx_0/d\omega = 0$. As a result, we obtain (6.7). For the calculation of the resonance curves, we directly determine the amplitude of the radius oscillation as a function of the reference radius R_0 (and equivalently f_{res}) and the driving frequency f as $\Delta R = R_0|x| = R_0|x_0|$, which corresponds to (6.4).

6.C Rectified diffusion and bubble removal at 110 kHz

The best working condition for our transducer is at $f = 110$ kHz, as we discussed in Appendix 6.A. We have performed additional experiments at that configuration, associated with a (smaller) resonant radius $R_{\text{res}} = 43 \mu\text{m}$. In this case, the pressure amplitude of the ultrasound wave produces much more powerful effects than the configuration at $f = 50$ kHz, even at the smallest signal amplitudes of the wave generator. Therefore, bubbles shake violently from the very beginning of their growth and are rapidly removed from the substrate. Their growth is also affected and does not follow any more the diffusive expected behaviour [Ch.2, 34] before reaching resonance, as can be noticed from figure 6.8. The ultrasound wave causes mixing and advective flows within the tank and generates a chaotic behaviour of the bubbles (which now appear on many different locations on the substrate). Hence, we decided to apply a more controlled signal at $f = 50$ kHz for the majority of our experiments. Nonetheless, further research at higher frequencies may be useful to achieve an optimal system which enforces an early detachment on bubbles and consequently releases the reacting surfaces from their detrimental presence.

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Figure 6.8: Bubble growth under a constant ultrasound wave of $f = 110$ kHz. Detachment is always achieved and the expected growth by diffusion is strongly altered.

Gas bubble evolution on microstructured silicon substrates ^{*} [†]

The formation, growth and detachment of gas bubbles on electrodes are omnipresent in electrolysis and other gas-producing chemical processes. To better understand their role in the mass transfer efficiency, we perform experiments involving successive bubble nucleations from a predefined nucleation site which consists of a superhydrophobic pit on top of a micromachined pillar. The experiments on bubble nucleation at these spots permit the comparison of mass transfer phenomena connected to electrolytically generated H_2 bubbles with the better-understood evolution of CO_2 bubbles in pressure-controlled supersaturated solutions. In both cases, bubbles grow in a diffusion-dominated regime. For CO_2 bubbles, it is found that the growth rate coefficient of subsequent bubbles always decreases due to the effect of gas depletion. In contrast, during constant current electrolysis the bubble growth rates are affected by the evolution of a boundary layer of dissolved H_2 gas near the flat electrode which competes with gas depletion. This competition results in three distinct regimes. Initially, the bubble growth slows down with each new bubble in the succession due to the dominant depletion of the newly-formed concentration boundary layer. In later stages, the growth rate increases due to a local increase of gas

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supersaturation caused by the continuous gas production and finally levels off to an approximate steady growth rate. The gas transport efficiency associated with the electrolytic bubble succession follows a similar trend in time. Finally, for both H_2 and CO_2 bubbles, detachment mostly occurs at smaller radii than theory predicts and at a surprisingly wide spread of sizes. A number of explanations are proposed, but the ultimate origin of the spreading of the results remains elusive.

7.1 Broader context

Bubbles are omnipresent in several entangled phenomena, particularly in electrolyzers or photoelectrochemical cells. Their influence in (photo)electrochemical and heat and mass transfer phenomena is still investigated in connection with the development of new devices including novel materials for renewable energy sources, specifically in solar fuel emerging technologies. In order to maximize the efficiencies of solar fuel generation such as hydrogen, a deep understanding of bubble evolution phenomena must be achieved. Once bubbles are formed, their attachment to the reacting surface can inhibit the desired production of the fuel. In this context, novel electrodes that could guarantee controlled release and transport of the fuel away from the active sites can improve significantly the overall efficiency of electrolyzers and (photo)electrochemical reactors. This chapter is concerned with pioneering work on the understanding of physicochemical processes required for the design of new types of structured

materials to control the formation of bubbles with increased mass transport efficiency.

7.2 Introduction

Hydrogen is a promising energy carrier that can be obtained via zero CO₂ emission techniques [186–188] such as solar-driven water splitting [189–192]. However, the chemical reactions involved in such processes result in bubble generation. Such bubbles can block the reacting surfaces and decrease the process efficiency [193, 194].

The formation of bubbles on liquid-immersed surfaces is relevant for many gas-producing processes such as boiling [195], catalysis [14, 196] and electrolysis [197, 198]. More specifically, the formation of bubbles during chemical processes may be either beneficial due to increased heat and mass transfer induced by convection upon bubble detachment [199], or detrimental due to overpotentials caused by blocked active sites on the electrodes [200–202].

Bubbles preferably nucleate in small defects such as pits or crevices, where gas can be easily entrapped and the energy barrier is smallest [84]. A certain control over the location at which bubbles are prone to nucleate can be achieved by modifying the topography of the solid surface with suitable microstructures that act as preferential nucleation sites. The robustness of this concept has been demonstrated during pressure pulse propagation [203], ultrasound exposure [204], turbulent boiling [205] and under liquid flow conditions [206]. For this purpose, pillars are fabricated as preferential nucleation sites for bubbles, as shown in figure 7.1(D), following a long-term line of research in our group with the aim of understanding and controlling the bubble evolution as a function of gas diffusion [Ch.2, Ch.8, 34, 37].

Three different phases can be distinguished during bubble evolution as shown in figure 7.1: bubble nucleation at the surface (figure 7.1(A)), growth (figure 7.1(B)) and detachment (figure 7.1(C)). In this study, we provide an in-depth comparative analysis between bubble evolution on a single pillar during electrolysis and the better-understood bubble evolution in pressure-controlled CO₂ supersaturated solutions on the same geometry, working out similarities and differences between the two processes. Our ultimate goal is to increase energy conversion efficiencies of solar-driven water splitting systems by controlling the gas bubble evolution on micromachined electrodes.

7.2.1 Outlook

In this fundamental study, we have investigated the isolated bubble evolution on artificial nucleation sites micromachined on electrodes. The knowledge

Figure 7.1: Various stages of bubble evolution on electrodes. (A) Heterogeneous bubble nucleation, here shown to occur in a crevice. The electron flux towards the electrode surface is indicated by ϕ_e . The flux $\phi_{H_2(aq)}$ indicates the diffusive transport of H_2 gas to the nucleating bubble. The highest gas concentration is at the electrode surface, indicated by a lighter blue color (the same colour pattern applies to the other plots). (B) Bubble growth on the electrode surface. The direction of the interfacial tension force F_σ and buoyancy force F_b are shown. (C) Detachment of bubbles by buoyancy overcoming the interfacial tension force which pins the bubble to a crack or crevice. (D) Artificial nucleation sites to facilitate successive bubble evolution. On the left panel, the H_2 bubble evolution during water splitting is shown. The dotted area shows the time-dependent area from which the bubble experiences influx of gas via diffusion. On the right panel, the CO_2 bubble evolves in a CO_2 supersaturated medium. The gas concentration is homogeneous in the liquid apart from the time-dependent area around the bubble where the gas becomes depleted as successive bubbles grow [Ch.2], indicated by a darker blue color.

achieved with our experimental and theoretical work can certainly assist in the design of novel devices in the future. These future works could use nucleation sites to prevent the crossover of species in configurations in which the electrodes could be used to drive the bubbles to different streams [207] or to facilitate buoyancy driven separation mechanisms [208]. Artificial nucleation sites could also be used to evolve bubbles in predefined locations, a scenario which has been suggested to give rise to increased flexibility in device design, optimization and operation [209]. The use of multiple nucleation sites on electrodes permits the definition of areas on the electrodes where bubbles are generated such that they do not compete for evolved gas as well as areas where they do. This could determine areas on the electrode surface where bubbles do not form, and dedicated areas where bubbles do form, allowing for controlled bubble formation at higher current densities. Major advantages could lie in designing electrodes where the catalytic surface is kept free from bubbles.

7.3 Materials and methods

7.3.1 Microfabrication of silicon substrates

Micropillars on the surface of the electrode increase the active area and contact with the liquid phase, ultimate characteristics which are desirable in photolysis applications [210, 211]. This approach encourages the construction of small and dense structures which work as light-harvesting areas. With the aim of understanding the fundamentals of bubble evolution on pillars, we focus on a single pillar microstructure of radius $R_p = 2.5 - 15 \mu\text{m}$ to study the succession of single bubbles generated on them. A superhydrophobic pit on top of the micropillar serves as the nucleation site [84].

Boron-doped silicon wafers with (100) crystal orientation, resistivity in the range of $0.01 \Omega\cdot\text{cm} - 0.025 \Omega\cdot\text{cm}$, thickness of $525 \mu\text{m}$ and single side polished, were covered by $1.7 \mu\text{m}$ Olin OiR 907-17 resist. Using photolithography, circular regions ranging $R_0 = 1 - 10 \mu\text{m}$ in radius were defined, as shown in step 1 in figure 7.2(D). The circular regions were etched with a deep reactive ion etching (DRIE) Bosch process (Adixen AMS100SE) to a depth of $\sim 20 \mu\text{m}$. Black silicon was formed at the bottom of the pits with DRIE, as shown in step 2 in figure 7.2(D). Black silicon is an important structure that allows for better gas trapping while immersing the substrates in liquid. Afterwards, additional fluorocarbons were deposited ($\pm 40 \text{ nm/min}$) inside the pits, turning them superhydrophobic [91]. The deposition times varied per set of samples between 7 s to 60 s.

The pillar radii were defined with photolithography as shown in step 3 in

figure 7.2(D). These pillars were etched with DRIE to various heights in the range of $0\ \mu\text{m} - 60\ \mu\text{m}$. An aluminium contact was created via DC-sputtering with a thickness of $100\ \text{nm}$ (99% Al, 1% Si) at the bottom of the substrate, as shown in step 4 in figure 7.2(D). An ultrasound (VWR Ultrasonic Cleaner USC-THD, 45 kHz) acetone bath was used to remove the resist. Afterwards, the wafers were diced (Disco DAD 321) into $10\ \text{mm} \times 10\ \text{mm}$ square substrates. Prior to the measurements, the samples were cleaned with another ultrasound acetone bath step. Figure 7.2(A,B) shows SEM images of fabricated micropillars and figure 7.2(C) shows the black silicon inside the superhydrophobic pit.

7.3.2 Experimental set-ups for bubble evolution

Figure 7.3 shows the electrolysis set-up, consisting of a custom-made acrylic holder, a camera and a power source. The acrylic holder is designed to keep the substrate in place, to hold a platinum wire counter electrode far away from the growing bubble and to contain the electrolyte. A circular area of the silicon substrate with radius $R_e = 3.5\ \text{mm}$ and sealed to the holder with a Teflon ring is in contact at all times with the electrolyte. This radius is approximately ten times the maximum bubble radius and, therefore, we can assume that the holder walls do not play any significant role during bubble growth on the pillars. The substrate contains an electrical contact at the bottom aluminium layer through which the current is supplied (not shown in figure 7.3 for simplicity). A Keithley 2410 power source is used to drive the constant-current electrolysis. For optical imaging, a Flea[®]3 Monochrome Camera, (optical resolution of $1.1\ \mu\text{m}/\text{pixel}$) is coupled to a 50/50 Beam-splitter Cube. For illumination, a Galvoptics KL2500 LCD 230V light source is used.

At the beginning of each experiment, the holder is filled with 20 mL of fresh electrolyte. The electrolyte consists of a solution of non-degassed Milli-Q water with 10 mM Na_2SO_4 salt and a pH 3 buffer of 1 mM anhydrous sodium acetate and 0.1 M acetic acid. The temperature remains constant at all times, $T \approx 20\ ^\circ\text{C}$. During each experiment, a constant current in the range of $10\ \mu\text{A} - 600\ \mu\text{A}$ is supplied. The resulting current density J falls in the range of $0.3\ \text{A}/\text{m}^2 - 15\ \text{A}/\text{m}^2$. The potentials during experiments were measured within a range of 1.8 V to 4.9 V.

To compare the evolution of H_2 bubbles generated by electrolysis with that of CO_2 bubbles growing in an initially uniformly supersaturated solution, identical silicon substrates are placed within a pressurized test chamber (pressure $P_0 \approx 9\ \text{bar}$) that is filled with carbonated water previously saturated at the same pressure. By lowering the pressure to approximate values of $P_l \approx 7.7$ bars, a supersaturation of $\zeta = P_0/P_l - 1 \approx 0.17$ is achieved following Henry's

Figure 7.2: Scanning Electron Microscope (SEM) images of (A) a micropillar with a 10 μm diameter, a pit diameter of 2 μm and a pillar height of 25 μm , viewed at a 45° angle, (B) a micropillar with a 30 μm diameter, a pit diameter of 15 μm and a pillar height of 30 μm viewed at a 20° angle, and (C) a close-up of black silicon at the bottom of the pit in panel (B) viewed under a 20° angle. (D) Sketch of the cross-sectional view (not to scale) of the substrate fabrication process. Step 1 shows the p⁺⁺ type silicon wafer on which a pattern is created via photolithography to mark the outline of the pit. With dry etching, a pit is created and black silicon formed at its bottom, step 2. Resist is applied and patterned via photolithography to mark the outline of the micropillar for dry etching, step 3, after which an aluminium backside contact is formed via DC sputtering. The resulting complete substrate is shown in step 4.

Figure 7.3: Schematic of the electrolysis set-up (not to scale). At the top, the optics consist of a camera, lens and light source. Below the optics, an acrylic holder (yellow) which contains the substrate (grey) is placed. A circular area of the substrate of radius $R_e = 3.5$ mm is in contact with the electrolyte (light blue), in which the counter electrode is placed (top right). A DC power source is used to drive the reaction.

law (at constant temperature) and, consequently, bubbles nucleate and grow on the predefined spots. A detailed description of this experimental set-up and procedure can be found elsewhere [Ch.2, 37].

7.4 Results and discussion

7.4.1 Bubble nucleation on a superhydrophobic pit

The superhydrophobic pit entraps a gas pocket upon submersion in a liquid[203] and hence acts as a site for heterogeneous nucleation. The interfacial or equilibrium concentration of dissolved gas at a liquid-gas interface can be written as $C = k_H P_g$ according to Henry's law, where k_H is Henry's constant (a decreasing function of temperature specific to each gas-liquid pair) and P_g is the partial pressure of the gas acting on the liquid surface [26]. For a pit with a circular opening of radius R_0 , the pressure threshold at which bubbles begin to grow is given by the condition [91]

$$P_v + P_g > P_l + \frac{2\sigma}{R_0} \equiv \frac{P_v}{P_l} + (\zeta + 1) > 1 + \frac{2\sigma}{P_l R_0}, \quad (7.1)$$

where P_v is the liquid vapor pressure, P_l is the liquid pressure and $\sigma = 0.07$ N/m is the liquid-gas interfacial tension (for simplification, we assume a con-

stant value for both H_2 and CO_2 cases). The radius R_0 in the Laplace pressure term (last term in (7.1)) is justified since, at the nucleation stage, the bubble can be assumed to be a hemispherical cap of radius R_0 growing from the pit with the same radius. Equation (7.1) reflects that the pressure inside the bubble must overcome the forces resulting from the liquid pressure and surface tension to achieve bubble growth. If a multicomponent solution of N volatile ideal gas species is considered, the condition for growth in (7.1) can be approximated as [212]:

$$\frac{P_v}{P_l} + \sum_{i=1}^N (\zeta_i + 1) > 1 + \frac{2\sigma}{P_l R_0}, \quad (7.2)$$

where $\zeta_i = C_i/(k_{H,i}P_l) - 1$ is the supersaturation of the dissolved gas species i (in general, position and time dependent), with C_i being the gas concentration in mol/m^3 . With this equation, we can calculate the critical minimum supersaturation level required to overcome the energy barrier due to surface tension.

For the electrolysis case, we perform experiments at $T = 20^\circ\text{C}$ and $P_l = 1$ bar. Under these conditions, the water vapour pressure can be neglected since $P_v/P_l \sim 0.02$ (the effect of dissolved gases on the vapour pressure has been considered negligible since their mole fraction is small enough to assume that there is no appreciable change in the boiling point of water). H_2 gas bubbles grow in a binary solution of H_2 and air since the electrolyte is not degassed (this condition is similar to that present in real electrolyzer applications) and it is permanently exposed to ambient air throughout its preparation, subsequent storage and finally during experiments. Therefore, it is reasonable to assume that it is air equilibrated, i.e. $\zeta_{air} = 0$ (assuming that air is a single component entity). Consequently and according to (7.2), the minimum supersaturation of H_2 required to trigger growth for a typical pit radius $R_0 = 2.5 \mu\text{m}$ corresponds to

$$\zeta_{H_2} = \frac{2\sigma}{P_l R_0} - 1 \approx -0.44. \quad (7.3)$$

In practical terms, the negative value above means that the presence of other dissolved species, i.e. air (which consists of a mixture of N_2 , O_2 and other gases), makes bubble nucleation easier and, consequently, it is possible to achieve bubble nucleation shortly after initiating the electrolysis. We can anticipate that somewhat higher concentrations are required in practice. There are many other factors that can inhibit bubble nucleation and growth. Those will be discussed later in the text.

In contrast, the experiments with CO_2 bubbles growing from pressure-controlled supersaturated carbonated water within a pressurized chamber are

performed at a liquid pressure $P_l \approx 7.7$ bars and isolated from the outside. The preparation procedure ensures that in the experimental chamber there are no other gas species present within the liquid apart from CO_2 . Therefore, the minimum supersaturation required for nucleation is

$$\zeta_{\text{CO}_2} = \frac{2\sigma}{P_l R_0} \approx 0.07. \quad (7.4)$$

Note that in this case a positive minimum supersaturation value is necessary. Supersaturation levels below $\zeta_{\text{CO}_2} = 0.07$ were tried and resulted in no bubble generation. The lowest CO_2 supersaturation for which we experimentally achieved bubble growth was indeed $\zeta_{\text{CO}_2} \approx 0.07$.

7.4.2 Bubble nucleation times

In constant-current electrolysis and in the absence of bubbles, the (molar) concentration of H_2 near the electrode can be estimated as

$$C(t) = \frac{2J}{Fz\sqrt{\pi D}}\sqrt{t}, \quad (7.5)$$

which is an increasing function of time obtained by solving the 1D diffusion equation in a semi-infinite domain with a constant flux boundary condition [Ch.8, 213]. Here, t denotes the time after the start of electrolysis, J is the current density, $z = 2$ is the valency of the H_2 evolution reaction, $F = 96485$ C/mol is Faraday's constant and $D = 4.5 \times 10^{-9}$ m²/s is the diffusivity of H_2 in water. Combining Henry's law, (7.3) and (7.5), we obtain the theoretical minimum time for a bubble nucleation after the start of electrolysis as a function of the current density:

$$t^* = \frac{\pi\sigma^2 k_{H,\text{H}_2}^2 F^2 z^2 D}{J^2 R_0^2}. \quad (7.6)$$

Here $k_{H,\text{H}_2} = 7.7 \times 10^{-6}$ mol/N·m. It stands to reason that as J increases, the gas formation rate also increases and, therefore, the minimum time to nucleate a bubble is achieved faster. There is evidence that the concentration at which the first bubble nucleates on a gas-evolving electrode also depends on the value of the current density [213]. [213] reported that the nucleation time does not depend on a constant concentration C , but rather on the applied current density J , with C increasing as J increases. They proposed the following empirical relation for the nucleation time of the first bubble spontaneously growing on a flat electrode in a presumably non-degassed electrolyte:

$$t^* = k\pi z^2 F^2 D J^{-1}, \quad (7.7)$$

with $k = 0.19 \text{ mol}^2/\text{m}^4\text{A}$ a fitting constant. The nucleation times of the first H_2 bubble in the succession on the predefined pits are plotted vs the current density in figure 7.4 and compared to the theoretical prediction in (7.6) with $R_0 = 5, 7.5$ and $10 \text{ }\mu\text{m}$, and the empirical relation in (7.7). The times are measured from the start of the electrolysis up to a threshold radius of $\sim 25 \text{ }\mu\text{m}$, following the method used by Tawfik and Diez [213]. The nucleation time, t^* , appears to generally decrease with J ; however, no clear trend can be appreciated. The significant variability in our experimental measurements can be attributed to three possible causes:

- (1) The pit topography is different from sample to sample. We measured deviations from the ideal circular pit opening in the radial direction of several hundreds of nanometers (refer to Appendix 7.A). Fluorocarbons within the pit may hinder mass transport of dissolved gas towards the gas pocket or enforce pinning at different contact angles and, thus, affect the effective value of R_0 .
- (2) The current density is likely far from being spatially uniform along the electrode surface [Ch.8, 214].
- (3) The electrolyte contains air, partially composed of O_2 . Oxygen reduction competes with H_2 formation. This implies that the net current density available for H_2 formation is less than the actually applied current density. By definition, the standard potential for H_2 formation is 0 V, whereas O_2 reduction occurs at 0.40 V. Consequently, higher current densities result in both more H_2 production and O_2 reduction. This fact means that H_2 is not efficiently produced (not all of the applied current is used for its generation) and, thus, the bubble nucleation time seems not to follow a clear decreasing trend with increasing J . Furthermore, this may be a cause of the scattering in figure 7.4, since O_2 levels at the start of each experiment may not be the same (although a fresh solution was employed for each experiment). The levelling off of the nucleation time at higher current densities in the same figure could be attributed to the influence of the dissolved O_2 reduction, the unequal distribution of gas production, the time required for the diffusion of the gases through the liquid towards the artificial nucleation site and the stochastic nature of nucleation. In addition to the influence of the parameters mentioned above, other factors unknown to us may play a rather significant role in the measured deviation between the nucleation times of the bubbles and of the predicted theoretical values.

Moreover, the empirical prefactor in (7.7) may correct for the growth of the bubble to the threshold size of $25 \text{ }\mu\text{m}$, even though the time needed to reach

Figure 7.4: Experimental nucleation time of the first H_2 bubble formed since the start of electrolysis as a function of current density. The blue diamonds, red circles and yellow squares show the measured nucleation times with $R_0 = 5, 7.5$ and $10 \mu\text{m}$, respectively. The blue, red, and yellow lines represent Equation (7.6) for $R_0 = 5, 7.5$ and $10 \mu\text{m}$, correspondingly. The dashed line shows the empirical relation by Tawfik & Diez (7.7) [213]. Generally, the nucleation time t^* decreases with current density J . Discrepancies between experiments and the theoretical prediction are more than apparent and explained in the text.

that threshold may be negligible compared to the time necessary to achieve nucleation. However, no such correction is performed in (7.6). Surface tension reduction due to dissolved gases in the solution can also explain why the experimental nucleation times differ from those predicted by theory [215]. For electrolysis, the nucleation times for the various applied currents in this research fall within the order of tenths of seconds. In comparison, the nucleation of CO_2 bubbles in carbonated water is observed to occur at or below the order of seconds after the pressure was reduced below the saturation value [Ch.2]. The differences may rely then on the different ways of bubble generation and not on the substrate surface properties.

7.4.3 Bubble growth

Bubble growth can be described as $R(t) \propto t^\alpha$, with R denoting the bubble radius, t the time after nucleation and α the time exponent [216]. For diffusive bubble growth, $\alpha = 1/2$ [25], whereas for reaction limited growth $\alpha = 1/3$ [11, 216].

In electrolysis, diffusion-limited growth occurs when the characteristic time of the diffusive transport of the evolved gas across the electrode, $t_e \approx R_e^2/D$

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Figure 7.5: (A) H_2 bubble evolution on a microstructured electrode with a pit radius of $R_0 = 5 \mu\text{m}$. The applied current densities are 5.2, 7.8, 10.4 and 13 A/m^2 from top to bottom, respectively. (B) H_2 bubble evolution at 15.6 A/m^2 on a pit of radius $R_0 = 5 \mu\text{m}$. The top figure shows the bubble radius as function of time whereas the bottom figure shows the experimental (pink) and theoretical (black) squared radii over time. (C) Successive growth of CO_2 bubbles in supersaturated carbonated water on a pit of $R_0 = 10 \mu\text{m}$ and supersaturation $\zeta = 0.17$. The left plot shows the time evolution of the bubble radius. On the right plot, the experimental (blue) and theoretical (black) squared radii over time are shown. The dashed red line indicates the squared detachment radius of the first bubble. The onset of natural convection at the late stages of the bubble growth explains the deviation between the experimental and theoretical curves [34].

(where D is the diffusion coefficient), is much larger than that of the diffusive gas transport to the bubble, $t_d \approx R_d^2/D$. The relation between these two characteristic diffusive times can be associated to the Damköhler number, which is defined as $Da = t_e/t_d = R_e^2/R_d^2$ and can be interpreted as the ratio of the diffusive transport across the characteristic electrode size and across the characteristic bubble size. Here, $R_e = 3.5 \text{ mm}$ is the electrode radius and $R_d \sim 0.3 \text{ mm}$ is the bubble experimental mean detachment radius of all experiments at all current densities, which results in $Da \approx 100$. Therefore, our research focuses on bubble growth during electrolysis controlled by diffusion.

Figure 7.5(A) and 7.5(B) (top plot) show the evolution of bubble radii over time of five series of successive H_2 bubbles produced at constant-current electrolysis. Each series corresponds to a different current density. At the beginning, each successive bubble evolves slower than the previous one ap-

proximately up to the 4th bubble, when the growth rate becomes faster. This acceleration is attributed to the evolution of the diffusive concentration boundary layer in which the bubbles grow [Ch.8] and the most-probable complete reduction of the dissolved O_2 in the electrolyte (see item (3) in the discussion above). With increasing current densities, the growth rates at the beginning of each succession increase due to the larger gas production, but the evolution trend remains unaltered since the early bubbles in the succession deplete the diffusive concentration boundary layer around them.

The unsteady nature of the electrolytic bubble growth becomes more apparent upon comparison with the bubble growth in pressure-controlled supersaturated carbonated liquid (figure 7.5(C)). In this figure, we present a succession of CO_2 bubbles in supersaturated water at $\zeta = 0.17$. The growth in this case continuously slows down with the successive bubble detachment due to the active depletion of the total amount of CO_2 gas available [Ch.2]. In contrast, for the electrolytically-generated bubbles, after the early depletion the H_2 gas concentration near the substrate continues to increase over time due to the continuous water splitting reaction resulting in a faster growth of the H_2 bubbles [Ch.8].

Both H_2 and CO_2 bubbles evolve via pure diffusive growth, namely

$$R(t) = \tilde{b}\sqrt{Dt}, \quad (7.8)$$

where $\tilde{b}$ is the dimensionless growth coefficient [Ch.8]. The straight slopes observed in R^2 plotted against time in figures 7.5(B) (bottom plot) and (C) (right plot) corroborate this behaviour. A short movie showing a succession of single H_2 bubbles during electrolysis can be found on-line along this article (Movie 1).

The gas boundary layer evolution during electrolysis results in three different growth regimes, which are further elucidated by taking a closer look at the growth coefficient $\tilde{b}$. Figure 7.6 shows the evolution of $\tilde{b}$ with time since the start of electrolysis calculated from the data in figure 7.5(A) and the top plot in 7.5(B). Note that each experimental point corresponds to the growth coefficient of a particular bubble in the succession. Initially, $\tilde{b}$ decreases as a consequence of the initial bubble locally depleting the boundary layer of gas, behaviour referred to as the ‘stagnation’ regime (I). Successive bubbles keep growing in a mildly supersaturated liquid until the boundary layer overcomes the depletion losses due to the constant gas production and evolves to higher gas concentrations. The accompanying increase in $\tilde{b}$ characterises regime II, in which bubbles grow faster. The transition between regimes depends on the applied current density: the higher the current density, the earlier the onset of increasing $\tilde{b}$. Finally, regime III shows a stabilization in the growth rate

for successive bubbles, reflected by $\tilde{b}$ increasing in small increments. In contrast, the growth coefficients corresponding to the CO₂ bubble succession in figure 7.5(C) always decrease due to gas depletion [Ch.2]. inset in figure 7.6, similar to the early H₂ bubbles in electrolysis (regime I). In this case, there is no influx of new gas which can counteract this depletion effect, resulting in a continuous smaller growth rate. The pillar height does not have any influence on the bubble growth coefficients [Ch.8]. For a more in-depth discussion on the different growth regimes and the influence that the boundary layer and its depletion have on the bubble growth dynamics, the interested reader is referred to Ch.8.

During both H₂ and CO₂ measurements, successive bubble growth could suddenly stop because of spurious pit deactivation. This may occur once liquid enters the pit during bubble detachment: the interface of the gas pocket in the pit can form a jet which can wet the surface inside the pit, displacing the air [91]. We found no consistency in how long bubbles can be generated before pit deactivation. The fastest deactivation in the measurements occurred after the growth and detachment of a single bubble.

7.4.4 Bubble detachment

The position of the triple contact line on the pit-pillar microstructure and the contact angle dynamics determine the size at which the bubbles detach from the microstructure [217, 218]. Since optical access to the contact line was not possible, we speculate on five probable pinning positions during the bubble evolution process, sketched in figure 7.7(A). The inner surface of the pit contains several artifacts as a result of the fabrication process that can pin the bubble interface. As shown in figure 7.7(B), needle-like structures of black silicon are present at the bottom of the pit, whereas the inner surface contains vertical and horizontal scallops resulting from the Bosch etching process [219]. Additionally, the fluorocarbon (FC) layer deposited for enhanced hydrophobicity can facilitate pinning. Typically, the FC layer will adhere to the pit wall; however, in figure 7.7(B) the layer detached prior to the FIB milling process (a video can be found on-line along this article) as observed with optical microscopy and SEM. This event could provide unpredictable pinning positions during the experiments and, consequently, end up in a different detachment radius. However, we have evidence that for the majority of the bubbles, the pinning is most likely to occur inside the pit (position I) throughout their whole lifetime, forming a bridging neck between the gas trapped in the pit and the bubble growing outside [Ch.2].

As the bubble grows and attains its detachment size, it is possible that the bubble contact line moves from position I up to V [220], as sketched in figure

Figure 7.6: The dimensionless growth coefficient $\tilde{b}$ per successive H_2 bubble as function of the time after the start of the electrolysis, t . The data are derived from the experimental results in figure 7.5(A) and the top plot in figure 7.5(B). The different regimes are marked by the shaded regions, where region I corresponds to the stagnation regime in which $\tilde{b}$ decreases due to the early depletion, region II shows the counteracting effect due to the continuous gas production and III marks the regime in which an approximated steady state is reached. The transition between regimes II and III is defined by the moment in which the derivative $d\tilde{b}/dt$ drastically decreases, i.e. $\tilde{b}$ approaches a quasi-steady state. With increasing current density, the transition between regimes occurs faster because of the increased gas formation and the faster bubble evolution and their corresponding boundary layer. The inset shows the single regime I for the CO_2 bubble growth coefficient in supersaturated carbonated water caused by continuous depletion due to the successive bubble growth.

Figure 7.7: (A) Schematic side view of a cross section showing a micropillar with micropit, indicating five possible pinning positions for the contact line of evolving bubbles. Position I is inside the pit, II is at its edge with an arbitrary contact angle θ shown in red, position III indicates a transition location, IV the outer edge of the pillar and V is on the pillar surface. (B) Focused ion beam (FIB) milled down pillar, under 52° angle with respect to the electron source. The inside of the pit shows the black silicon needle structure at the base and a detached fluorocarbon layer. Etching defects (vertical lines along the pillar) on the inside and on the outside are present. A video recording of the milling process can be found on-line along this article (Movie 2).

7.7(A). The departure size is an indirect way of estimating the position of the contact line. The maximum theoretical value of the bubble detachment radius growing from a pit of radius R_0 is given by Fritz's formula [70],

$$R_d^* = \left(\frac{3R_0\sigma}{2\Delta\rho g} \right)^{1/3}, \quad (7.9)$$

with $\Delta\rho$ the difference in density between the liquid and gas phases and $g = 9.81 \text{ m/s}^2$ the gravitational acceleration. Equation (7.9) can be derived from the balance between buoyancy and capillary forces, assuming that the contact line is at position II with a contact angle of 90° with respect to the horizontal at the moment of detachment, as sketched in figures 7.1(B) and 7.7(A). Net charges present on bubbles due to the solvent pH or absorbed species, such as surfactants [221], may affect the pinning position of the bubble to the pit and consequently, its final detachment radius. Our electrolysis experiments are carried out in a medium with a pH 3 buffer and with no absorbent species to ensure a point of zero charge on the bubble. We can thus exclude electrostatic forces from the detachment force balance.

Figure 7.8 shows the detachment radius for electrolysis at various current densities. The measured radii are smaller than what equation (7.9) predicts, as

Figure 7.8: (A) Successive H₂ bubble detachment radii over time, normalized by the Fritz radius (7.9) for various levels of applied current density. The inset shows the normalized detachment radii of successive CO₂ bubbles over time for $\zeta = 0.17$. In this case, the detachment radii slightly decrease with time due to induced density-driven convection, which does not occur in electrolysis. (B) Histograms of the measured detachment radius for various applied current densities (from top to bottom, 5.2 A/m², 7.8 A/m², 10.4 A/m², 13 A/m² and 15.6 A/m²). The red bars at current densities 10.4 A/m² and 13 A/m² have values of $N=15$ and $N=40$, respectively.

one would expect from the contact line pinned somewhere inside the pit (position I) and a potential necking process [Ch.2]. Histograms of the detachment radii per current density applied to the same sample are included in figure 7.8(B). The detachment radius does not seem to be affected by the current density. The inset in figure 7.8(A) likewise shows that the detachment radii of successive CO₂ bubbles always fall below the theoretical value. Moreover, the measured radii slightly decrease with each successive bubble formed due to the onset of buoyancy-driven convection near the bubbles [34]. However, in general terms, bubble detachment radii remain stable and reproducible, especially in the short term (below 1 hour) [Ch.2].

Figure 7.9 shows two histograms of the detachment radii R_d normalized with the theoretical maximum detachment radius R_d^* . The top histogram shows that the detachment radii of CO₂ bubbles spread over a range with a mean value of $\sim 0.6 R_d/R_d^*$. The lower histogram shows a peaked distribution for the H₂ bubble detachment radii, also with a mean value of $\sim 0.6 R_d/R_d^*$.

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The same mean range of R_d/R_d^* for the H_2 and CO_2 measurements is not accidental since both scenarios make use of similar microstructures with the same pit-pillar configuration. The spread in the measured radii must arise from the fact that the contact line may differ from experiment to experiment, and thus the necking before pinch-off occurs differently. Preferred adhesion sites or defects within the pit or on the pillar could be responsible for this. Since roughness of flat electrodes has been shown to influence the detachment radii of bubbles [85, 222, 223], we expect that pit roughness might play a role in the detachment radii of evolving bubbles. We measured the roughness in radial direction but found no apparent correlation between the detachment radii and the radial roughness (see Appendix 7.A). For some bubbles, $R_d/R_d^* > 1$, probably due to the fact that the bubbles were not pinned to the pit (positions I or II in figure 7.7(A)) but rather to defects on the pillar or the outer rim (position III, IV or V in figure 7.7(A)). In our experiments, we have measured detachment radii up to $1.5R_d^*$, especially for the case of the smallest pit to pillar radii ratio. This case is particularly interesting, since such a small ratio could be used for future designs of pillars in which the pit functions as the gas trapping source and the pillar as the outer pinning geometry for the bubble. Convective forces, electrostatic charges induced by local pH changes, and the dependency of surface tension and liquid density with concentration of dissolved gases may also influence the force balance and final detachment radius in a complex way. Although we provide several possible scenarios and parameters which could cause the deviation between the measured detachment radii and theory, the influence of other unknown factors can not be excluded. Nonetheless, a full analysis of the force balance and other factors influencing detachment is beyond the scope of this study.

7.4.5 Gas transport efficiency

The efficiency of gas transported away from the electrode surface by the bubbles can be quantified as the ratio between the amount of gas moles within each bubble after detaching from the nucleation site, n_b , and the total amount of electrolytically produced moles of H_2 , n_g . Note that this efficiency is not constant in time since it changes as the subsequent bubbles grow at different rates and depends on the amount of dissolved O_2 which is reduced at the electrode. The efficiency after the n -th bubble in the succession has detached is thus calculated as

$$\frac{n_b}{n_g} = \frac{\sum_{i=1}^n \frac{4\pi P_{b,i} R_{d,i}^3}{3R_u T}}{Q/(Fz)}. \quad (7.10)$$

Figure 7.9: The top histogram shows the detachment radii of CO_2 bubbles normalized by the Fritz radius (7.9) formed at $0.16 < \zeta < 0.18$. Values below $R_d/R_d^* < 1$ are shown in purple whereas larger values are shown in red. The bottom histogram shows the detachment radii of H_2 bubbles evolved on various substrates at different current densities. Here the same color palette as in the top figure has been used. Even though the histograms have different distributions, both correspond to a mean value of bubble detachment $R_d/R_d^* \approx 0.6$.

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Here, $R_{d,i}$ denotes the detachment radius of the i -th bubble, $P_{b,i} = (2\sigma/R_{d,i}) + P_l$ is the internal pressure of the i -th bubble, $F = 96485$ C/mol, $z = 2$ is the valency of the H_2 evolution reaction, $Q(t_n) = J\pi R_e^2 t_n$ is the total electric charge supplied at the detachment time of the n -th bubble t_n , $R_u = 8.314$ J/K·mol is the universal gas constant and $T = 293$ K the absolute temperature. Note that this definition of the efficiency is limited to the gas transported away in each bubble and, therefore, does not consider the gas transport from the electrode in the form of convective plumes caused by bubble detachment or in the form of parasitic bubbles growing in other spots within the set-up.

Figure 7.10 shows the H_2 transport efficiency of the bubble succession as a function of time. A single substrate is used for the measurements of the various current densities. The efficiency evolves as a parabola in time for all current densities, i.e. a similar trend as that of $\tilde{b}$ in time, figure 7.6. This originates from the definition of the transport efficiency, equation (7.10), which fundamentally corresponds to a discrete integral of $\tilde{b}$ in time. Consequently, the efficiency initially decreases due to the effect of depletion during the stagnation regime, region I in figure 7.6. During the stagnation, the efficiency is surprisingly higher for lower current densities. This may originate from larger depletion losses caused, for instance, by the formation of parasitic bubbles. However, the efficiency becomes larger with increasing current densities as the concentration boundary layer evolves with time to higher gas concentrations. This is expected since the current density is directly proportional to the generation rate of molecular hydrogen. The produced gas does not diffuse fast enough into the bulk electrolyte, but accumulates instead around the bubble and electrode, increasing the local supersaturation. This results in faster bubble formation frequencies and higher transport rates. We find the highest experimental efficiency (5.7 %) for a current density of 7.8 A/m² after 270 minutes of constant electrolysis operation. A general optimal efficiency value could not be determined due to the eventual pit deactivation or parasitic bubble formation blocking optical access.

Future designs of electrodes with multiple nucleation sites may increase the amount of gas that is transported away by the bubbles, resulting in higher transport efficiencies. The size of the nucleation sites and the spacing over the surface would be crucial since they determine to what degree the bubbles compete for gas and how the gas concentration boundary layer evolves with time.

Figure 7.10: The ratio of gas transported out of the liquid phase by the bubbles and the amount of electrolytically generated gas as function of time for various current densities. For the measurement at 5.2 A/m^2 , the current density is so low that only regime I appears within our experimental time. It is expected that the other regimes (II & III) would occur with prolonged reaction time. The inset shows the efficiency ratio for the full length of the 7.8 A/m^2 measurement up to 270 minutes. A maximum efficiency of 5.7 % is obtained at the end of the experiment. The employed nucleation site has a radius of $R_0 = 5 \text{ }\mu\text{m}$.

7.5 Conclusions

The microfabrication of artificial nucleation sites (in the form of pillar-pit microstructures on flat silicon substrates) allowed us to experimentally study bubbles evolving in water. By observing the succession of single bubbles, we compared the differences between the pressure-controlled supersaturated CO_2 and electrolytic H_2 bubbles, focusing on the evolution of the concentration boundary layer and its effect on the bubble growth rate, the detachment radius and the gas transport efficiency.

The time taken for the first H_2 bubble to nucleate after the start of electrolysis at various current densities coincides with previous electrolysis nucleation studies and covers a wide spread ranging from the order of seconds to tens of seconds (most probably affected by the presence of dissolved O_2 at the beginning of the experiment) whereas the CO_2 nucleation occurs generally in the order of seconds once the carbonated solution becomes supersaturated. By studying the growth coefficient $\tilde{b}$, we determine that a system with a finite amount of gas available will experience continuously slower bubble evolution over time due to gas depletion, whereas in the case of electrolytically generated bubbles, their growth experiences different phases depending on the concentration of available gas as a function of time. The height of the pillars does

not seem to play any significant role during bubble evolution in any of the cases studied here.

Bubble detachment usually occurs around 60% of the maximum theoretical radius (see equation (7.9)) for both cases. This fact indicates that bubble detachment is mainly governed by the pillar-pit geometry. The smaller detachment value originates from the structural imperfections of the pits that lead to random adhesion sites of the contact line. The contact angle, the force balance and the neck formation of the bubbles are thus affected. For CO₂ bubbles, detachment occurs at slightly decreasing radii over time because of the onset of density driven convection [34] and a neck formation between the trapped gas in the pit and the growing bubble on top [Ch.2]. In electrolysis, the detachment of H₂ bubbles does not follow any clear trend.

Finally, the gas evolution efficiency follows a parabolic trend with time. A matching trend is observed for the bubble growth rates. We conclude that the efficiency first decreases due to depletion losses, and then increases after a certain supersaturation is achieved and the dissolved O₂ is reduced. Surprisingly, during the stagnation regime the efficiency is higher for lower current densities. This effect is counteracted later in time, such that higher current densities J imply higher efficiencies. The maximum efficiencies range from 1 to 5 %, values which could be further increased with the use of multiple nucleation sites and flow conditions, closer to real life applications where continuous flow reactors are desirable. The aspects of nucleation, growth, and detachment considered here certainly warrant future studies toward higher transport efficiencies of (photo)electrolytic devices.

7.A Roughness study and its effect on the bubble detachment radius

The roughness in the radial direction at the top of the pits is measured by imaging the apex from the top using Scanning Electron Spectroscopy (SEM). A circle-line is fitted over the pit apex and deviations from the ideal circumference are measured. We then calculate the roughness in radial direction as:

$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i|, \quad (7.11)$$

where y_i is the deviation per measurement point. For these calculations, we take points with equal spacing over each circle. We calculate R_a for various DRIE conditions and fluorocarbon deposition times, but a correlation to the detachment radius could not be found.

To illustrate the complexity of taking the surface roughness into account, we image various substrates. Figure 7.11(A) shows partially the inside of a pit with a $7.5\ \mu\text{m}$ radius. Here the black silicon is visible at the bottom half of the image, the top half shows part of the inner wall of the $20\ \mu\text{m}$ deep pit where fluorocarbons have been deposited for 37 seconds after the pit formation. The wall shows non-homogeneity in the surface created during the pit fabrication, which could play an important factor if the bubble is pinned within the pit. A top view of a pillar with a $15\ \mu\text{m}$ radius is shown in figure 7.11(B), which contains a defect on the outer edge at the bottom right side, providing an irregularity that could influence the bubble detachment size if the contact line moves to the pillar edge. Figure 7.11(C) shows a close-up of the pit in the pillar of subfigure (B), in which the pit apex is shown in bright white. The pit has a radius of $7.5\ \mu\text{m}$, $R_a = 0.004\ \mu\text{m}$ averaged by three measurements, and due to the substrate not being levelled under the electron source, a small part of the wall is shown at the right side of the image between the dark black silicon and the bright pit apex. Figure 7.11(D) shows a top view of a $30\ \mu\text{m}$ tall micropillar, with a radius of $15\ \mu\text{m}$ and pit radius of $5\ \mu\text{m}$. Before imaging, this substrate was used in an electrolysis experiment, during which an unknown substance precipitated on the pillar surface near the pit, creating additional pinning locations for bubbles. Subfigure (E) shows a close-up of this pit with $R_a = 0.008\ \mu\text{m}$ averaged by three measurements. Similar to subfigure (C), a part of the pit wall is shown on the right side between the dark black silicon and bright apex. Although in our experiments roughness does not seem to play any significant role during bubble growth and detachment, its influence warrants further investigation which does not only take into account the pit apex but the roughness of the pit inner wall, the pillar outer wall and the top pillar surface, as well as other defects.

Figure 7.11: (A) The inside of a micropit of $20\ \mu\text{m}$ depth and $7.5\ \mu\text{m}$ radius is partially shown. The substrate is under a 20° angle with respect to the electron beam source. At the bottom of the image, black silicon is visible. At the top, the wall on the inside of the pit shows roughness, a result of the DRIE process. In all subfigures, the white scalebars indicate a $5\ \mu\text{m}$ length. (B) A top view of a pillar with a $15\ \mu\text{m}$ radius and $7.5\ \mu\text{m}$ radius pit is shown. A defect from the fabrication of the substrate on the outer edge at the bottom right side of the pillar is present. (C) Close-up of the pit shown in (B). Here the radial roughness is $R_a = 0.004\ \mu\text{m}$. (D) A micropillar of $30\ \mu\text{m}$ height, $15\ \mu\text{m}$ radius and a pit radius of $5\ \mu\text{m}$ is shown. A deposit on the surface of the pillar can be noticed near the pit aperture. (E) Close-up of the pit from subfigure (D). Here, $R_a = 0.008\ \mu\text{m}$.

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Control over the bubble growth rates forming on the electrodes of water-splitting cells or chemical reactors is critical with respect to the attainment of higher energy efficiencies within these devices. This study focuses on the diffusion-driven growth dynamics of a succession of H_2 bubbles generated at a flat silicon electrode substrate. Controlled nucleation is achieved by means of a single nucleation site consisting of a hydrophobic micropit etched within a micrometer-sized pillar. In our experimental configuration of constant-current electrolysis, we identify gas depletion from (i) previous bubbles in the succession, (ii) unwanted bubbles forming on the sidewalls, and (iii) the mere presence of the circular cavity where the electrode is being held. The impact of these effects on bubble growth is discussed with support from numerical simulations. The time evolution of the dimensionless bubble growth coefficient, which is a measure of

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the overall growth rate of a particular bubble, of electrolysis-generated bubbles is compared to that of CO_2 bubbles growing on a similar surface in the presence of a supersaturated solution of carbonated water. For electrolytic bubbles and under the range of current densities considered here ($5\text{--}15\text{ A/m}^2$), it is observed that H_2 bubble successions at large gas-evolving substrates first experience a stagnation regime, followed by a fast increase in the growth coefficient before a steady state is reached. This clearly contradicts the common assumption that constant current densities must yield time-invariant growth rates. Conversely, for the case of CO_2 bubbles, the growth coefficient successively decreases for every subsequent bubble as a result of the persistent depletion of dissolved CO_2 .

8.1 Introduction

At sufficiently large voltages, gas bubbles are produced on the electrodes in electrochemical reactors [224–226], in water-splitting cells during the electrolysis of water for hydrogen production [227], in the study of nanobubbles [214, 228, 229], and during photoelectrolysis by solar-driven cells [230, 231], a topic that recently has gained interest. The formation of unwanted nucleation sites or large bubble departure sizes may lead to an excessive coverage of electrodes by bubbles. This ultimately results in increased electrical resistance [227, 232] within the aforementioned devices. Thus, proper control over the nucleation, growth and detachment of bubbles is expected to play a key role in the progress toward higher energy efficiencies [233]. Moreover, such control should allow us to efficiently harvest the produced gas bubbles [234] without further need of energy input, e.g., in the form of pumping- or vibration-based mechanical systems.

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Control over the bubble growth rates is a critical aspect that should be achieved after properly understanding the underlying physical problem. Bubble growth kinetics in electrolytic systems has been generally described in the form of [11, 23, 80, 216, 235–239]

$$R = bt^\alpha, \quad (8.1)$$

where R is the bubble radius and t is the actual residence time of the bubble, which starts growing at $t = 0$, on the electrode before detachment. Here, b is the dimensional growth coefficient whereas α is the scaling exponent. Throughout the majority of the bubble lifetime, except for a very fast inertia-controlled initial growth [216] (on the order of 0.1 s in our experiments), b and α can be approximated as constants. The scaling exponent α is typically $1/2$ or $1/3$, depending on the experimental conditions.

The occurrence of one scaling exponent is determined by a quantity of immediate interest, A_e/R_d^2 , namely, the ratio of the active surface area, A_e , of the electrode upon which the bubble grows to the characteristic bubble surface at the moment of detachment (at a bubble radius of R_d). This coefficient represents the ratio between the characteristic time of the diffusive transport of the evolved gas across a region of the size of the electrode, $t_t \approx A_e/D$, and that of the diffusive transport of gas to the bubble, namely, $t_d \approx R_d^2/D$, which in turn limits the bubble growth rate. Here, D denotes the gas diffusivity in the liquid. Alternatively, if the exsolution of dissolved gas into the bubble is considered to be a chemical reaction, then the quantity A_e/R_d^2 can be interpreted as a Damköhler number representing the ratio between the diffusive transport time to the bulk fluid and the diffusive transport time of gas into the bubble. This ratio is geometrically imposed by the experimental configuration, and it essentially specifies the growth mechanism that determines the nature of b and α [239]. Two limiting cases [11, 239] are to be identified:

- (i) Surface-reaction-controlled (or production/reaction-limited) growth for relatively small active electrode surfaces, $A_e/R_d^2 \ll 1$, where $R = bt^{1/3}$.
- (ii) Diffusion-controlled (or diffusion-limited) growth for relatively large active electrode surfaces: $A_e/R_d^2 \gg 1$, where $R = bt^{1/2}$.

Bubbles generated at microelectrodes [80, 216, 238] by catalysis and at laser-irradiated photoelectrodes [78, 239] or plasmonic nanoparticles [240] are common scenarios of case (i). Here, bubble growth is directly limited by the gas production rate and hence by the supplied current. Essentially, all of the gas produced at the electrode surface is directly transferred into the bubble adhered to it by diffusion and by coalescence with smaller (nano)bubbles that

nucleate at the rim of the microelectrode [238, 240]. Gas diffusion into the bulk electrolyte is negligible in comparison. The gas evolution efficiency [241], namely, the fraction of gas contained within the departing bubble(s) with respect to the total amount of gas produced at the electrode, has been reported to be close to 100% [238]. For these reasons, microelectrodes enable the production of well-controlled successions of single bubbles that nucleate, grow, and detach in a highly periodic and repetitive fashion. In the case of a single microelectrode, multiple bubble interactions or bubble coalescence events are suppressed. Moreover, the effect of convection induced by the detachment of previous bubbles on the growth rate is negligible because viscous dissipation limits detachment-induced flow to a short time interval of around 0.1 s [238]. The mathematical formulation of the growth dynamics in case (i) is trivial. Provided that the growing bubble remains spherical as it grows and that the contact angle is small, a simple mass balance yields the following experimentally confirmed relation [80, 216, 238, 242]

$$R = bt^{1/3} = \frac{3R_u T_\infty I}{4\pi F v P_0} t^{1/3} \quad (8.2)$$

where R_u is the universal gas constant, T_∞ and P_0 are the liquid pressure and temperature, I is the electric current, F is Faraday's constant, and v is the number of electrons transferred in the electrochemical cell per molecule of evolved gas.

The mechanism behind case (ii), the case of bubbles growing on electrodes with relatively large surfaces, is substantially different. The growth is almost entirely driven by the Fickian diffusion of gas into the bubble from the surrounding supersaturated electrolyte. Mass is now transferred across the entire bubble surface. Direct gas diffusion from the substrate to the bubble is, on the other hand, usually small in comparison. We then expect very similar behavior to the diffusive, quasi-static growth of bubbles in uniformly supersaturated solutions [34, 85]. Diffusion-limited growth has been found to be well described by the classical theories by [25] or [42]. These theories, which can be extended to the growth of surface (nano)bubbles [15], coincide in that diffusive growth may be described by $R = bt^{1/2}$. The scaling $R \propto t^{1/2}$ is in full agreement with reported electrolysis experiments for case (ii) [23, 235–237].

The diffusive growth coefficient b is now determined by the local degree of supersaturation of the nearby liquid, by the gas solubility, and by the gas diffusivity. The local degree of supersaturation and, as a consequence, the average bubble growth rate and gas evolution efficiency are all expected to increase with the current density [241]. Most studies reporting bubble growth dynamics [11, 23, 235, 239] or analyzing mass transfer from electrodes [241, 243, 244] assume a constant, time-independent value of the local supersaturation for a

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given current density. This therefore would entail a unique growth coefficient b common to all bubbles, regardless of the time of nucleation after the onset of electrolysis. However, it follows that the gas supersaturation near the electrode depends not only on the current density but also on the elapsed time of electrolysis. This stands to reason because from simple mathematical considerations [236] the imposition of a constant gas flux at the electrode surface must lead to an accumulation over time of dissolved gas near the electrode. The concentration of dissolved gas increases with time until an approximately steady-state profile is reached. Consequently, b is expected to increase for subsequent bubbles until a steady-state value is reached, even under the imposition of a constant current density.

The constant-electrolysis scenario has some similarities to the diffusion-driven growth of a succession of bubbles from a nucleation site in a supersaturated liquid. In both scenarios, the behavior $R = bt^{1/2}$ holds for each individual bubble, and the value of the coefficient b is observed to vary discretely from bubble to bubble in the succession. However, in the latter scenario the growth coefficient b of subsequent bubbles continuously gets smaller and smaller, as opposed to becoming increasingly larger as seen during electrolysis. This effect has been recently studied for a succession of CO_2 bubbles in carbonated water kept at constant pressure under supersaturation conditions [Ch.2].

With all of these ideas in mind, the aim of this work is to explore in detail the time evolution of the growth coefficient for a succession of H_2 bubbles produced by constant-current electrolysis. In our configuration, the electrode is much larger than the bubble, and hence $R = bt^{1/2}$ is expected. We make use of flat silicon electrodes with a single microstructure upon which a succession of single bubbles may form. In this way, the effect on b of bubble electrode coverage, convection and diffusive interactions between multiple bubbles [244] is intentionally minimized. This is done in view of future applications in photoelectrolysis, where silicon is becoming an increasingly popular material for photoelectrodes [21, 245], considering that it may be feasibly etched with micrometer- or nanometer-sized pillars [210] as a means to increase the light-harvesting efficiencies and gas production rates. Finally, some interesting conclusions will be drawn by comparing the growth coefficient of electrolysis bubbles with that of CO_2 bubbles in carbonated water in a pressure-controlled (P-C) setup.

Figure 8.1: SEM image of a micropillar protruding from the silicon substrate. In this particular sample, the pillar height is $H_p = 30 \mu\text{m}$, the pit (inner) radius is $R_0 = 5 \mu\text{m}$ and the pillar (outer) radius is $R_p = 15 \mu\text{m}$.

8.2 Experiments

8.2.1 Microstructured substrates

A single active site for bubble formation was defined at the center of flat boron-doped silicon substrates ($10 \times 10 \times 0.525 \text{ mm}^3$). This nucleation site, fabricated through reactive ion etching after photolithography, consists of a micrometer-sized hydrophobic cylindrical pit [203] (about $20 \mu\text{m}$ deep) etched within a cylindrical micrometer-sized pillar [210]. Details of the fabrication process may be found elsewhere [233].

Figure 8.1 shows a scanning electron microscope image of a micropillar containing the superhydrophobic pit. The pit radius, R_0 , was set in the range of $1\text{-}10 \mu\text{m}$ over the various experimental samples, values that ensure successful bubble nucleation [91]. Similarly, the pillar radius, R_p , was set to $5\text{-}15 \mu\text{m}$. The pillar heights considered were $H_p = 0, 15$, and $30 \mu\text{m}$, in view of potentially identifying any influence that the distance from the electrode to the bubble nucleation spot may have on bubble growth. The case $H_p = 0 \mu\text{m}$ corresponds to a micropit in an otherwise flat substrate; i.e., the pillar is absent in this case.

8.2.2 Experimental method

The experimental setup, sketched in figure 8.2, comprises a 3D-printed acrylic holder and a mounting plate designed to hold the silicon substrate (electrode)

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Figure 8.2: Sketch of the electrolysis setup. The dimensions of the substrate, cavity, and holder are not drawn to scale to highlight, within a single schematic, the different dimensions playing a crucial role in electrolytic bubble growth. Note that the pit and pillars are much smaller in reality.

in place. The substrate is at the base of a circular cavity (of radius $R_e = 3.5$ mm and depth $H_c = 2$ mm) that determines the active electrode surface in contact with the electrolyte. A rubber ring, placed between the silicon substrate and the substrate holder, creates a liquid-tight seal. A counter electrode in the form of a platinum wire is then placed at the corner of the holder far away from the substrate.

At the beginning of each experiment, the holder is filled with 20 mL of fresh electrolyte. The resulting electrolyte level depth is $H \approx 12$ mm. The electrolyte consists of a solution composed of nondegassed Milli-Q water with 10 mM Na_2SO_4 salt and a pH 3 buffer (sodium acetate anhydrous and acetic acid), giving the bubbles a neutral electric charge [216]. During each experiment, a constant current I in the range of 200-600 μA is supplied. The corresponding current density, computed as $j = I/(\pi R_e^2)$, falls in the range of 5-15 A/m^2 . In this way, a constant molar flux of hydrogen gas, $J_w = j/(Fv)$, is uniformly released from the substrate by electrolysis. Here, $F = 96485$ C/mol is Faraday's constant, and $v = 2$ is the number of electrons taken up per molecule of evolved H_2 gas.

A few seconds after the start of electrolysis, the electrolyte is sufficiently saturated with hydrogen and a single bubble grows from the pit on top of

the micropillar. Eventually, the bubble reaches a critical size and detaches. Shortly afterward, a new bubble nucleates and the process starts over again. Images of the succession of growing bubbles are acquired from the top by a digital camera mounted with an axial light source for 1–5 hours.

The radius of the gas-evolving substrate is about 10 times larger than the typical detachment radius of the bubble ($R_d < 0.4$ mm), which gives a Damköhler number of $D_e = R_e^2/R_d^2 \gtrsim 80 \gg 1$. As discussed in the Introduction, it is expected that the bubble dynamics then follows diffusion-limited growth.

8.2.3 Experimental observations: electrolysis-induced bubbles

Figure 8.3 shows the typical evolution of the bubble radius for a succession of bubbles captured during the first hour of constant j . Several effects come into view. First, the bubble growth rates eventually increase with time. This stands to reason because imposing a constant flux J_w leads to an accumulation of dissolved H_2 gas in the bubble surroundings. In other words, there is a net increase of the average H_2 concentration in the region where the bubble grows. The fact that repetitive, steady-state growth is not reached immediately is very striking and significant. The time required to reach the steady state in the absence of bubbles (see Appendix 8.A) can be very roughly estimated as $t_{ss} \approx H^2/D_{H_2}$, where $D_{H_2} = 4.2 \times 10^{-9}$ m²/s is the diffusivity of H_2 in the electrolyte [246]. To do so, we have assumed a 1D concentration profile of $C(z, t)$ with a constant flux at $z = 0$ together with a zero-concentration boundary condition at the free surface, $C(H, t) = 0$. Taking $H = 10$ mm, this gives approximately 6 h. In our experiments, it will be seen that the steady state is attained somewhat faster, within the order of 0.5–3 h.

Second, the radius dynamics are affected by transient effects. This is especially evident in the very first bubble(s) of figures 8.3(a)–(d), whose growth dynamics displays fast temporal variations. This is attributed to the unsteadiness and nonuniformity of the evolving concentration field, which makes it more susceptible to perturbations during the first minutes after the onset of electrolysis. In time, these transient effects diminish as the boundary layer of evolved H_2 gas grows and the local concentration field surrounding the pillar becomes more uniform. The effect of the contact angle dynamics on bubble growth is discarded because the detachment radius is always found to be below the maximum theoretical Fritz radius [70] calculated using the pit circumference as the reference contact line. This implies that bubbles do not adhere to the top surface of the pillar. Instead, they are attached to the inside of the pit and detach through a necking process [Ch.2].

Third, electrolytically driven bubble evolution is not perfectly reproducible for a number of reasons that will be discussed later. Premature detachment of

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Figure 8.3: Time evolution of the bubble radius for a succession of bubbles captured during the first hour after the start of the electrolysis. Each individual curve represents a distinct bubble. Four different experiments are shown, in which the supplied current density is set to (a) 5.2, (b) 7.8, (c) 10.4 and (d) 13.0 A/m². The pit and pillar radii are 5 and 15 μ m, respectively, whereas the pillar height is 30 μ m. Using $R_d \approx 0.3$ mm and $R_e = 3.5$ mm yields a Damköhler number of $De = R_e^2/R_d^2 \approx 136$. The dotted horizontal line marks the etching defect size below which it was not possible to optically detect the bubbles.

particular bubbles is a commonly observed phenomenon in our experiments, especially for large current densities or supersaturations, as seen in figure 8.3(d) for $t = 24$ and 35 min.

8.2.4 Experimental observations: pressure-controlled bubbles

It is of interest to see how the growth dynamics obtained in the electrolysis experiments compares with those found in pressure-controlled (P-C) experiments entailing a succession of CO₂ bubbles produced in uniformly supersaturated water. To do so, a silicon chip, identical to those used in electrolysis experiments, is placed in the center of a pressurized test chamber (pressure $P_s \approx 9$ bar) that is then filled with carbonated water previously saturated under the same pressure. A detailed description of the experimental setup and procedure may be found in [Ch.2, 37], to which the reader is referred. At the beginning of the experiment, the pressure is lowered to a value $P_0 \approx 8$ bar, which yields a supersaturation of $\zeta = P_s/P_0 - 1 \approx 0.17$. Shortly afterward, a single bubble nucleates and grows on top of the micropillar. As in the case of the electrolysis experiments, a succession of bubbles then follows. The time evolution of the bubble radii for a particular experiment is shown in figure 8.4.

Two differences become immediately apparent upon comparison of figures

Figure 8.4: Pressure-controlled growth for a succession of CO_2 bubbles for $\zeta = 0.17$ during the first 100 min after the pressure drop. The dotted vertical lines indicate bubble detachment and nucleation of the following bubble. The pit and pillar radii are 10 and 15 μm , respectively, whereas the pillar height is 30 μm .

8.3 and 8.4. In the first place, the P-C growth rate and detachment radius are more repeatable and stable than for the electrolysis experiments. In the second place, in the P-C experiments, the time taken for each bubble to detach grows with time, and thus the growth coefficient decreases. This is in contrast to what is observed in electrolysis, where the continuous dissolution of H_2 in the bubble surroundings enhances the growth rate. In the case of P-C bubble growth, [Ch.2] showed that the slowing down of the bubble growth is caused by the local depletion of CO_2 near the bubble. Such a depletion phenomenon was attributed to buoyancy-driven convection and mixing due to bubble detachment.

8.2.5 Numerical model

As a means to provide further insight into the growth dynamics of the electrolytic bubbles studied here, a numerical model for the growth of a spherical bubble attached to a micropillar of height H_p protruding from a (gas-evolving) substrate has been developed. It is an extension of the (pillarless) numerical model described in [Ch.1]. The governing equations are solved through a second-order finite-difference discretization in space and an implicit Euler method in time. The 2D axisymmetric grid is portrayed in figure 8.5. The grid is divided into two regions that use different coordinate systems: a bulk region for $z > H_p$ and a microlayer region below. In the bulk region, the advection-diffusion equation coupled with the streamfunction-vorticity equations [Ch.1] are solved, imposing a no-slip boundary condition at $z = H_p$. In the microlayer region, only the diffusion equation is solved. The concentration and its gradient are matched at the coupling plane $z = H_p$. If required, a constant and uniform molar flux can be imposed at the substrate wall ($z = 0$) and pillar surface. Details about the simulation equations may be found in Appendix 8.C.

The limitations of the simulation regarding the electrolysis experiments are

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Figure 8.5: Schematic of the simulation grid for a pillar with dimensions $H_p/R_0 = 4$ and $R_p/R_0 = 2$. The simulation points fall on the intersection of the contour lines. The simulation is axisymmetric around the z axis. The bulk region in tangent-sphere coordinates (η, ξ) applies to $z > H_p$. The microlayer region in pseudocylindrical coordinates (ρ, ζ) applies to $0 < z < H_p$. A matching condition is imposed at $z = H_p$. Coordinates η , ξ , and ρ evolve with the bubble so that $\xi = 1$ (in blue) always maps the bubble surface, regardless of the actual bubble size. Here, the bubble size has been arbitrarily set to $R/R_0 = 3$. The separation of the contours is uniform. Here, $\Delta\eta = \Delta\xi = \Delta\rho = 0.1$ and $\zeta = 0.5$. Coordinate $\eta = 0$ lies on the z axis, $\eta \rightarrow \infty$, at the contact point.

that it considers neither the real finite size of the electrode nor the presence of a cavity (figure 8.2). Moreover, we assume a spatially uniform flux along the electrode. Finally, we must estimate the initial H_2 field corresponding to a bubble nucleating at some time after the start of electrolysis. To do so, we use the 1D analytical concentration profile in the absence of bubbles provided in Appendix 8.A. Thus, this idealized initial concentration profile depends on just two input parameters, namely, the effective current density (which establishes the flux of dissolved H_2 gas that is evolved at the electrode) and the elapsed time of electrolysis. We must finally remark that when modeling the growth of electrolytic bubbles a binary system of H_2 gas and air is considered. The electrolyte is not degassed; in fact, it was kept in a container openly exposed to ambient air. Hence, we make the approximation that the electrolyte surrounding the micropillar is perfectly equilibrated with air at the beginning of bubble growth. The presence of dissolved air explains why the first hydrogen bubbles nucleate and grow just a few seconds after the start of electrolysis when the electrolyte close to the electrode is still undersaturated in H_2 . Nonetheless, the small molar fractions of air typically present in the bubbles (<15 %) can be neglected for all other purposes.

8.3 Results and discussion

We begin this section with a theoretical description of the key quantity used to characterize the bubble growth dynamics, namely, the diffusive growth coefficient. The experimental results are then discussed, giving special attention to the effect that the different sources of depletion have on the measured growth coefficients. For the electrolysis experiments, the time evolution of the growth coefficients allows us to distinguish two sequential stages: an initial stagnation regime, where the bubble growth rates are nearly constant or slower than that of the very first bubbles, and a later supersaturation regime, where the bulk liquid contains enough H_2 to sustain large bubble growth rates. Finally, the growth dynamics of each stage is quantitatively described.

8.3.1 Significance of the diffusive growth coefficient

Assuming diffusion-limited growth, the n th bubble in the succession grows as $R_n(t_n) = b_n \sqrt{t_n}$, where b_n is its associated diffusive growth coefficient and $t_n = t - t_{0,n}$ is the current time after nucleation at $t = t_{0,n}$. In the spirit of the theories for monocomponent bubble growth by [25] or [42], it is convenient to recast this law in terms of the dimensionless growth coefficient $\tilde{b}_n = b_n / \sqrt{D}$ such that

$$R_n(t_n) = \tilde{b}_n \sqrt{Dt_n}, \quad (8.3)$$

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where D denotes the gas diffusivity. Indeed, if the bubble grows to a radius R_n much larger than the size of the nucleation site (the pit on the pillar in our case), then its growth will be given by the Epstein & Plesset equation [25], that determines the quasi-static diffusive growth of an isolated spherical bubble:

$$\frac{dR_n}{dt_n} = \frac{DR_u T_\infty}{P_0} (\bar{C}_n - k_H P_0) \left[\frac{1}{R_n} + \frac{1}{\sqrt{\pi D t_n}} \right]. \quad (8.4)$$

In this expression, R_u and k_H are the universal gas constant and Henry's constant, respectively. Moreover, T_∞ and P_0 are the liquid temperature and pressure during growth, and $\bar{C}_n$ is the gas concentration far away from the bubble. Finally, note that surface tension has been neglected, as even the largest capillary (or Laplace) pressure $2\gamma_{lg}/R \approx 0.05$ bar is negligible in comparison to the pressure involved in bubble growth, $P_0 \geq 1$ bar. Here, we have considered surface tension $\gamma_{lg} = 0.07$ N/m and the smallest trackable bubble size, $R = 30$ μm .

In the case of electrolysis within our air-equilibrated electrolyte, the Epstein & Plesset equation will be valid for sufficiently large concentrations of H_2 such that the flux of other species (N_2 , O_2) into the growing bubble is small in comparison. In such cases, the ratio of H_2 -to-air fluxes can be shown to be roughly equivalent to $D_{\text{H}_2} k_{H,\text{H}_2} \zeta / (D_{\text{air}} k_{H,\text{air}}) \approx 2\zeta$, where ζ is the supersaturation of H_2 , to be defined in (8.7b).

At times $t_n \gg R_0^2/D$, this corresponds to roughly $t_n \gtrsim 1$ s in our experiments, equation (8.4) allows for the following solution (neglecting surface tension):

$$R_n(t_n) \approx \sqrt{Ja_n/\pi} \left[\sqrt{Ja_n} + (2\pi + Ja_n)^{1/2} \right] \sqrt{Dt_n}. \quad (8.5)$$

This solution is essentially that provided by [25] formulated for the n th bubble in the succession and, correspondingly, using the mass-transfer Jakob number [11, 246] related to the n th bubble,

$$Ja_n = \frac{R_u T_\infty}{P_0} (\bar{C}_n - k_H P_0) = \Lambda \zeta_n. \quad (8.6)$$

The Jakob number is a measure of the driving force for bubble growth induced by a solubility parameter Λ , commonly known as the Ostwald coefficient, and the degree of supersaturation ζ_n . These are defined as follows:

$$\Lambda = k_H R_u T_\infty, \quad \zeta_n = \frac{\bar{c}_n}{k_H P_0} - 1. \quad (8.7a, b)$$

We expect the Jakob number to be smaller than unity in our experiments. Indeed, for the P-C experiments, multiplying the supersaturation of CO_2 ($\zeta_n \approx$

	CO ₂	H ₂	Air ^c
D (m ² /s)	1.78×10^{-9} ^a	4.2×10^{-9} ^b	2.0×10^{-9} ^b
k_H (mol m ⁻³ Pa ⁻¹)	3.36×10^{-4}	7.7×10^{-6}	8.5×10^{-6}
Λ	0.824	0.0188	0.0207

^a Pressure ≈ 8 bar. ^b Pressure = 1 bar. ^c Air is considered only in the simulation.

Table 8.1: Gas properties in our experimental conditions ($T_\infty = 20^\circ\text{C}$).

0.17) by the corresponding solubility tabulated in table 8.1 results in $Ja_n \approx 0.14$. For the H₂ electrolysis experiments, $\zeta_n < 12$ according to simulations; therefore, $Ja_n < 0.23$. Equation (8.5) then simplifies to

$$R_n(t_n) = \sqrt{2Ja_nDt_n} \quad (8.8)$$

because $Ja_n \ll 2\pi$ always holds. Within this diffusive regime, the Jakob number can be readily shown to be equivalent to the Péclet number, $Pe_n = R_n\dot{R}_n/D$, which expresses the relative significance of advective over diffusive mass transport. The quantity $\dot{R}_n = dR_n/dt_n$ can be computed by differentiating (8.8) with respect to time. One then gets that $Pe_n \equiv Ja_n$, which is consistent with the fact that the Péclet number must also be smaller than unity. Finally, the direct comparison of (8.8) with (8.3) gives that the square of the dimensionless growth coefficient scales as the Jakob number:

$$\tilde{b}_n^2 = 2Ja_n = 2\Lambda\zeta_n. \quad (8.9)$$

It should be pointed out that, strictly speaking, (8.9) is valid only for a spherical bubble far from any boundary. Nonetheless, taking into account the presence of the substrate will not modify any of the scalings but will change only the numerical coefficient relating $\tilde{b}_n^2$ and Ja_n , as shown by [34] for P-C growth. In P-C growth, this coefficient is expected to be lowered by the presence of the inert substrate, which has a hindering effect on bubble growth (as seen in [Ch.1, 34]). This is perceived upon inspection of the CO₂ concentration field displayed in figure 8.6(d) obtained from simulation. The concentration isocontours are farther apart closer to the substrate compared to those near the apex.

The opposite occurs for the first bubbles in the case of electrolysis-driven growth, where H₂ transfer rates (concentration gradients) are highest in the portion of the bubble interface located closest to the electrode, as can be inferred from the accumulation of isoconcentration lines in the region closer to the substrate (figures 8.6(a,b)). Here, the bubbles are set to nucleate shortly after the onset of electrolysis; consequently, the H₂ supersaturation in the bulk

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Figure 8.6: Simulation snapshots of (a-c) H₂ or (d) CO₂ concentration isocontours around four distinct growing bubbles. The contour labels display the local supersaturation value, $C/(k_H P_0) - 1$. The simulations are performed for $R_0 = 7.5 \mu\text{m}$, $R_p = 15 \mu\text{m}$ and $H_p = 30 \mu\text{m}$. The snapshots correspond to the early growth stage of the bubbles when $R = 2H_p = 60 \mu\text{m}$. Panels (a-c) show H₂ bubbles growing in an air-saturated electrolyte assuming an effective current density of 1.56 A/m^2 that provides a similar H₂ flux as the highest nominal current density used in our experiments (figure 8.14). The bubble nucleation time after the start of electrolysis, t_0 , the corresponding initial degree of H₂ supersaturation (in the absence of bubbles), ζ , and the time after nucleation at which the snapshot is taken, t , are (a) $t_0 = 30 \text{ s}$, $\zeta \approx 0$, $t \approx 31 \text{ s}$, (b) $t_0 = 2 \text{ min}$, $\zeta \approx 1$, $t \approx 16 \text{ s}$, and (c) $t_0 = 20 \text{ min}$, $\zeta \approx 5.3$, $t \approx 3 \text{ s}$. Panel (d) portrays a CO₂ bubble growing in an initially uniform supersaturated solution, $\zeta = 0.17$ at $P_0 = 7.75 \text{ bar}$. The bubble is $t \approx 5 \text{ s}$ old.

electrolyte is still low. One may note that as the degree of supersaturation in the bulk liquid increases with time (figure 8.6(a) to 8.6(b) to 8.6(c)), the boundary layer evolves to the form attained in the P-C case (figure 8.6(d)). Most of the H₂ flux occurs at the apex of the bubble, as observed for P-C growth.

Finally, we must remark that the pillar height H_p is much smaller than the radius of the growing bubble except for the initial seconds of bubble growth. Therefore, the effect of the pillar height on the aforementioned coefficient is expected to be small.

8.3.2 Growth dynamics

The experimental diffusive growth coefficient for each electrolytic bubble in the succession was obtained by fitting the experimental data to (8.3), namely, $R_n(t_n) = \tilde{b}_n \sqrt{D t_n}$. More specifically,

$$\tilde{\beta}_{\text{H}_2}^2 = \frac{1}{D_{\text{H}_2}} \left\langle \frac{dR^2}{dt} \right\rangle_{R \rightarrow R_d}. \quad (8.10)$$

Here, $\tilde{\beta}_{\text{H}_2}$ is the asymptotic growth coefficient [23] at which the bubble reaches its detachment size. Even so, $\tilde{\beta}_{\text{H}_2}$ should be regarded, by all accounts, as the

Figure 8.7: Bubble radius dynamics at three different time periods after the onset of electrolysis with 7.8 A/m^2 . The measured bubble radii (dots) are plotted in (a, c, and e), whereas the corresponding square of the measured radii are plotted in (b, d, and f). Panels (a and b) correspond to the stagnation regime, (c and d) correspond to the supersaturation regime, and (e and f) correspond to the advected growth regime. The dashed black curves are the fits from which the asymptotic growth coefficient $\tilde{\beta}_{\text{H}_2}$ is obtained. The pit and pillar radius are 5 and $15 \text{ }\mu\text{m}$, respectively. The plots in (a)-(d) belong to the same experiment where $H_p = 30 \text{ }\mu\text{m}$. The plots in (e and f) belong to a different experiment where $H_p = 15 \text{ }\mu\text{m}$. The dotted horizontal line marks the size below which it was not possible to optically determine the size of the bubble accurately.

experimentally obtained $\tilde{b}$ for the electrolytic bubbles.

The theoretical fits are plotted in figure 8.7 for three different time periods after the start of electrolysis. Three regimes with distinct growth dynamics can be identified depending on the elapsed time of electrolysis. At early times, we devise a characteristic stagnation regime (see figure 8.7(a)), in which the second and third bubbles usually grow slower than the very first. Here, the accumulation of H_2 gas that one would expect from the continuous flux at the electrode is in fact exhausted or overridden by local gas depletion effects induced by the growth of the first bubbles and other sources that will be later discussed. The duration of this stagnation regime is shortened with increasing current density (figure 8.9). It stands to reason that no depletion regime may be observed if the current density is sufficiently large.

Thus, provided that the current density is large enough, the flow of H_2 into the bubble liquid surroundings eventually overrides the flow of gas lost through depletion effects. This results in a net accumulation of H_2 and, consequently,

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a vertical H_2 concentration boundary layer that develops from the electrode.

In such a case, a supersaturation regime (figure 8.7(c)) is eventually attained. The local supersaturation of the surrounding electrolyte is now more uniform. The expected diffusive behavior, $R_n^2 \propto t_n$, can be corroborated in figure 8.7(d). If, at later times, the supersaturation becomes large enough, an advective growth regime (figure 8.7(e)) is manifested. It is characterized by discontinuous dR/dt dynamics caused by the appearance of boundary-induced advection in bubble growth and departure [244]. Furthermore, a fast initial growth is observed. It is attributed to the presence of a thin boundary layer of excess H_2 gas near the gas-evolving electrode that quickly gets adsorbed into the bubble. As a consequence, the initial growth is observed to be more pronounced for pillar heights of 0 or 15 μm as opposed to 30 μm .

In slightly supersaturated water- CO_2 solutions, bubbles are known to diffusively grow before density-driven convection sets in during the final stages of their growth [34]. As a consequence, the diffusive growth coefficient for the CO_2 bubbles in the P-C experiments was similarly computed as

$$\tilde{\beta}_{\text{CO}_2}^2 = \frac{1}{D_{\text{CO}_2}} \left\langle \frac{dR^2}{dt} \right\rangle_{R < 3R_d/4}, \quad (8.11)$$

where R_d denotes the bubble radius at detachment. The upper limit of $3R_d/4$ is established in order to restrict the fitting of $\tilde{\beta}_{\text{CO}_2}$ to just the initial diffusive growth regime.

The theoretical fit (extrapolated to span the full bubble lifetime) is compared to a typical experiment ($\zeta = 0.17$) in figure 8.8. The initial diffusive growth, where $R \propto \sqrt{t}$, can be perfectly distinguished. One may also note a deviation between the theoretical fits and experiments as the bubble radius reaches its detachment size. This deviation is expected because it is related to the onset of natural convection at the end of bubble growth (as explained in [Ch.2, 34]). The prominent effect of density-induced convection on bubble growth observed here is, on the other hand, negligible for the case of H_2 bubbles.

The computation of $\tilde{\beta}_{\text{H}_2}$ and $\tilde{\beta}_{\text{CO}_2}$ for each individual bubble essentially allows for a quantitative measure of the evolution of the growth rate of the bubble succession as a whole. The fact that the evolution of $\tilde{\beta}_{\text{H}_2}$ in time for a succession of bubbles under constant-current electrolysis is far from uniform is immediately corroborated in figure 8.9. An illustrative movie of the electrolysis experiment with $j = 10.4 \text{ A/m}^2$ can be found online along this article. In the video, the time evolution of the bubble radii and the growth coefficient are also plotted in real time.

The first few bubbles fall under what we have referred to as the stagnation

Figure 8.8: (a) Pressure-controlled bubble radius dynamics and (b) the corresponding squared radius. The dashed curves are the (extrapolated) fits from which $\tilde{\beta}_{\text{CO}_2}$ is computed. The pit and pillar radii are 10 and 15 μm , respectively, whereas the pillar height is 30 μm .

Figure 8.9: $\tilde{\beta}_{\text{H}_2}$ for a succession of electrolytic bubbles exposed to constant current densities. Each point corresponds to a distinct bubble in the succession. Time t_m is the mean time (after the start of electrolysis) of the fitting period used to compute $\tilde{\beta}_{\text{H}_2}$. The bubbles evolved on a pit with a radius of 5 μm , a pillar radius of 15 μm and a pillar height of 30 μm .

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regime, in which $\tilde{\beta}_{\text{H}_2}$ is observed to decrease or remain fairly constant. The stagnation regime occurs as a result of the partial depletion of the evolving boundary layer of dissolved gas. There are three main sources of depletion that will soon be described. These are responsible for the ever-present loss of gas dissolved in the cavity where the electrode is held (cf. figure 8.2). This loss is most noticeable and even dominant in the early stages of electrolysis. This stands to reason because, as mentioned before, the local concentration of dissolved H_2 gas near the pillar is relatively small at the beginning of the electrolysis. Accordingly, gas losses due to depletion constitute a proportionally large reduction of the small amount of gas dissolved.

The subsequent bubbles experience a fast increase in $\tilde{\beta}_{\text{H}_2}$. This is a sign of the net accumulation of dissolved H_2 gas in the cavity. In other words, the flow rate of evolved H_2 into the cavity overrides the smaller flow rate losses due to depletion. Figure 8.10 displays the same experimental values of $\tilde{\beta}_{\text{H}_2}$ as a function of the total electric charge that has been in circulation before a given time, which is a direct measure of the total mass of H_2 supplied. For a given charge $Q = jt$, during the initial transient stage of electrolysis, we conclude that $\tilde{\beta}_{\text{H}_2}$ is higher for larger current densities. It is expected that the gas evolution efficiency increases with current density because the diffusion length of dissolved H_2 , which scales as $\sqrt{D_{\text{H}_2}Q/j}$, is smaller. In other words, mass is supplied faster and H_2 does not diffuse fast enough into the bulk electrolyte above the cavity in which the bubble evolves. Consequently, the gas supersaturation in the cavity surrounding the electrode is higher.

Naturally, in the P-C experiments, the absence of gas production must translate into a permanent depletion regime. [Ch.2] developed a theoretical depletion model for this particular scenario. On the basis of this model (Appendix 8.B), the evolution of the experimental growth coefficient should approximately satisfy

$$\frac{1}{\tilde{\beta}_{\text{CO}_2}^2(t)} - \frac{1}{\tilde{\beta}_{\text{H}_2}^2(0)} = \frac{2\pi}{3} \frac{D_{\text{CO}_2}t}{R_d^2}. \quad (8.12)$$

The experimental evolution in time of $\tilde{\beta}_{\text{CO}_2}$ is plotted in figure 8.11(a). In figure 8.11(b), these are compared to the best fitting law $1/\tilde{\beta}_{\text{H}_2}^2(t) = mt + c$. According to (8.12), the slope is $m = 0.027 \text{ s}^{-1}$. This estimate agrees well with experiments, where $m \approx 0.03 \text{ s}^{-1}$. Similarly, constant $c = 2.93$ from theory falls close to the experimental values that lie within 2.6-2.9. The small differences may be associated with the many simplifications and approximations that the theoretical model is based upon. Nonetheless, the good overall agreement between the model and experiments indeed suggests that in the P-C configuration there is only depletion from previous bubbles in the succession.

Figure 8.10: Diffusive growth coefficient as a function of charge for different current densities (caption of figure 8.9). The efficiency of gas evolution in the transient regime increases with the current density j .

Figure 8.11: (a) Diffusive growth coefficient, $\tilde{\beta}_{CO_2}$, as a function of time for four different P-C experiments. The time measurement for each bubble n is associated with its moment of detachment. (b) Plot of $1/\tilde{\beta}_{CO_2}^2$ as a function time. The straight solid line shows linear (8.12), with a slope of $m = 2\pi D_{CO_2} t / (3R_d^2) = 0.027 \text{ s}^{-1}$.

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Figure 8.12: Photograph showing the parasitic bubbles forming on the circular corner where the electrode (black surface) meets the sidewall of the cavity and at the sharp upper edge of the cavity wall (cf. the large bottommost bubble). These bubbles visibly surround the bubble that forms on top of the micropillar in the center of the electrode. The electrode diameter is 7 mm.

Depletion sources in the electrolysis experiments

In our electrolysis experiments, however, the electrolyte in the cavity suffers H_2 gas depletion from (i) previous bubbles in the succession, from (ii) parasitic bubbles (eventually millimeter-sized) forming all around the circular sidewall of the cavity (figure 8.12), and from (iii) the cavity opening, toward which H_2 is transported by diffusion. Regarding the latter, it is worth noticing that the cavity perimeter is much smaller than the perimeter of the holder above (cf. figure 8.2). In addition, the volume of electrolyte in the tank above the cavity is almost 3 orders of magnitude larger than the volume of the cavity itself. The opening of the cavity therefore initially acts as a zero H_2 concentration boundary condition (a pseudofree surface) because H_2 is essentially diffusing into an infinite reservoir.

The effect of these depletion sources on the bubble growth dynamics will be discussed next for the electrolysis experiments, discerning between the stagnation regime and supersaturation (eventually steady-state) regime that follows.

Stagnation regime

In the stagnation regime, the bulk concentration of dissolved H_2 gas within the cavity is small. We can then make the rough approximation that the H_2 gas in these bubbles be entirely supplied by the molar flux J_w that is evolved within a harvest area $\pi\delta^2$ on the flat electrode. The characteristic harvest length

Figure 8.13: Minimum squared value of $\tilde{\beta}_{H_2}$ plotted versus the product of current density and detachment radius. Each point corresponds to a single bubble in a unique succession. The linear regression fit is also plotted.

δ is the effective electrode length required to sustain a bubble growing at a particular rate in a degassed liquid and assuming a gas evolution efficiency of unity. Consequently, δ is always smaller than the electrode radius, $\delta \leq R_e$ (or an equivalent length). Indeed, the aforementioned depletion sources tend to decrease the growth rate and hence also δ . Thus, δ constitutes an important design parameter in electrolytic systems and should be investigated in future studies. In fact, δ/R_e can be regarded as a direct measure of the gas evolution efficiency of the system.

Assuming then that these bubbles are entirely composed of H_2 , a simple mass balance scaling yields

$$\frac{4\pi}{3} \frac{P_0}{R_u T_\infty} \frac{R_d^3}{\Delta t} \approx J_w \pi \delta^2, \quad (8.13)$$

where Δt denotes the bubble lifetime prior to detachment. As a first approximation, we expect the harvest length to scale as $\delta \approx R_d$. If we further assume purely diffusive growth, $R_d = \tilde{\beta}_{H_2} \sqrt{D_{H_2} \Delta t}$, and note that $J_w \propto j$, then (8.13) suggests that the asymptotic growth rate must scale as $\tilde{\beta}_{H_2}^2 \approx j R_d$. This relation is compared against experimental values in figure 8.13. The experimental dispersion is expected as a result of the random variability of the harvest length (primarily due to the spatial nonuniformity of the H_2 flux at the electrode) and the depletion strength from one experiment to the other.

Within the stagnation regime or transient regime that follows, the diffusive depletion at the cavity opening has an important retardation effect on the bub-

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Figure 8.14: Comparison between simulation (curves) and the experimental growth dynamics of the third bubble for three nominal current densities: (a) 7.8, (b) 10.4 and (c) 15.6 A/m^2 . Simulations employ effective current densities of (a) 1.04, (b) 1.30 and (c) 1.56 A/m^2 . Using (8.17) in Appendix 8.A, these yield initial supersaturations, ζ , of approximately (a) 1.5, (b) 3.3, and (c) 3.1. The black curves are computed by imposing a zero-concentration boundary condition at heights of (a) 1.0, (b) 1.3, and (c) 1.3 mm to model the effect of the cavity. The red dashed curves are computed without imposing the aforementioned boundary condition.

ble growth rate as the bubble grows larger and gets closer to the opening. This retardation can be noted upon inspection of figures 8.3 and 8.7(a). This claim is supported by numerical simulations as seen in figure 8.14. The simulation curves predict the experimental behavior once a zero-concentration boundary condition is imposed at a height somewhat lower, but close to the actual cavity depth of 2 mm. However, this is expected, because a lower height also accounts for other losses such as parasitic bubble formation at the cylindrical sidewall of the cavity.

It is imperative to note that the effective current density (which establishes the molar flux of dissolved H_2 at the electrode) employed in the simulation is in fact taken as a free parameter. The effective current density and the experimental time of nucleation of a particular bubble are put into (8.17) in Appendix 8.A to obtain the initial concentration field in which that particular bubble grows. The effective current density is thus chosen so that the numerical solution matches the experimental radii at the initial growth stage of the bubble. Surprisingly, the effective current densities are 7 to 10 times smaller than the nominal (experimental) values. Accordingly, the growth rates obtained by simulations at the nominal current densities were exceedingly high. A similar discrepancy in theoretical versus measured H_2 diffusive fluxes was observed by [247], who argued that most of the gas may not actually dissolve

in hydrated form. They reported that H_2 gas preferentially resides in the form of stable bulk nanobubbles ($R \approx 400$ nm) instead [247, 248].

Although at the moment we cannot give a precise answer to this discrepancy, we propose two plausible, not mutually exclusive, explanations. First, not all of the H_2 flux put into dissolution remains in the electrolyte or eventually goes to the bubble nucleating at the pit. Indeed, we observe that large bubbles unavoidably form at the cylindrical cavity sidewall. Second, the numerical model assumes a spatially uniform current density along the substrate. In practice, this may not be so. In fact, the current density can be highly non-homogeneous for planar electrodes [214]. Moreover, one may note that the actual boundary condition occurring at the electrode is of constant potential and not of uniform current density. Thus, close to the base of the pillar the local current density must be smaller than the average on the electrode surface.

Supersaturation regime

In the supersaturation regime, the gas concentration in the cavity is relatively more uniform at the beginning of the bubble growth, especially for sufficiently high supersaturations, $\bar{C}_n/(k_H P_0) \gg 1$. By making use of (8.6) $\bar{C}_n$ can be made continuous in time by setting $\bar{C}(t)$ equal to the wall concentration $C(z = 0, t)$ in the absence of bubbles assuming a 1D profile. The expression is provided in (8.17) in Appendix 8.A. In such a case, the growth coefficient exhibits the following behavior at long times:

$$\tilde{\beta}_{\text{H}_2}^2(t) \approx \frac{2R_u T_\infty}{P_0} \bar{C}(t; H_{\text{eff}}, J_{w,\text{eff}}). \quad (8.14)$$

The local concentration $\bar{C}(t)$ depends on the effective molar flux $J_{w,\text{eff}}$, or, equivalently, on the effective current density j_{eff} . These will be smaller than the nominal values in order to account for the aforementioned discrepancy between the experimental and theoretical concentrations. Furthermore, $\bar{C}(t)$ is also dependent on the effective electrolyte liquid column height H_{eff} that is expected to be lower than $H = 12$ mm. H_{eff} accounts for the geometry of the electrolysis holder and cavity and losses from growing and departing bubbles at the cavity perimeter. For high current densities, H_{eff} is also limited by the maximum supersaturation of dissolved H_2 that the electrolyte can withstand at the experimental pressure. The steady-state growth coefficient can be shown to directly depend on these two quantities:

$$\tilde{\beta}_{\text{H}_2,ss}^2 \approx \frac{2R_u T_\infty F v}{D_{\text{H}_2} P_0} j_{\text{eff}} H_{\text{eff}}. \quad (8.15)$$

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Figure 8.15: Evolution in time of the diffusion growth rate for $j = 7.8 \text{ A/m}^2$ for three different experiments. The pit radius is $R_0 = 5 \mu\text{m}$ for $H_p = 0$ and $30 \mu\text{m}$, whereas $R_0 = 1 \mu\text{m}$ for $H_p = 15 \mu\text{m}$. The green curve is a theoretical approximate solution given in (8.14) with $j_{\text{eff}} = 1.04 \text{ A/m}^2$ (same value as in simulations) and $H_{\text{eff}} = 8 \text{ mm}$.

Figure 8.15 compares this theoretical model for the behavior of $\tilde{\beta}_{H_2}$ at long times against three experiments with different pillar heights but performed under the same current density. A similar steady-state value is attained in all cases after about 150 min. However, it is evident that the transient behavior of $\tilde{\beta}_{H_2}$ is not repetitive across experiments. The deviations arise presumably from differences in the flux distribution across the electrode samples and especially from gas losses from the random formation and subsequent detachment of large parasitic bubbles on the cavity sidewall. The bubbles in the succession must then compete against the parasitic bubbles for the available H_2 gas. The formation of the parasitic bubbles ultimately has a hindering effect on the growth rates of the bubbles growing on the pillar. This effect increases over time as the solution becomes more supersaturated and the parasitic bubbles increase in size and hence in proximity with respect to the micropillar. For instance, the sudden decrease in $\tilde{\beta}_{H_2}$ at around 110 min in the experiment with $H_p = 30 \mu\text{m}$ in figure 8.15 is a consequence of a particular large parasitic bubble that expanded quite close to the pillar. After its detachment at approximately 130 min, $\tilde{\beta}_{H_2}$ is observed to recover quickly.

The radius dynamics of two bubbles belonging to this particular succession are compared with simulations in figure 8.16. The agreement is quite good once the (a priori unknown) initial supersaturation level ζ is adjusted. Note that ζ corresponds to the mean value of the initial concentration profile close

Figure 8.16: Comparison between simulation (curves) and the experimental growth dynamics for the (a) 48th and (b) 74th bubble of the succession with $H_p = 30 \mu\text{m}$ (cf. figure 8.15). The nominal current density is $j = 7.8 \text{ A/m}^2$, whereas simulations employ an effective current density of 1.04 A/m^2 . The red dashed curves are expected growth for a bubble in an infinitely long electrode that nucleates at the experimental time t in the absence of any previous bubbles. The initial concentration profile is given by (8.17) evaluated at time t . The resulting local supersaturations are $\zeta_{48} \approx 9.25$ and $\zeta_{74} \approx 11.0$. For the black curves, the time is adjusted to (a) $0.5t$ and (b) $0.6t$, resulting in $\zeta_{48} \approx 7.25$ and $\zeta_{74} \approx 8.4$.

to the electrode wall. As before, ζ , or rather the initial concentration profile, is computed from (8.17), and it is a function of the current density and time of nucleation after the onset of electrolysis. The value of the effective current density employed is 1.04 A/m^2 , the same as the one obtained by fitting the initial growth rate of the third bubble in the succession (as done for figure 8.14(a)). Thus, the nucleation time after the onset of electrolysis is now the sole free parameter. Setting it equal to the experimental nucleation time clearly overestimates the growth rates, as seen from the zero-loss prediction curves in figure 8.16. One can then account for depletion losses by decreasing the time of nucleation used to calculate ζ . After a suitable reduction in the nucleation time and hence ζ , the bubble growth behavior is reasonably well reproduced.

One may note that in the supersaturation regime the zero-concentration boundary condition is not required because the entire cavity, and possibly a small region above it, will be homogeneously supersaturated to a good degree. As the bubble approaches departure, a retardation in its growth is noticeable nonetheless. This is attributed to H_2 deprivation due to the presence of parasitic bubbles. The deviation for the 48th bubble is greater than for the 74th bubble. This is consistent with the fact that the 48th bubble is derived

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from the H_2 available to a greater extent by the aforementioned large parasitic bubble.

8.4 Conclusions

The growth dynamics of a succession of H_2 bubbles driven by constant-current electrolysis on a large electrode has been studied. The bubbles form within a hydrophobic pit on top of a single micropillar etched on a flat silicon electrode. The large surface area of the electrode ensures that the bubble growth is diffusion-limited. As such, growth can be suitably described in terms of an experimentally determined dimensionless growth coefficient $\tilde{\beta}_{\text{H}_2}$ according to $R(t) = \tilde{\beta}_{\text{H}_2} \sqrt{D_{\text{H}_2} t}$.

The accumulation of dissolved H_2 near the gas-evolving electrode is hindered by several depletion sources. We identify depletion from (i) previous bubbles in the succession, from (ii) unwanted parasitic bubbles forming on the cavity sidewall, and from (iii) the mere presence of the cavity where the electrode is being held. It follows that the degree of supersaturation near the electrode (and consequently $\tilde{\beta}_{\text{H}_2}$) is largely unsteady. For the range of current densities considered in our experiments (5-15 A/m²), the H_2 bubble succession first experiences a stagnation regime where depletion effects are most noticeable. Here, $\tilde{\beta}_{\text{H}_2}$ remains fairly constant or decreases. A fast growth in $\tilde{\beta}_{\text{H}_2}$ then follows before the steady state is reached. Conversely, for the case of CO_2 bubbles in our P-C experiments, persistent depletion (exclusively from previous bubbles in the succession) is observed. The analogous growth coefficient $\tilde{\beta}_{\text{CO}_2}$ decreases in such a way that the quantity $1/\tilde{\beta}_{\text{CO}_2}^2(t)$ increases linearly with time.

Furthermore, in the electrolysis experiments, the depletion effect of the cavity opening and of parasitic bubbles forming on the cavity sidewall accounts for the growth retardation observed as bubbles approach their departure size. Oppositely, CO_2 bubbles experience enhanced growth as they approach detachment. This is attributed to the onset of density-induced natural convection.

The comparison of both case scenarios serves to highlight the important effect of depletion, omnipresent in the growth of a succession of bubbles. The knowledge obtained can be further expanded by conducting electrolysis experiments with two main variations. First, we have nucleated bubbles within a cavity with no flow (stagnant conditions). In real-life scenarios, however, it may be desirable to have continuous flow. This will change the force balance keeping the bubbles pinned at the surface and influence mass transport through advection. Second, closed systems that could be pressurized (as op-

posed to open systems, such as the one presented here) will be very similar to the actual utilization of microfluidic electrochemical reactors [226]. Both cases are expected to entail distinct bubble growth dynamics and certainly warrant further study.

8.A One-dimensional concentration profile from a gas-evolving surface

The one-dimensional diffusion equation governing the evolution of the dissolved gas concentration profile

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (8.16)$$

applies to the liquid region $0 < z < H$. A constant molar flux J_w enters the region at $z = 0$. At the free surface, $C(z = H, t) = 0$. Initially we assume that $C(z, t = 0) = 0$. The concentration profile has the following analytical solution [249]:

$$C(z, t) = 2J_w \sqrt{t/D} \sum_{n=0}^{\infty} (-1)^n \left\{ \text{ierfc} \left(\frac{nH + z/2}{\sqrt{Dt}} \right) - \text{ierfc} \left(\frac{(n+1)H - z/2}{\sqrt{Dt}} \right) \right\}, \quad (8.17)$$

where the integral of the complementary error function is defined as

$$\text{ierfc}(x) = \int_x^{\infty} \text{erfc}(u) du = \frac{e^{-x^2}}{\sqrt{\pi}} - x \text{erfc}(x). \quad (8.18)$$

Equation (8.17) converges in time to the linear profile of the steady state solution, $C(z, t \rightarrow \infty) = J_w(H - z)/D$. Profiles computed from (8.17) are plotted in figure 8.17, whereas the evolution in time of the concentration at the gas-evolving surface ($z = 0$) is plotted in figure 8.18. Note that for the case of infinite height, $H \rightarrow \infty$, the solution in (8.17) simplifies to

$$C(z, t) = 2J_w \sqrt{t/D} \text{ierfc} \left(\frac{z}{\sqrt{4Dt}} \right). \quad (8.19)$$

In this particular case, no steady-state solution exists, and the concentration at the wall increases unboundedly as $2J_w \sqrt{t/(\pi D)}$. Furthermore, if small heights or short times are considered such that $z/\sqrt{4Dt} \ll 1$, then (8.19) can be approximated as

$$C(z, t) = \frac{2J_w}{\sqrt{\pi D}} \left(\sqrt{t} - \frac{z}{2} \sqrt{\pi/D} \right). \quad (8.20)$$

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Figure 8.17: Universal plot of the time evolution of the 1D concentration profiles for different instants in dimensionless time. The profiles marked in blue correspond to $\log_{10}(Dt/H^2) = -3, -2, -1$, and 0 . The profile in red is the steady-state profile.

Figure 8.18: Invariant, dimensionless plot of the time evolution of the concentration at the electrode wall ($z = 0$).

8.B Depletion model for the growth coefficient

Let subscript n refer to the n -th bubble. Let $t_n = t - t_{0,n}$, where $t_{0,n}$ is the nucleation time of such a bubble and $t_{0,n=1} = 0$. Let $\theta_n(r, t) = C(r, t) - \bar{C}_n$, where

$$\bar{C}_n = C_n(r, t_n = 0) = C_{n-1}(r = \delta_{n-1}, t_{n-1} = \Delta t_{n-1}) \quad (8.21)$$

is the characteristic (homogeneous) concentration field (left behind by bubble $n-1$) in which bubble n immediately grows. It is essentially the concentration field evaluated at the characteristic diffusion length δ_n and time Δt_n corresponding to the previous bubble, where $\Delta t_n = t_{d,n} - t_{0,n}$ is the bubble residence time. Note that we assume a negligible time between detachment and nucleation of the subsequent bubble: $t_{n-1} = \Delta t_{n-1}$ is equivalent to $t_n = 0$. Furthermore, the detachment radius $R_d = \tilde{b}_n \sqrt{D \Delta t_n}$ is assumed to be constant for all bubbles.

Following the model proposed in [Ch.2], we treat each bubble in the succession as a point source of molar strength

$$\dot{n}_n = -\frac{4\pi P_0 R_d^3}{3R_u T_\infty \Delta t_n} \quad (8.22)$$

which acts as a boundary condition to the diffusion equation,

$$\frac{\partial \theta_n}{\partial t_n} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \theta_n}{\partial r} \right), \quad (8.23)$$

together with a second boundary condition $\theta_n(r \rightarrow \infty, t) = 0$ and initial condition $\theta_n(r, t_n = 0) = 0$. Let $\bar{\theta}_n$ be the characteristic solution for θ_n evaluated at $r = \delta_n$ and $t = \Delta t_n$. Then,

$$\bar{\theta}_n = -\frac{4\pi P_0 R_d}{3R_u T_\infty} \frac{\tilde{b}_n^2}{\delta_n} \operatorname{erfc} \left(\frac{\delta_n \tilde{b}_n}{2R_d} \right). \quad (8.24)$$

Let $\Delta \bar{C}_n = \bar{C}_n - k_H P_0$ be the characteristic concentration field strength relative to the interfacial concentration. One then has that

$$\Delta \bar{C}_n = \bar{C}_1 - k_H P_0 + \sum_{m=2}^n \bar{\theta}_m. \quad (8.25)$$

Making use of (8.9) we know that $\Delta \bar{C}_n = P_0 \tilde{b}_n^2 / (2R_u T_\infty)$. Substituting this expression along with (8.24) into (8.25) yields

$$\tilde{b}_n^2 = \tilde{b}_1^2 - \frac{8\pi}{3} \sum_{m=2}^n R_d \frac{\tilde{b}_m^2}{\delta_m} \operatorname{erfc} \left(\frac{\delta_m \tilde{b}_m}{2R_d} \right), \quad (8.26)$$

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where $\tilde{b}_1^2 = 2R_u T_\infty \Delta \bar{C}_1 / P_0$ is just the known growth rate of the first bubble (corresponding to the initial, undepleted supersaturation $\Delta \bar{C}_1$). From experimental evidence in [Ch.2], we can make the approximation that $\delta_n \approx 4R_d$. Moreover, because $\tilde{b}_m \approx 0.1$ is small, the complementary error function can be approximated as unity. Equation (8.26) then simplifies to

$$\tilde{b}_n^2 = \tilde{b}_1^2 - \frac{2\pi}{3} \sum_{m=2}^n \tilde{b}_m^2. \quad (8.27)$$

The above expression can be made continuous in time through

$$\tilde{b}^2(t) = \tilde{b}^2(0) - \frac{2\pi}{3} \int_0^t \tilde{b}^2(t') \frac{dn}{dt'} dt' \quad (8.28)$$

where $dn/dt = D\tilde{b}^2(t)/R_d^2$ is simply the continuous form of the bubble nucleation frequency. Differentiating (8.28) in time yields

$$2\tilde{b} \frac{d\tilde{b}}{dt} = -\frac{2\pi D}{3R_d^2} \tilde{b}^4. \quad (8.29)$$

Upon integration, we obtain

$$\frac{1}{\tilde{b}^2(t)} - \frac{1}{\tilde{b}^2(0)} = \frac{2\pi}{3} \frac{Dt}{R_d^2}. \quad (8.30)$$

8.C Mathematical formulation of the mass transfer problem

This appendix provides the mathematical formulation of the mass transfer problem in addition to the equations employed by the numerical model. In particular we focus on (a) the electrolytic growth of a single H_2 bubble attached to a micropillar protruding from a H_2 gas-evolving substrate in an air-saturated, H_2 -containing, electrolyte and (b) the growth of a CO_2 bubble attached to a micropillar in mildly supersaturated carbonated water.

8.C.1 Formulation of the mass transfer problem

The transport of dissolved gas species in liquids is governed by the mass transport equation, usually referred to as the advection–diffusion equation. The bubbles evolving in the electrolysis experiments are immersed in a binary system of dissolved hydrogen gas and air. We choose to model air as a single species. The advection–diffusion equation for each gas species reads

$$\frac{\partial C_k}{\partial t} + \mathbf{U} \cdot \nabla C_k = D_k \nabla^2 C_k, \quad k = 1, 2 \quad (8.31)$$

where $C_k(\mathbf{x}, t)$ is the molar-based concentration field of dissolved hydrogen gas ($k = 1$) or air ($k = 2$). The concentration field and the velocity vector field $\mathbf{U}(\mathbf{x}, t)$ are both functions of the position vector $\mathbf{x}$ and time t . The gas diffusivities are denoted by D_k .

The pressure-controlled (P-C) experiments obviously involve monocomponent CO_2 bubbles. In this case, the problem is simplified to a single gas species. Therefore, $k = 1$ in (8.31) refers to CO_2 gas, whereas $k = 2$ is not applicable. From hereon forth, the problem shall be formulated for the electrolysis problem. The P-C problem is identical, except that the molar flux of CO_2 at the substrate is zero ($J_w = 0$), and species $k = 2$ should be removed from the formulation. The initial conditions are somewhat different. These shall be pointed out correspondingly.

The H_2 gas generated at the gas-evolving electrode can be suitably described through a constant flux boundary condition at the electrode surface,

$$\nabla C_1 \cdot \hat{\mathbf{n}} = -J_w/D_1 \quad (8.32)$$

where $\hat{\mathbf{n}}$ is the outward-pointing unit normal from the electrode surface. One would expect a zero-flux boundary condition along the impermeable holder and cavity walls, whereas at the free surface a zero-concentration boundary condition applies. For air, we expect a zero-flux boundary condition along the walls of the substrate and holder. At the free surface, the electrolyte is perfectly saturated with air. The boundary condition for the dissolved gas concentration at the bubble surface, $C_{k,i}(t)$, is given by Henry's Law,

$$C_{k,i}(t) = k_{H,k} \frac{n_k}{n} \left(P_0 + \frac{2\gamma_{lg}}{R} \right), \quad (8.33)$$

where $n_k(t)$ is the number of moles of species k inside the bubble, $n(t) = n_1(t) + n_2(t)$ is the total number of moles, P_0 is the ambient pressure, γ_{lg} is the liquid-gas surface tension and $R(t)$ is the bubble radius.

The bubble gas volume is related to the gas content and pressure via the equation of state for an ideal gas,

$$\frac{4}{3}\pi R^3 \left(P_0 + \frac{2\gamma_{lg}}{R} \right) = n R_u T_\infty, \quad (8.34)$$

where R_u denotes the universal gas constant and T_∞ is the ambient temperature. Finally, the mass transfer rate across the bubble surface S is given by Fick's first law. The molar rate of gas within the bubble is thus

$$\frac{dn}{dt} = \sum_{k=1}^2 \frac{dn_k}{dt} = \sum_{k=1}^2 D_k \int_S \nabla C_k \cdot \hat{\mathbf{n}} dS \quad (8.35)$$

where dS is an infinitesimal area element of the bubble surface, and here $\hat{\mathbf{n}}$ is the outward-pointing unit normal from the bubble surface.

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8.C.2 Nondimensionalization

It is convenient to rewrite the time, radius, Cartesian coordinates, mole number and concentration in dimensionless form:

$$\tau = \frac{D_1}{R_0^2} t, \quad a = \frac{R(t)}{R_0}, \quad \tilde{\mathbf{x}} = \frac{\mathbf{x}}{R_0}, \quad \mu_k = \frac{R_u T_\infty}{4/3\pi R_0^3 P_0} n_k(t), \quad c_k = \frac{C_k(\mathbf{x}, t) - C_{k,\infty}}{k_{H,k} P_0}. \quad (8.36a-e)$$

We also normalise the pillar height $h_p = H_p/R_0$, pillar radius $r_p = R_p/R_0$ and the free surface height $h = H/R_0$ using the pit radius R_0 . The reference concentrations are $C_{1,\infty} = 0$ for H_2 and $C_{2,\infty} = k_{H,2} P_0$ for air. Moreover, the species diffusivity, reference concentration and solubility, in addition to the surface tension and H_2 flux, may all be written in dimensionless form,

$$\Gamma_k = \frac{D_k}{D_1}, \quad \Upsilon_k = \frac{C_{k,\infty}}{k_{H,k} P_0}, \quad \Lambda_k = k_{H,k} R_u T_\infty, \quad \sigma = \frac{2\gamma l g}{R_0 P_0}, \quad j_w = \frac{R_0 J_w}{D_1 k_{H,1} P_0}. \quad (8.37a-e)$$

One may note that $\Upsilon_1 = 0$ whereas $\Upsilon_2 = 1$. For the P-C problem, $\Upsilon_1 = P_s/P_0$ (approximately 1.17 in the experiments), where P_s denotes the saturation pressure.

8.C.3 Simulation overview

As discussed in the main manuscript, neither the geometry of the holder and cavity, nor the free surface, is directly modelled. The simulated scenario is simplified to that of a bubble growing on a pillar upon an a substrate of infinite area in a semi-infinite liquid. The simulation solves the mass transfer problem for this simplified configuration. The computational grid, sketched in figure 8.5, is divided into two regions that use different coordinate systems: a bulk region for $z > H_p$ and a microlayer region below. In the bulk region, the advection–diffusion equation (1) coupled with streamfunction–vorticity equations are solved imposing a no-slip boundary condition at $z = H_p$. In the microlayer region, only the diffusion equation is solved, taking into account the flux boundary condition (2) across the substrate wall and the pillar surface. The concentration and its gradient are matched at the coupling plane $z = H_p$.

Overall, the numerical model is an extension of the (pillar-less) numerical model described in [Ch.1]. A detailed description of the numerical model and procedure may be found there. The novelties here are (a) the consideration of multiple species, (b) the addition of the microlayer region (as a means to overcome the geometrical difficulty imposed by the pillar) and (c) the non-zero H_2 flux boundary condition at the substrate. These additions or changes strictly affect only the mass transfer equations or their boundary conditions.

The streamfunction–vorticity formulation and numerical procedure remains unchanged. For this reason, expressions for just these particular mass transfer equations shall be provided next.

8.C.4 Equations for the bulk region

The mass transfer problem is recast in dimensionless tangent-sphere spatial coordinates (η, ξ, ϕ) , where

$$\tilde{x} = 2a \frac{\eta}{\eta^2 + \xi^2} \cos \phi, \quad \tilde{y} = 2a \frac{\eta}{\eta^2 + \xi^2} \sin \phi, \quad \tilde{z} = 2a \frac{\xi}{\eta^2 + \xi^2} + h_p. \quad (8.38a-c)$$

The scale factors

$$\tilde{h}(\eta, \xi) = \tilde{h}_\eta = \tilde{h}_\xi = \frac{2a}{\eta^2 + \xi^2}, \quad \tilde{h}_\phi(\eta, \xi) = \frac{2a\eta}{\eta^2 + \xi^2}. \quad (8.39a, b)$$

also depend on the instantaneous bubble radius $a(\tau)$. The dimensionless advection-diffusion equation for $c_k(\tilde{\mathbf{x}}, \tau)$ reads

$$\frac{\partial c_k}{\partial \tau} + \mathbf{u} \cdot \tilde{\nabla} c_k = \nabla^2 c_k, \quad (8.40)$$

and, for $c_k(\eta, \xi, \tau)$, it transforms to

$$\frac{\partial c_k}{\partial \tau} = F \frac{\partial c_k}{\partial \eta} + G \frac{\partial c_k}{\partial \xi} + H \left(\frac{\partial^2 c_k}{\partial \eta^2} + \frac{\partial^2 c_k}{\partial \xi^2} \right), \quad (8.41)$$

where

$$F = -\Gamma_k \frac{\eta^2 - \xi^2}{2a\tilde{h}\eta} - \frac{da}{d\tau} \frac{\eta}{a} - \frac{u_\eta}{\tilde{h}}, \quad G = -\Gamma_k \frac{\xi}{a\tilde{h}} - \frac{da}{d\tau} \frac{\xi}{a} - \frac{u_\xi}{\tilde{h}}, \quad H = \frac{\Gamma_k}{\tilde{h}^2}. \quad (8.42a-c)$$

The velocity field components $u_\eta(\eta, \xi, \tau)$ and $u_\xi(\eta, \xi, \tau)$ are computed as detailed in [Ch.1]. The boundary conditions for the concentration at the bubble surface, axis of symmetry and triple contact point are

$$c_k(\eta, 1, \tau) = \frac{\mu_k}{\mu} \left(1 + \frac{\sigma}{a} \right) - \Upsilon_k, \quad \frac{\partial c_k}{\partial \eta}(0, \xi, \tau) = 0, \quad \frac{\partial c_k}{\partial \eta}(\infty, \xi, \tau) = 0. \quad (8.43a-c)$$

At the coupling plane, we prescribe the flux $j_{w,k}$ at the pillar top surface, and we force a coupling flux $j_{cp,k}(\eta)$ in the liquid phase equal to the flux obtained from the microlayer region:

$$\frac{\partial c_k}{\partial \xi}(\eta, 0, \tau) = \begin{cases} -\tilde{h}(\eta, 0)j_{w,k}, & \text{if } \eta > 2a/r_p, \\ -\tilde{h}(\eta, 0)j_{cp,k}(\eta), & \text{otherwise.} \end{cases} \quad (8.44)$$

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The dimensionless molar flow rate across the bubble surface is

$$\frac{d\mu}{d\tau} = -3a \sum_{k=1}^2 \Gamma_k \Lambda_k \int_0^\infty \frac{\eta}{1+\eta^2} \left. \frac{\partial c_k}{\partial \xi} \right|_{\xi=1} d\eta. \quad (8.45)$$

Finally, the dimensionless ideal gas law simply reads: $(1 + \sigma/a)a^3 = \mu$.

8.C.5 Diffusion equation for the microlayer region

In the microlayer region bounded by $\tilde{x}^2 + \tilde{y}^2 > r_p^2$ and $0 \leq \tilde{z} \leq h_p$, the diffusion equation is recast in dimensionless pseudo-cylindrical coordinates (ρ, ϕ, ζ) ,

$$\tilde{x} = \frac{2a}{\rho} \cos \phi, \quad \tilde{y} = \frac{2a}{\rho} \sin \phi, \quad \tilde{z} = h_p \zeta. \quad (8.46a-c)$$

The scale factors are

$$\tilde{h}_\rho = \frac{2a}{\rho^2}, \quad \tilde{h}_\phi = \frac{2a}{\rho}, \quad \tilde{h}_\zeta = h_p. \quad (8.47a-c)$$

One may note that coordinate ρ behaves identically to η in the coupling plane defined by $(\rho, \phi, \tilde{z} = h_p)$ or $(\eta, \xi = 0, \phi)$. The microlayer region is bounded by $0 < \rho \leq \rho_p(\tau)$ and $0 \leq \zeta \leq 1$ where $\rho_p = 2a/r_p$. The diffusion equation for $c_k(\rho, \zeta, \tau)$ then reads

$$\frac{\partial c_k}{\partial \tau} = A \frac{\partial c_k}{\partial \rho} + B \frac{\partial^2 c_k}{\partial \rho^2} + C \frac{\partial^2 c_k}{\partial \zeta^2}, \quad (8.48)$$

where

$$A = \frac{\Gamma_k}{\rho \tilde{h}_\rho^2} - \frac{da}{d\tau} \frac{\rho}{a}, \quad B = \frac{\Gamma_k}{\tilde{h}_\rho^2}, \quad C = \frac{\Gamma_k}{\tilde{h}_\zeta^2}. \quad (8.49a-c)$$

The boundary conditions are

$$\frac{\partial c_k}{\partial \rho}(0, \zeta, \tau) = 0, \quad \frac{\partial c_k}{\partial \rho}(\rho_p, \zeta, \tau) = 2aj_{w,k}/\rho_p^2, \quad \frac{\partial c_k}{\partial \zeta}(\rho, 0, \tau) = -h_p^2 j_{w,k}. \quad (8.50a-c)$$

At the coupling plane, we impose the concentration found at the coupling plane in the bulk region:

$$c_k(\rho, \zeta = 1, \tau) = c_k(\eta, \xi = 0, \tau). \quad (8.51)$$

The flux obtained the coupling plane of the microlayer region is then imposed as the flux boundary condition for the bulk region at the coupling plane,

$$-j_{cp,k}(\eta, \tau) = \frac{1}{\tilde{h}(\eta, 0)} \frac{\partial c_k}{\partial \xi}(\eta, 0, \tau) = \frac{1}{h_p} \frac{\partial c_k}{\partial \zeta}(\rho, 1, \tau). \quad (8.52)$$

8.C.6 Initial conditions of the numerical model

Let us consider a bubble that grows at time $\tau = \tau_0$ after the start of electrolysis. The initial condition for the concentration of air is assumed always to be $c_2(\eta, \xi, \tau_0) = 0$, i.e. the electrolyte is uniformly equilibrated with air. Furthermore, we approximate the initial H_2 concentration field as the 1D vertical profile that would be obtained in the total absence of previous bubbles (cf. Appendix 8.A):

$$c_1(\eta, \xi, \tau_0) = 2j_w \sqrt{\tau_0} \sum_{n=0}^{\infty} (-1)^n \left\{ \text{ierfc} \left(\frac{nh + \tilde{z}_i/2}{\sqrt{\tau_0}} \right) - \text{ierfc} \left(\frac{(n+1)h - \tilde{z}_i/2}{\sqrt{\tau_0}} \right) \right\}. \quad (8.53)$$

where $\tilde{z}_i = 2\xi a_i/(\eta^2 + \xi^2) + h_p$. Here, $a_i = a(\tau_0)$ is the initial bubble radius which must be set to a small but finite size (typically around two times the pit radius). The initial bubble composition, $\mu_1(\tau_0)$ and $\mu_2(\tau_0)$ (whether purely H_2 , purely air, or a mixture of both), was seen to have a negligible effect on the bubble growth dynamics

The initial concentration condition for the P-C problem is that the water is homogeneously supersaturated with CO_2 , $c_1(\eta, \xi, \tau_0) = 0$. Moreover, the initial time can be set to $\tau_0 = 0$ since its value is of no consequence.

The nucleation rate of single O₂ nanobubbles on Pt nanoelectrodes *

Nanobubble nucleation is a problem that affects efficiency in electrocatalytic reactions since those bubbles can block the surface of the catalytic sites. In this article, we focus on the nucleation rate of O₂ nanobubbles resulting from the electrooxidation of H₂O₂ at Pt disk nanoelectrodes. Bubbles form almost instantaneously when a critical peak current, i_{nb}^{P} , is applied, but for lower currents, bubble nucleation is a stochastic process in which the nucleation (induction) time, t_{ind} , dramatically decreases as the applied current approaches i_{nb}^{P} , a consequence of the local supersaturation level, ζ , increasing at high currents. Here, by applying different currents below i_{nb}^{P} , nanobubbles take some time to nucleate and block the surface of the Pt electrode at which the reaction occurs, providing a means to measure the stochastic t_{ind} . We study in detail the different conditions in which nanobubbles appear, concluding that the electrode surface needs to be preconditioned to achieve reproducible results. We also measure the activation energy for bubble nucleation, E_{a} , which varies in the range from (6 to 30) kT , and assuming a spherically cap-shaped nanobubble nucleus, we determine the footprint diameter $L = 8 - 15$ nm, the contact angle to the electrode surface $\theta = 135 - 155^\circ$ and the number of O₂ molecules contained in the nucleus (50 to 900 molecules).

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9.1 Introduction

The generation of bubbles in chemical reactions is a process that has been well known by scientists throughout history. When these bubbles are extremely small (on the order of nanometers), the problem becomes much more challenging to analyze [15, 250, 251]. However, the technology used to visualize such surface nanobubbles has been very recently developed [15, 252–254]. The biggest concern that surface nanobubbles cause is their generation in chemical reactions, such as electrolysis [11] and catalysis [14]. Nanobubbles nucleating on top of reacting surfaces or electrodes influence the efficiency of chemical reactions since they partially block the reactive surface and consequently impede the reaction of interest [197]. A similar situation occurs in the case of nanodroplet and nanocrystal nucleation [255]. In other scenarios, such as redox reactions in cells, the nanobubbles can form within the nanoprobe and induce current amplification [256]. The high internal pressures of nanobubbles make their behavior rather different from that of micro- or macrobubbles [15, 257]. Nanobubbles often adhere to the surface at which they originate, forming a spherical cap that strongly attaches to the active surface [15, 258]. Without pinning, i.e., when the nanobubbles are not attached to a specific location on the surface, due to the high pressure inside them [259, 260], nanobubbles would dissolve extremely rapidly once the reaction stops. However, if there are pinning sites and constant gas supersaturation is provided at the surface, then nanobubbles on reacting surfaces are very stable [261, 262] and do not dissolve [15]. Molecular dynamics simulations [263] support this view.

In this article, we measure the nucleation rate of single O_2 nanobubbles generated at Pt nanodisk electrodes by the electro-oxidation of H_2O_2 . When the local dissolved O_2 concentration at the nanoelectrode is sufficiently high [264], a nanobubble nucleates and blocks the reacting surface, as depicted in figure 9.1. We study the factors affecting the nucleation rate of O_2 nanobubbles under different applied currents.

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Figure 9.1: O_2 nanobubble generation by electro-oxidation of H_2O_2 . When the O_2 concentration at the nanoelectrode is sufficiently high, a nanobubble nucleates after some time and partially blocks the electrode surface.

9.2 Experimental methods

The fabrication and measurement of the size of Pt nanoelectrodes are described in detail in Appendix 9.A. All experiments were performed in an aqueous solution of 1 M H_2O_2 and 1 M $HClO_4$, prepared using purified deionized water ($18.2\text{ M}\Omega\cdot\text{cm}$).

A HEKA EPC10 patch clamp amplifier was used to collect current, i , voltage, E , and time, t , data, which were filtered with a 4-pole Bessel low-pass filter at 10 kHz and sampled at 50 kHz. A LabVIEW program employing a FPGA card (National Instruments, PCIe-7852) was used to monitor the voltage and to control current steps for galvanostatic experiments. The program was capable of lowering the current to 0 nA within 80 μs after the detection of nanobubble nucleation. A mercury sulfate electrode (BASi) was employed ($E = +0.64\text{ V}$ relative to a normal hydrogen electrode, NHE) as a reference/counter electrode in a two-electrode configuration. For convenience, all potentials are presented vs NHE.

9.3 Results and discussion

9.3.1 Cyclic voltammogram in a solution of 1 M H_2O_2 and 1 M $HClO_4$

The generation of a single nanobubble at a Pt nanoelectrode can be observed in cyclic voltammetric measurements, as reported in previous work [265, 266]. Figure 9.2 shows the cyclic voltammogram of a 6-nm-radius electrode in an aqueous solution of 1 M H_2O_2 and 1 M $HClO_4$.

The $i - E$ response reflects several potential-dependent electrochemical reactions [266], as labeled in figure 9.2:

Figure 9.2: Cyclic voltammogram of a 6-nm-radius Pt nanoelectrode in a solution of 1 M H_2O_2 and 1 M HClO_4 . The red dot on the close-up area corresponds to the peak current i_{nb}^{p} at which a nanobubble nucleates and then grows to block the electrode surface. The scan rate is 200 mV/s.

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1. $\text{H}_2\text{O}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^- + \text{O}_2$: above 0.8 V, H_2O_2 is electrochemically oxidized to produce dissolved O_2 . The higher the current, the faster the rate of O_2 production and the higher the local supersaturation [264].
2. O_2 nanobubble formation: when the current reaches the peak value, i_{nb}^{p} , the concentration of O_2 is sufficiently high that a nanobubble nucleates at the nanoelectrode, grows, and blocks it, as depicted in figure 9.1. Consequently, the current rapidly drops to a residual current, i_{nb}^{r} , which corresponds to the balance of the steady-state O_2 dissolution from the bubble to the bulk with the O_2 production at the circumference of the nanoelectrode (which is not fully covered by the nanobubble) [265, 267]. Increasing the voltage from that point on causes no change in the current, which remains constant at i_{nb}^{r} [265]. This current also stays constant when we subsequently reduce the voltage until O_2 electrogeneration ceases and the nanobubble dissolves.
3. $\text{H}_2\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \longrightarrow 2\text{H}_2\text{O}$: from 0.8 to 0 V, H_2O_2 is reduced to form H_2O , resulting in a cathodic current.
4. $\text{H}^+ + \text{e}^- \longrightarrow \text{Pt} - \text{H}$: a monolayer of $\text{H}\cdot$ is reductively adsorbed at the Pt surface [268], reducing the rate of H_2O_2 reduction, resulting in a decrease in the cathodic current.
5. $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$: from -0.1 to -0.4 V, protons are reduced to produce H_2 .
6. H_2 nanobubble formation: when enough H_2 molecules cluster together, a H_2 nanobubble nucleates at the nanoelectrode, as indicated by a sudden decrease in current to a potential-independent residual current.
7. As the electrode potential is scanned toward positive voltages (from 0 to 0.8 V), $\text{H}\cdot$ desorbs from the Pt and the rate of H_2O_2 reduction increases.

This cyclic voltammogram may be scanned hundreds of times, with repeated formation and dissolution of the O_2 and H_2 nanobubbles on each scan [215]. However, large variability in i_{nb}^{p} is observed after an extensive repetition of voltammetric cycles. This is likely due to the restructuring of the surface in the repetitive scans, as the voltammetric responses involve $\text{H}\cdot$ absorption and desorption (from 0 to 0.8 V, steps 3 and 7 in figure 9.2) and the oxidation and reduction of H_2O_2 involve the generation of PtO_x as well as the reduction of PtO_x to Pt [268]. However, the self-decomposition of H_2O_2 to O_2 caused by the Pt surface [163, 269] does not play a significant role in the case of eventual bubble nucleation since the O_2 generation rate is negligible compared to the

Figure 9.3: Multiple voltammetric cycles demonstrating the generation of O₂ and H₂ nanobubbles. Note that the curves show a large variation. More specifically, the current i_{nb}^P at which an O₂ nanobubble forms varies significantly from cycle to cycle. The voltammograms were recorded at a 6-nm-radius electrode at a scan rate of 200 mV/s.

gas production rate once a certain current is applied [266]. The electrode apparent radius a is also affected during the application of the conditioning cycles (refer to Appendix 9.A), and consequently, i_{nb}^P may be affected [266, 267, 270]. Figure 9.3 shows several cyclic voltammograms recorded at the same electrode, displaying a different i_{nb}^P in every cycle. However, by reducing the scan range or applying a ‘conditioning cycle’, a reproducible electrode surface and a constant apparent radius, and therefore a consistent i_{nb}^P , can be achieved. We can thus influence the surface chemistry of the Pt electrode, achieving a more reproducible i_{nb}^P [214]. Figure 9.4 presents several voltammograms of the same electrode covering different scan ranges, with the resulting variability of i_{nb}^P shown in figure 9.4(d). It is important to notice the different mean values of i_{nb}^P for different scan ranges, which emphasizes the importance of the surface chemistry on bubble nucleation.

Once we have secured a reproducible i_{nb}^P , we can turn to the objective of our story: the measurement of the different rates at which nanobubbles nucleate if a certain current below i_{nb}^P is applied.

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Figure 9.4: (a-c) Multiple cycles of voltammograms performed over different potential scan ranges for the determination of experimental conditions giving rise to reproducible i_{nb}^p for O_2 nanobubble formation on a 6-nm-radius electrode. (d) i_{nb}^p vs cycle number for O_2 nanobubble formation for different scan ranges corresponding to voltammograms in panels (a,b,c) and figure 9.3. The voltammetric cycle shown in panel (c) is the one that involves the least surface chemistry and thus, results in the most reproducible results (green diamonds in panel (d)). Note that the mean value of i_{nb}^p changes for different scan ranges, again highlighting the importance of the surface chemistry.

9.3.2 Measurement of the nucleation rate

Our experiments aim at measuring the time to nucleate a nanobubble as a function of the applied current i_{app} . In the experiments described above, the nanobubbles nucleate ‘instantaneously’ on the voltammetric time scale when the current reaches i_{nb}^{p} (which is approximately linearly related to the electrode apparent measurable radius a [266, 267]). However, if i_{app} is lower than i_{nb}^{p} , then a measurable stochastic induction time is required for nucleation [266].

As shown in figure 9.4(d), at least 40 cycles need to be performed before a good i_{nb}^{p} reproducibility is reached. Therefore, we designed the conditioning cycle shown in figure 9.5(a) to obtain reproducible results during the nucleation rate experiments. First, the voltage is swept positively until an O_2 nanobubble nucleates and blocks the electrode. The voltage is then stepped to $E = 0.64$ V for a defined time, t_{dis} , to allow the nanobubble to dissolve; this dissolution is followed by a stabilization process in which the electrode surface is conditioned by holding it at a voltage, E_{stab} , for a time, t_{stab} . Finally, we let the electrode rest at $E = 0.64$ V for a time t_{rest} before repeating the cycle. Conditioning waveforms using different combinations of t_{dis} , t_{stab} , E_{stab} , and t_{rest} have been experimentally tried and are presented in the table in figure 9.5(c). The optimized conditions correspond to $t_{\text{dis}} = 1$ s, $t_{\text{stab}} = 2$ s, $E_{\text{stab}} = 0.89$ V, and $t_{\text{rest}} = 1$ s, corresponding to conditioning protocol #4 (green diamonds) in figure 9.5(b), where we represent i_{nb}^{p} vs the cycle number corresponding to the most representative data among 20 different conditioning configurations. The different $i - E$ vs t plots of these conditioning cycles have been included in Appendix 9.B.

Now we can measure the nucleation rate at different supersaturation levels, which are directly controlled by the applied current [271]. We chose to control current rather than voltage because the experiment is very sensitive to any drift in the voltage. For example, in the region very close to i_{nb}^{p} , a change of 20 mV generated a change of 8% in current, as can be seen in figure 9.6(a), in which we plot a voltammogram for O_2 nanobubble nucleation. Such an apparent ‘small’ variation in current causes a significant variation in the nucleation rate of nanobubbles. Control of the voltage is difficult to achieve with the desired precision. Therefore, we decided to control the current, which can be precisely adjusted to the level of pA.

A LabVIEW script was used to control the current i_{app} applied to the electrode. By subsequent step increases from $\sim 0.7i_{\text{nb}}^{\text{p}}$ to $\sim 1.0i_{\text{nb}}^{\text{p}}$, we can measure different nucleation times, which become smaller the closer i_{app} is to i_{nb}^{p} . The applied current loop is represented in figure 9.6(c), in which i_{stab} corresponds to the current response obtained during the application of E_{stab} in the course of electrode conditioning (figure 9.5(a)). Once a nanobubble forms,

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Figure 9.5: (a) Voltammetric electrode conditioning cycle used to rapidly achieve a state where the O_2 nanobubble forms at a consistent current. (b) i_{nb}^{p} for the most representative combinations of t_{dis} , t_{stab} , E_{stab} , and t_{rest} as indicated in the table in panel (c). The configuration with the smallest standard deviation used throughout this article corresponds to configuration 4, with $t_{\text{dis}} = 1$ s, $t_{\text{stab}} = 2$ s, $E_{\text{stab}} = 0.89$ V, and $t_{\text{rest}} = 1$ s. (c) Table with the different configurations for conditioning the electrode to obtain reproducible results. The configuration which achieves the lowest standard deviation is highlighted in blue (diamond symbol) and is used in the remainder of the article and is referred to as ‘the electrode conditioning cycle’.

Figure 9.6: (a) Forward scan of a voltammogram for bubble formation at a 41-nm-radius Pt electrode. Inset: the range of i_{app} where bubble nucleation times are measured. (b) Experimental sequence used to determine bubble nucleation time as a function of i_{app} . (c) Applied current cycle (top) and measured potential (bottom) for determining the bubble nucleation time at the same electrode as in panel (a). The different times are defined similarly to the intervals in figure 9.5(a), whereas i_{stab} is the measured value of the current obtained during the application of E_{stab} in the same figure.

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according to the voltammogram presented in figure 9.6(a), if i_{app} is maintained fixed at a certain value, then the voltage will dramatically increase to values that correspond to water oxidation, damaging the nanoelectrode. Therefore, a threshold voltage $E_{\text{thres}} = 1.5$ V is established, so when a nanobubble nucleates and the voltage spikes, i_{app} will automatically return to zero.

We design a full experiment as shown in the flowchart of figure 9.6(b). First, the electrode surface is conditioned by applying the cycle in figure 9.5(a) over a hundred times with voltage control. Afterwards, we switched to current control, applying a fixed i_{app} until a nanobubble nucleates and blocks the electrode, while measuring the corresponding nucleation time t_{ind} . For the purpose of avoiding electrode surface reconditioning, if no bubble nucleated after 30 s, the current was manually set to zero and the process continued as designed. We repeated this loop for different currents 10 times before conditioning the electrode surface again. Several voltage responses are shown for a 41-nm-radius electrode corresponding to different i_{app} values in figure 9.7 (see more results for different currents and different electrodes in Appendix 9.C). It can be perfectly appreciated that the closer i_{app} is to i_{nb}^{p} , the shorter t_{ind} becomes, e.g., $t_{\text{ind}} \approx 15$ s at $i_{\text{app}} = 11.3$ nA (figure 9.7(a)), whereas when i_{app} is increased by 0.8 nA, t_{ind} drastically decreases to ~ 7 ms (figure 9.7(d)). An increase of 7% in i_{app} causes a decrease in the nucleation time of 3 orders of magnitude. We report the different nucleation times t_{ind} for different i_{app} values on an $a = 41$ nm electrode in figure 9.8(a) (refer to Appendix 9.C for the results corresponding to different electrodes). The stochasticity of the process can be appreciated in the different nucleation times measured at the same i_{app} . Notably, the closer i_{app} is to i_{nb}^{p} ($i_{\text{nb}}^{\text{p}} = 12.2$ nA for this case), the lower the variability of t_{ind} , i.e. the curves for different repetitions lie closer together. This effect originates from the shorter exposure time to a certain i_{app} , thus avoiding any reconditioning of the electrode surface. The shorter the exposure, the less the surface chemistry and consequently the more reproducible the results. For values of i_{nb}^{p} of approximately $0.9i_{\text{nb}}^{\text{p}}$, the stochastic variability in t_{ind} ranges over 2 to 3 orders of magnitude [271], moving toward values with variability within 1 order of magnitude for $0.99i_{\text{nb}}^{\text{p}}$.

The cumulative probability of a nanobubble nucleating at a nanoelectrode can be expressed as $P = N(t)/N_{\text{T}}$, where $N(t)$ represents the number of nanobubbles whose nucleation occurs before a specific time t and N_{T} is the total number of nucleation events recorded at a certain i_{app} [272]. This cumulative probability can be theoretically expressed by an exponential relationship [272, 273]:

$$P = 1 - e^{-J(t-t_{\text{limit}})}, \quad (9.1)$$

where J refers to the nucleation rate at a specific current and t_{limit} is the

Figure 9.7: Potential-time measurements to determine the time needed to nucleate an O_2 nanobubble. Each panel shows a different $i_{app} < i_{nb}^p = 12.2$ nA and is presented on a different time scale. The electrode was 41 nm in radius. In some repetitions, for the lowest i_{app} , bubble nucleation did not occur within 30 s; therefore, the process was manually stopped. Panel (c) illustrates the interval in which the nucleation time, t_{ind} , is measured, from the moment in which the current is applied until the moment in which the nanobubble nucleates (indicated by a sudden increase in the voltage as the bubble blocks the surface of the nanoelectrode). The arrows indicate the cycle number.

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Figure 9.8: (a) Experimentally measured t_{ind} for different i_{app} values on a 41-nm-radius Pt electrode. (b) Corresponding cumulative probability P of a nanobubble nucleation event for $i_{app} = 11.4, 11.6, 11.7, 11.8, 11.9$ and 12 nA (other currents have similar results but are not shown, aiming for clarity in the figure). The theoretical curves correspond to the best fit of (9.1) to the data. The curves become increasingly vertical with increasing i_{app} : the higher the current, the higher the nucleation rate J .

shortest accessible experimental time, which can be physically associated with the response time of the electronic circuit coupled to the capacitance of the electrochemical cell [271] and determines the minimum experimentally achievable t_{ind} . By fitting (9.1) to the data in figure 9.8(a), the nucleation rate, J , for each value of i_{app} can be measured as a best-fitting parameter. An estimate can be calculated as $J \approx 1/(\bar{t}_{ind} - t_{limit})$, where $\bar{t}_{ind}$ is the mean value of the nucleation time at a certain i_{app} . A single value of t_{limit} was fit to all measurements with each electrode. The probability distribution for the different i_{app} values in figure 9.8(a) is represented in figure 9.8(b). The best match between the fits and experiments occurs for intermediate levels of i_{app} since for the lower values, nanobubbles take a longer time to nucleate and therefore the nanoelectrode surface can be reconditioned to a different state, whereas for i_{app} very close to i_{nb}^P the process is so fast that any uncertainty in t_{limit} may result in a very significant uncertainty in J .

The nucleation rate, J , depends on i_{app} , increasing its value as i_{app} increases, as can be depicted from the more vertical sigmoidal curves in figure 9.8(b) for higher values of i_{app} . From Classical Nucleation Theory (CNT), the nucleation rate of a nanobubble at the surface of the electrode can be

expressed as [197, 257, 261, 274, 275]

$$J = J_0 e^{-\frac{16\pi\gamma^3\phi(\theta)}{3kT(P_s - P_0)^2}}, \quad (9.2)$$

where J_0 is the pre-exponential factor which describes the statistical molecule-by-molecule process of nucleus growth (which can be considered to be constant with respect to i), γ is the surface tension of the gas–liquid interface (variations in the surface tension at molecular length scale, which have been shown to be minimal down to 10 nm [265], are not considered), $\phi(\theta) = (1 + \cos(\theta))^2(2 - \cos(\theta))/4$ is a geometric function which depends on the nanobubble contact angle θ to the electrode surface [196, 215, 276] (which implicitly accounts for the minute effect of the surface tension between the electrode and the bubble [277]), $kT = 4.11 \times 10^{-21}$ J is the product of Boltzmann constant k and thermodynamics temperature $T = 298$ K, and P_s and P_0 refer to the pressure in the bubble and the ambient pressure in the bulk liquid, respectively. Note again that in the derivation of (9.2), a spherical cap shape of the bubble nucleus has been assumed. Once van der Waals forces and thus the disjoining pressure play a role, this is no longer the case and the nanobubble shape may differ from that of a perfect spherical cap [278]. Given the nanometric size of the bubbles, these considerations may apply. These deviations from a perfect spherical-cap shape are nevertheless known to be very small [278], so our assumption may still be valid.

Assuming Fickian diffusion on a planar disk electrode, we can relate the steady-state current i to the local concentration of O_2 being produced at the electrode surface, $C_{O_2}^{\text{surface}}$ [196, 266, 267]:

$$i = 4nFD_{O_2}a(C_{O_2}^{\text{surface}} - C_{O_2}^{\text{bulk}}). \quad (9.3)$$

In (9.3), $n = 2$ is the number of exchanged electrons per molecule of O_2 generated, $F = 96485$ C/mol is Faraday's constant, $D_{O_2} = 1.67 \times 10^{-9}$ m²/s is the diffusivity of O_2 [279], and $C_{O_2}^{\text{surface}}$ and $C_{O_2}^{\text{bulk}}$ are the O_2 concentrations locally at the surface of the electrode and in the bulk, respectively. $C_{O_2}^{\text{bulk}}$ is approximately zero compared to $C_{O_2}^{\text{surface}}$ in our experiments. Applying Henry's law, we can relate this supersaturated concentration at the electrode surface to P_s and therefore [196]

$$J = J_0 e^{-\frac{16\pi\gamma^3\phi(\theta)}{3kT\left(\frac{i}{K_H 4nFD_{O_2}a} - P_0\right)^2}}, \quad (9.4)$$

where $K_H = 1.283 \times 10^{-5}$ mol/m³Pa is Henry's constant for O_2 [280]. Equation (9.4) can be rewritten as

$$\ln\left(\frac{J_0}{J}\right) = B\left(\frac{i}{K_H 4nFD_{O_2}a} - P_0\right)^{-2}, \quad (9.5)$$

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Figure 9.9: Logarithmic linear relation between nucleation rate J and the inverse of the squared supersaturated pressure difference for (a) $a = 3$ nm, (b) $a = 41$ nm, and (c) $a = 51$ nm. An outlier in (a) has been indicated by a black circle.

where $B = 16\pi\gamma^3\phi(\theta)/3kT$ and J_0 are calculated as best-fit parameters. Figure 9.9 shows experimentally measured nucleation rates vs the bracketed expression in (9.5) for three different electrodes, indeed displaying the linear behavior suggested by this equation. From the slope B , we can extract the contact angle θ , see below.

The nucleation rate is related to the activation energy E_a of a nanobubble nucleation by Arrhenius' law [274]. Therefore, we can achieve a one-to-one relation between both physical magnitudes [271]

$$E_a = \frac{16\pi\gamma^3\phi(\theta)}{3\left(\frac{i}{K_H 4nFD_{O_2}a} - P_0\right)^2} = \frac{BkT}{\left(\frac{i}{K_H 4nFD_{O_2}a} - P_0\right)^2}. \quad (9.6)$$

E_a thus decreases with increasing current; i.e., E_a decreases with increasing supersaturation $\zeta = (c_s - c_0)/c_0$, where c_s and c_0 refer to the O₂ concentration at supersaturation and under ambient conditions. These concentrations are related to pressure by Henry's law at constant temperature, thus ζ can be rewritten as the pressure difference, $\zeta = (P_s - P_0)/P_0$. Associating this definition with (9.2) and (9.4), we obtain an expression for the supersaturation level at the nucleation time for a bubble:

$$\zeta = \frac{i}{K_H P_0 4nFD_{O_2}a} - 1 \quad (9.7)$$

The different E_a for different electrodes are represented in figure 9.10(a) vs the corresponding levels of ζ achieved at different i_{app} values and tabulated in table 9.1. As expected, the increase in supersaturation causes a decrease in the activation energy for every case.

a (nm)	B (Pa ²)	$\ln(J_0 \cdot s)$	E_a/kT	ζ
3	$9.0 \pm 1.0 \times 10^{16}$	14.3 ± 1.1	$12.5 - 7.9 \pm 1.2$	835-1,050
41	$8.3 \pm 1.3 \times 10^{15}$	32.2 ± 4.2	$30.3 - 26.4 \pm 4.2$	160-175
51	$1.6 \pm 0.5 \times 10^{16}$	12.1 ± 2.1	$9.5 - 5.7 \pm 2.1$	410-525

Table 9.1: Fitting parameters B and J_0 in equation (9.5), activation energy E_a from equation (9.6), and supersaturation ζ at bubble nucleation from equation (9.7) for different electrodes. The tolerances in B , $\ln(J_0 \cdot s)$ and E_a/kT indicate the error measurement when fitting equations (9.5) and (9.6). The intervals shown in ζ represent the calculated supersaturation level at the different applied currents for each electrode.

a (nm)	i_{nb}^p (nA)	θ (°)	L (nm)	h_{nb} (nm)	n_{nb}
3	5.3	144 ± 12	11.4 ± 3.2	2.0 ± 1.2	550-900
41	12.1	156 ± 1	4.1 ± 1	0.9 ± 0.1	50-85
51	45	151 ± 2	4.8 ± 0.3	1.2 ± 0.1	100-170

Table 9.2: Geometrical dimensions of different nanobubble nuclei: apparent electrode radius, a ; peak current, i_{nb}^p ; contact angle, θ ; nucleus footprint, L ; nucleus height, h_{nb} ; and number of O₂ molecules in the nucleus, n_{nb} . The tolerances are the standard deviations which are derived from the calculation of the contact angle, θ , from the fitting parameter B .

From figure 9.10(a), there is no apparent relation between the different values of the activation energy E_a and the apparent radius of the electrode a nor is there a clear relation between a and fitting parameters B and J_0 , as indicated in table 9.1.

As mentioned above, the contact angle θ can be calculated from the slope B , namely, by the implicit equation:

$$B = \frac{16\pi\gamma^3}{3kT} \phi(\theta) = \frac{4\pi\gamma^3}{3kT} (1 + \cos(\theta))^2 (2 - \cos(\theta)). \quad (9.8)$$

For all the different electrodes, θ ranges from 135° to 155° (inset in figure 9.10(b)), similar to the case of H₂ nanobubbles [271]. The radius of curvature of the nucleus for an O₂ nanobubble has been reported to be $r_{nb} = 10$ nm [266, 267, 281], which implies a Laplace pressure of $P_{nb} = 2\gamma/r_{nb} = 14.2$ MPa. The extremely high pressure within the nanobubble justifies the surprisingly high supersaturation levels achieved locally around it at nucleation. Knowing r_{nb} and θ , the nanobubble nucleus geometry is fully determined, assuming a spherical cap shape [267, 275, 281] (figure 9.11 and table 9.2).

From the small size of the bubble nucleus footprint, L , when compared to the electrode radius, a (table 9.2), we conclude that the nanobubble nucleus

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Figure 9.10: (a) Activation energy, E_a , as a function of the supersaturation, ζ , at different electrodes. E_a decreases with increasing i , i.e., increasing ζ . (b) Sketch of a surface nanobubble nucleus under the assumption of a spherical cap shape. The contact angle, θ , is defined on the water side, where h_{nb} corresponds to the nucleus height and L determines the nucleus footprint. Inset: geometric relation $\phi(\theta) = (1 + \cos(\theta))^2(2 - \cos(\theta))/4$ needed for the calculation of the nucleus volume assuming a spherical cap shape. The framed region indicates the domain in which all of the nanobubbles studied in this article are situated.

covers a very small portion of the electrode. There is one exception to this case: $a = 3$ nm. In this particular case, the nucleus of the nanobubble is larger than the electrode. This result has several possible origins: either the nucleus is attached to some irregularities on the nanoelectrode surface, i.e., the electrode has a very nonflat surface, or the Pt disk is recessed within the glass seal [229], providing an apparent radius determined volumetrically to be much smaller than the actual electrode size, or the disjoining pressure within the nanobubble deforms its shape in a high manner such that the assumption of a spherical cap is no longer applicable. On the other hand, the total volume occupied by the number of molecules contained in the nuclei ($\sim 50 - 900$) is small compared to the presumed initial bubble volume. From the drawing to scale in figure 9.11, we can appreciate this fact: within the nanobubble nucleus volume, there is empty space which cannot be occupied by the number of molecules present. This may result in a deformed shape of the nanobubble nucleus due to the disjoining pressure [278]. From our results in tables 9.1 and 9.2, we can conclude that there is a direct relationship between the supersaturation level ζ and the number of molecules in the nucleus n_{nb} . However, there is no apparent relation between n_{nb} and i_{nb}^p nor a . This issue can be due to the electrode surface properties and especially the surface chemistry that applies to the electrode during its conditioning to achieve reproducible results.

Figure 9.11: (a) Scale drawing [282] of a nanobubble nucleus at an $a = 41 \text{ nm}$ electrode. The white circles (best seen in panel (b)) represent Pt atoms, whereas the red ones represent O atoms. The molecular structure is defined in detail in panel (c). The close-up view of the area covered by the nanobubble nucleus is depicted from the top and the side in panel (b). The nucleus (as shown) initially covers a very small portion of the electrode surface before growing and blocking the majority of the electrode. The volume occupied by the O_2 molecules contained in the nucleus is small compared to the total nucleus volume, which may suggest that the nucleus shape may be deformed by the disjoining pressure [278].

9.4 Conclusions

The nucleation of single O₂ nanobubbles at a Pt nanoelectrode has been studied in detail. The importance of surface chemistry has been exposed throughout all of this research. The necessary treatment of the Pt surface to generate a reproducible peak current i_{nb}^{p} at which nanobubbles are formed is of extreme importance if good stochastic results are to be obtained concerning the nucleation rate of nanobubbles (the corresponding analysis for a non-preconditioned electrode can be found in Appendix 9.D). In a region very close to i_{nb}^{p} , the nucleation time t_{ind} rapidly changes with a small variation on the order of tenths of a nA in the applied current i_{app} . The nucleation rate $J(i_{\text{app}})$ can be calculated from the different induction times for bubbles to nucleate when i_{app} is fixed at a certain level below i_{nb}^{p} . The Classical Nucleation Theory (9.2) provides an accurate mathematical expression for J . Because of stochasticity, the nucleation time can vary for the same i_{app} within 2 orders of magnitude. The higher the i_{app} , the higher the supersaturation ζ and consequently the higher the nucleation rate. ζ values are large in an area local to where the nanobubble nucleates, which results from the high Laplace pressure of the nanobubble nucleus due to its small radius. From the different measured J at different ζ , the activation energies E_{a} have been derived, along with the contact angle θ between the bubble and the electrode surface if the geometry of the nucleus of the nanobubble is approximated as a spherical cap. We can estimate the number of O₂ molecules contained in the critical bubble nucleus, which is higher for higher ζ ; i.e., the more molecules are locally produced, the more molecules will form the nanobubble nucleus. Though disjoining pressure may affect the nanobubble final shape [278], for the scope of this research the assumption of a spherical cap is more than justified since the disjoining pressure barely causes the bubble shape to deviate from a spherical cap.

9.A Fabrication of nanoelectrodes

Nanoelectrodes were fabricated using a previously reported procedure [283], shown schematically in figure 9.12. Briefly, a Pt wire (Alfa Aesar) of 25 μm diameter was glued to a W rod (A-M Systems) using silver epoxy (Alfa Aesar). The wire was then inserted in a borosilicate glass capillary (Prism Glass Capillaries) of 0.5 mm inner diameter and 1.0 mm outer diameter, which serves to insulate the electrode. The Pt wire was then etched with sodium cyanide (6 M) to obtain a sharpened tip. The Pt wire and the W rod were afterwards sealed inside the glass capillary by heating with a hydrogen torch. Finally, a polishing process exposes the tip of the Pt nanowire, producing a Pt inlaid

Figure 9.12: Fabrication of nanoelectrodes: (a) the Pt wire glued to a W rod is inserted into a glass capillary, (b) the Pt is etched by cyanide, achieving a pointed tip of nanometer size, (c) the Pt is sealed in the glass capillary by heating with a hydrogen torch, and (d) the seal is polished until exposure of the Pt tip.

Figure 9.13: Voltammograms of ferrocene oxidation to ferrocenium used to measure the size of the nanoelectrodes. Note that the current scale is different on each plot. The solution contains 5 mM Fc and 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile.

disk in the insulating glass plane.

The apparent size of the electrode was determined by measuring the limiting current for ferrocene oxidation to ferrocenium [196, 254, 265, 266]. This method is reliable for nanodisk electrodes [283]. The diffusion limited current i_{lim} to a disk electrode is:

$$i_{\text{lim}} = 4nFD_{\text{Fc}}C_{\text{Fc}}a, \quad (9.9)$$

where $n = 1$ is the number of electrons exchanged, $F = 96485 \text{ C/mol}$ is Faraday's constant, $D_{\text{Fc}} = 2.4 \times 10^{-9} \text{ m}^2/\text{s}$ is the ferrocene diffusivity [284], $C_{\text{Fc}} = 5 \text{ mM}$ is the ferrocene bulk concentration and a is the apparent radius of the nanoelectrode. Voltammograms used to determine the size of the three nanoelectrodes used in the main text are presented in figure 9.13.

Figure 9.14 shows the voltammograms before and after 50 nucleation cycles on conditioned and non-conditioned electrodes. On conditioned electrodes, Figure 9.14(a), the voltammograms did not apparently differ, i.e. the apparent

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Figure 9.14: Voltammograms of ferrocene oxidation to ferrocenium used to measure the size of the nanoelectrodes before (blue) and after (red) 50 nucleation cycles. The solution contains 5 mM Fc and 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. (a) On conditioned electrodes, the voltammograms remain the same, indicating that the apparent electrode radius a remains quasi-constant throughout the experiments. (b) On non-conditioned electrodes, a increases significantly and consequently, experiments performed with these electrodes result in non-reproducible peak current values i_{nb}^p and nucleation times t_{ind} .

radius a remained constant throughout the nucleation cycles. That was not the case for the electrodes in which a conditioning cycle was not performed prior to the nucleation cycles, figure 9.14(b). In those situations, the electrode apparent radius could increase up to $\sim 5a$. This fact adds up to the surface chemistry affecting the reproducibility of peak current values i_{nb}^p , since i_{nb}^p and a are directly proportional to each other [266, 267, 270].

9.B Nanoelectrode conditioning

Best reproducibility of i_{nb}^p was observed when great care was exercised to control the potential waveform prior to applying a current, i_{app} . This requirement is related to the formation and stripping of the surface oxide on Pt at potentials where H_2O_2 is oxidized [268, 285]. As we discussed in the main text, at least 40 nanobubble nucleation repetitions need to be performed in order to achieve a reproducible peak current i_{nb}^p . To obtain reproducible results with lower standard deviation within fewer repetition, we designed a new potential waveform, in which we can control certain parameters, defined in the main text as t_{dis} , t_{stab} , E_{stab} and t_{rest} in figure 9.5(a). Figures 9.15(a)-(e) show the current response after 100 repetitions for different conditioning cycles corresponding to various combinations of those parameters. Figure 9.15(f) represents the

evolution of i_{nb}^{P} with the number of nucleated bubbles for the different conditioning waveforms. We conclude that the best reproducibility is obtained with $t_{\text{dis}} = 1$ s, $t_{\text{stab}} = 2$ s, $E_{\text{stab}} = 0.89$ V, and $t_{\text{rest}} = 1$ s, corresponding to figure 9.15(d), green diamond curve in figure 9.15(f).

9.C Nucleation rate measurements for additional values of i_{app} and electrodes

A nanobubble nucleates almost immediately when i_{nb}^{P} is reached. However, nanobubbles take a longer time to nucleate, grow, and block the electrode when a current i_{app} , whose value is very close to but lower than i_{nb}^{P} , is applied. The lower the i_{app} compared to i_{nb}^{P} , the longer it takes for nanobubbles to nucleate [271]. In the main text, several results of nucleation induction times for a 41 nm radius electrode are shown, figure 9.7. Figure 9.16 shows the corresponding results of nucleation induction times for other current levels not shown in the main text. Figure 9.16(a) indicates the interval from which the nucleation time t_{ind} is measured. The interval begins at the moment in which the current is applied and ends at the moment in which the nanobubble nucleates (indicated by a large increase in the voltage as the bubble blocks the surface of the nanoelectrode).

Figures 9.17 and 9.18 show voltage-time responses for bubble nucleation for two different nanoelectrodes with corresponding apparent radii $a = 3$ and 51 nm, respectively. In figures 9.19 and 9.20, we show the corresponding plots for t_{ind} as a function of i_{app} and the probability distribution P for these electrodes.

9.D Bubble nucleation measurements without electrode surface conditioning

If the electrode surface is not conditioned before performing the nucleation rate experiments, large variability of i_{nb}^{P} is observed (as shown in figure 9.4(d) in the main text). In this case it is impossible to assure that we are measuring a stochastic nucleation time corresponding to i_{app} , since the nucleation time depends very sensitively on the proximity of the applied current i_{app} to i_{nb}^{P} . Voltage-time curves for bubble nucleation at a non-conditioned, $a = 6$ nm radius electrode are presented in figure 9.21. In this example, the mean value of the measured nucleation times decreases systematically with increasing i_{nb}^{P} . However, the individual values are highly scattered with a very large mean deviation, thus indicating that these data do not correspond to a stochastic process.

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Figure 9.15: (a)-(e) Different electrode conditioning cycles. In blue, the controlled voltage is shown, whereas the red curve corresponds to the current response after 100 repetitions. The difference between panel (a) and (b) resides in the different nanobubble nucleation cycle: for the first case, the slope corresponds to $\Delta E = 0.5$ V in $t = 1$ s, whereas for the second case, and all other conditioning cycles, $\Delta E = 0.8$ V in $t = 1.6$ s. In panel (e), we used a ramp model to reach E_{stab} to avoid the sudden increase of current. The optimal empirical configuration corresponds to conditioning cycle (d). (f) Corresponding peak current i_{nb}^p for different conditioning procedures vs. the repetition number during conditioning.

Figure 9.16: (a) Voltage-time plot during the nucleation of a nanobubble indicating how the nucleation time t_{ind} is measured. The current is stepped from 0 nA to i_{app} nA at 0 ms and returned to 0 nA after the electrode surface is blocked (b-f) Voltage-time plots used for measuring t_{ind} for a $a = 41$ nm electrode at different i_{app} (labelled). Note that different responses are plotted with different time scales. This figure is complementary to figure 9.7. The numbers indicate the sequence of the t_{ind} measured.

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Figure 9.17: Voltage-time plots used to measure t_{ind} for multiple nucleation rate experiments performed at different i_{app} (labelled), corresponding to (a) $0.8i_{nb}^P$, (b) $0.85i_{nb}^P$, (c) $0.95i_{nb}^P$ and (d) i_{nb}^P . The electrode has an apparent radius of 3 nm. The numbers indicate the sequence of the t_{ind} measured. Note that different timescales are shown for the different applied currents.

Figure 9.18: Voltage-time plots used to measure t_{ind} for multiple nucleation rate experiments performed at different i_{app} (labelled), corresponding to (a) $0.75i_{\text{nb}}^{\text{P}}$, (b) $0.85i_{\text{nb}}^{\text{P}}$, (c) $0.95i_{\text{nb}}^{\text{P}}$ and (d) i_{nb}^{P} . The electrode has an apparent radius of 51 nm. The numbers indicate the sequence of the t_{ind} measured. Note that different timescales are shown for the different applied currents.

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Figure 9.19: (a) Experimentally measured t_{ind} for different i_{app} at an electrode with apparent radius $a = 3$ nm. (b) Cumulative probability distribution P for nanobubble nucleation derived from the values of t_{ind} reported in panel (a) for different i_{app} . The theoretical curves correspond to the best fit using equation (1) in the main text. t_{lim} is the shortest accessible experimental time.

Figure 9.20: (a) Experimentally measured t_{ind} for different i_{app} at an electrode with apparent radius $a = 51$ nm. (b) Cumulative probability distribution P for nanobubble nucleation derived from the values of t_{ind} reported in panel (a) for different i_{app} . The theoretical curves correspond to the best fit using equation (1) in the main text. t_{lim} is the shortest accessible experimental time.

Figure 9.21: (a-c) Measurements of nanobubble nucleation time for increasing i_{app} on a non-conditioned, $a = 6$ radius nm electrode. (d) Scattered plot of nucleation times t_{ind} for different i_{app} . The scatter is so high that no proper probability analysis can be done. This is due to a changing i_{nb}^p from cycle to cycle, since the electrode surface has not been previously conditioned. The numbers on the arrows in (a)-(c) indicate the sequence of the t_{ind} measured.

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Conclusions

Throughout this thesis, we have deeply researched the fundamentals of bubble nucleation, growth and detachment in many different configurations. In the first six chapters [Chs.1-6], we have gained the ample insight of bubble evolution in a very well-controlled set-up in which the supersaturation level can be precisely adjusted. That way, the analysis of the bubble dynamics is greatly facilitated, since many spurious effects, such as impact vibrations, partial pressure of other residual gases or intricacies related to chemical reactions, can be avoided. The analysis presented in Chs.1-4 and Ch.6 exhibits the remarkable importance of the concentration boundary layer developing and evolving as bubbles grow.

Starting from a stable bubble of a certain radius in a homogeneous medium, a shrinkage phase generates an enriched gas concentration area very local to the bubble front, and hence, a rapid change to a growth phase causes an enhanced mass transfer towards the bubble. This is known as the history effect and has been thoroughly discussed in Ch.1. As bubbles absorb the gas from their surroundings, the gas concentration locally decreases and so does, consequently, the density of the solution. Therefore, a buoyant region around the bubble develops and grows in time, which causes density-driven (natural) convection to set in from the middle stages of the bubble growth [Ch.3]. If we let bubbles grow in succession from a single location in a uniformly supersaturated medium [Ch.2, Ch.4], gas depletion originates from the fact that bubbles absorb and transport the gas away with them at detachment. Diffusion through the bulk alone cannot compensate for this extracted gas,

and hence, subsequent bubbles grow in a medium which has less dissolved gas available. In accordance, the growth rate is significantly affected. These events appear as a result of rapid but significant transitions, such as fast changes from a growth to a dissolution phase in the case of the history effect. For the depletion effect, subsequent bubbles nucleate and grow in a matter of seconds after the previous bubble has detached. If the waited time during these transitions would be long enough, all those phenomena would vanish since the concentration boundary layer around the bubble would be able to return to an equilibrium or, at least, a steady state due to the diffusion of gas towards or from the bulk.

The analysis of the coalescence of two nearby growing bubbles in Ch.5 provides insight in

- the growth of two neighbouring bubbles in a diffusive regime (which need to compete for the available gas), and
- the necking and wave mechanics distorting the bubble shape when the two bubbles merge into a single entity.

As a by-product, we also showed that the ultimate detachment radius can be modified by forcing the bubbles to coalesce, information which may prove extremely useful for many applications in which one wants to free surfaces from the presence of bubbles. This knowledge becomes even more relevant if we combine it with the results in Ch.6, which provides a useful configuration in which an ultrasound transducer successfully removes bubbles from surfaces by applying different wave frequencies, pressure amplitudes and number of cycles. By means of applying ultrasound waves, we can enhance the mass transfer towards the bubble, which grows considerably in the order of milliseconds. This enhancement originates from the bubble response and agitation when its resonant frequency matches the ultrasound frequency. By calculating the different resonant curves, we can program decreasing frequency chirps which allow for longer mass transfer enhancement.

Following the layout presented in the introduction [Ch.0], we subsequently move towards more applied science, which relates to bubbles growing in chemical reactions. In Chs.7 and Ch.8, we provide a geometry to which bubbles preferentially attach and focus on the nucleation, growth and detachment of single bubbles growing on pillars in an electrolytic reaction. That way, it becomes feasible to compare results with what was obtained in the previous chapters [Chs.1-6]. This analogy facilitates the understanding of the evolution of the concentration boundary layer around the bubbles within a medium in which gas is constantly generated. Three different domains have been identified: stagnation, compensation and saturation, corresponding to a decrease in

the bubble growth rate caused by an initial depletion, a counteracting increase due to the accumulation of produced gas and an equilibration of the growth rate to quasi-constant values as the production rate and the speed at which bubbles absorb gas become of the same order. We observed clear differences from the previous experiments in which the supersaturation level is caused by a well-controlled pressure decrease and the available gas in dissolution is fixed, such that the background concentration level is uniform. We also find that the geometry of the pillars to which the bubbles attach has a profound influence on the final bubble detachment radius. The two cases, i.e. bubbles generated by pressure-drop and by electrolysis, have similar detachment mechanics through a necking process, and therefore, we conclude that detachment is determined by the way in which bubbles pin to the structures and not by the process through which they grow.

Finally, the last chapter [Ch.9] deals with even more realistic applications: the generation of bubbles on electrodes during chemical reactions and the effects they cause. Those bubbles are detrimental to the reactions since they block the reacting surfaces, a situation which nowadays causes a huge reduction of the efficiency of electrolytic and catalytic applications. As a result, overpotentials which may damage the electrodes and partial inhibition of the chemical reaction are a few of the undesired consequences which may occur. However, for the scope of our study, it is essential that these bubbles block the electrodes because that fact provides a means of measuring the nucleation rate and the time bubbles take to grow and block the reacting site. We conclude that bubbles nucleate and grow almost instantaneously when a certain peak current is applied. By applying lower values, in the order of a few nA below that peak current, nanobubbles take exponentially-increasing more time to nucleate and block the reacting surface.

The fundamental insight gained throughout this series of experiments opens a window to further research which may facilitate the fabrication of tools to improve chemical reaction efficiencies. The fabrication of reacting surfaces with micropillars may drive the nucleation of bubbles to specific spots, releasing the reacting surfaces from bubbles and therefore, increasing the reaction rate since the impediment caused by the bubble block would no longer exist. The distribution of pillars may be the appropriate design parameter: the distance in between them should compromise growth detriment by the presence of neighbouring bubbles and the achievement of coalescence at earlier times (Chs.2-5 are of relevance to this end, together with Chs.7 and 8). The application of ultrasound at larger scales may excite the resonant frequencies of bubbles and therefore, enhance bubble detachment from the different surfaces or increase bubble growth rates by rectified diffusion, so that the correspond-

ing detachment radius is reached faster. For the later case, the gas removal from the solution is also increased. For this application, Ch.6 is essential to understand the bubble response to ultrasound pressure waves. Future research should focus on the configuration of an optimal frequency chirp which may excite the bubble resonant radius from the very beginning of its nucleation up to detachment. Following that path, we would be in the position to force a much earlier bubble detachment from any surface. The question whether it is energetically and economically favourable to use ultrasound to release bubbles from surfaces remains however open to discussion. Ultimately, by applying current levels below certain values, we can prevent or delay the generation of (nano)bubbles which inhibit the chemical reaction at some point. Of course, real life applications make use of much higher voltages and current levels than the ones applied along this thesis. The problem is much more serious in those cases, where we encounter the presence of nanobubbles, microbubbles and mm-sized bubbles, or even larger. The mechanics are rather different and much more complex in those scenarios. However, the first milestone to achieve better chemically-efficient applications is set with this work. The future is still open and challenging.

As a concluding quote, I would love to cite the Greek philosopher Socrates: *'the only thing I know is that I know nothing'*. The scientific community should always bear in mind these words as a motivation to continue doing science even though sometimes the path seems unclear and scary. Anyway, as well written by George R. R. Martin in his famous novel Game of Thrones, *'the man who fears losing has already lost'*.

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Summary

Bubbles are present in a very wide and extensive variety of processes. The motivation for this work originates from the fact that in chemical reactions, such as electrolysis or catalysis, bubbles attach to the reacting surfaces or electrodes, inhibiting or impeding the reaction to continue. The analysis of the bubble nucleation, growth and detachment is consequently essential for future applications that may want to avoid the formation of bubbles or, at least, transport the bubbles away by different means. We provide in this thesis different studies of the fundamentals of bubble behaviour in different configurations. These different case scenarios deepen the knowledge about the different phases during the bubble evolution, such as the way they nucleate and attach to specific locations, the way they deplete their surroundings as they grow and extract the gas from the bulk, the different stages they undergo when coalescence occurs, and the response they have when ultrasound are applied. The first six chapters of this thesis concern the just mentioned behaviour in a domain in which the supersaturation level of a solution of liquid (water) and gas (CO_2) can be precisely controlled by pressure drop. We perform experiments regarding the so-called history effect, the depletion caused by bubbles growing in a succession, the transition to convection during their diffusive growth, the extensive depletion caused by confinement, the coalescence of two neighbouring bubbles, and the rectified diffusion and bubble removal from surfaces by means of ultrasound.

The acquired knowledge through these experiments allow us to compare this now well-understood behaviour to the less known evolution on electrodes.

Consequently, two full chapters of this thesis reflect the direct comparison between the bubbles generated by pressure decrease and the electrolytically-generated bubbles. We find that for the two cases the geometry of the substrates is extremely influential on the final bubble radius before detachment. The evolution of the concentration boundary layer is however remarkably different in electrolysis, since bubbles in chemical reactions are generated in a medium which is continuously producing new gas. The fabrication of microstructured substrates with the presence of micropillars allow us to gain some control on the location in which bubbles nucleate and grow, releasing the reacting surface from their detrimental block. The fact that bubbles block the reacting surfaces is curiously useful if the nucleation rate of such bubbles needs to be calculated. The time that bubbles take to nucleate and grow until blocking the electrodes can be then measured with precision and provides very useful quantitative data which can be used in many future applications.

This book opens many doors to continue widening the knowledge of bubble nucleation on electrodes with the perspective of achieving in the near future different ways to transport gas away from electrolytic/catalytic surfaces and, as a result, improve the efficiency of chemical reactions.

Samenvatting

Luchtbellen zijn aanwezig in een zeer brede en uitgebreide verscheidenheid van processen. De motivatie voor dit werk komt voort uit het feit dat in chemische reacties, zoals elektrolyse of katalyse, bellen zich hechten aan reagerende oppervlakken of elektroden, waar zij de reactie remmen of belemmeren. De analyse van de belnucleatie, -groei en -loslating is daarom essentieel voor toekomstige toepassingen die de vorming van bellen willen voorkomen of, in ieder geval, de bellen weg te voeren door verschillende methoden. Wij bieden in dit proefschrift verschillende onderzoeken van de fundamenteën van het gedrag van bellen in verschillende situaties. Deze verschillende situaties verdiepen de kennis over de verschillende fasen tijdens de belontwikkeling, zoals de manier waarop ze nucleëren en zich hechten aan specifieke locaties, de manier waarop ze hun omgeving uitputten als ze groeien en het gas uit de bulk halen, de verschillende stadia die zij ondergaan wanneer coalescentie voor komt, en de reactie die zij hebben wanneer ultrasoon geluid wordt toegepast. De eerste zes hoofdstukken van dit proefschrift hebben betrekking op het bovengenoemde gedrag in een domein waarin het oververzadigingsniveau van een oplossing van gas (CO_2) in een vloeistof (water) nauwkeurig kan worden gecontroleerd door drukdaling. Wij voeren experimenten uit met betrekking tot het zogenaamde geschiedenis-effect, de uitputting veroorzaakt door achtereenvolgend groeiende bellen, de overgang naar convectie tijdens hun diffuse groei, de uitgebreide uitputting veroorzaakt door opsluiting, de coalescentie van twee naburige bellen, en de geredificeerde diffusie en de verwijdering van bellen van oppervlakken door middel van ultrasoon.

De verworven kennis uit deze experimenten stellen ons in staat om dit nu goed begrepen gedrag te vergelijken met het minder bekende gedrag van bellen op elektroden. Vervolgens behandelen twee volledige hoofdstukken van dit proefschrift de directe vergelijking tussen de bellen in de eerder genoemde samenstellingen en de elektrolytisch geproduceerde bellen. De geometrie van de substraten heeft voor de twee configuraties een zeer grote invloed op de straal van de zeepbel voor onthechting. De ontwikkeling van de grenslaag van de concentratie rond de bellen is echter opmerkelijk anders in electrolyse, aangezien de bellen in chemische reacties in een middel worden geproduceerd dat onophoudelijk nieuw gas produceert. De fabricage van micro-structuur substraten met micro-pilaren stelt ons in staat om enige controle te krijgen over de locatie waar bellen nucleëren, groeien en loslaten van het reagerende oppervlak, wat hun schadelijke blokkade opheft. Het feit dat bellen de reagerende oppervlakken blokkeren is opmerkelijk handig als de nucleatiesnelheid van dergelijke bellen berekend en gemeten moet worden. De tijd die de bellen nodig hebben om te nucleëren en te groeien totdat zij de elektroden blokkeren kan met precisie worden gemeten en verstrekt zeer nuttige kwantitatieve gegevens die in vele toekomstige toepassingen kunnen worden gebruikt.

Dit proefschrift laat veel deuren open tot verbreding van de kennis van bel-nucleatie op elektroden met het oog op het bereiken van verschillende manieren om gas uit de buurt van elektrolytische/katalytische oppervlakken te vervoeren en, als gevolg daarvan, het verbeteren van de efficiëntie van chemische reacties in de toekomst.

Resumen

Existen muchos y muy variados tipos de procesos que se ven influenciados por la presencia de burbujas. La motivación para emprender este trabajo de investigación se origina por el hecho de que durante reacciones químicas, tales como electrólisis o catálisis, aparecen burbujas que se adhieren a las superficies reactantes o a los electrodos, dificultando o impidiendo que la reacción continúe. El análisis sobre la nucleación, crecimiento y desprendimiento de burbujas se vuelve comprensiblemente esencial para futuras tecnologías que requieran evitar la formación de burbujas, o al menos, el bloqueo que pueden llegar a producir. En esta tesis intentamos acercarnos a ese posible futuro mediante diversas investigaciones en diferentes configuraciones que ahondan en las distintas fases del comportamiento de las burbujas, tales como la manera en la que nuclean y se adhieren a lugares específicos, la forma en la que agotan el gas a su alrededor en fluidos que contienen gas disuelto, las diferentes fases dentro de un proceso de coalescencia, y, por citar algún ejemplo más, su reacción a los ultrasonidos. Los primeros seis capítulos de esta tesis se focalizan en el recién mencionado comportamiento en un medio tal que la supersaturación se consigue mediante una bajada de presión de manera controlada y precisa en una solución de agua y CO_2 . Realizamos experimentos que tratan sobre el nombrado efecto de historia, el agotamiento producido por burbujas que crecen sucesivamente, la transición a convección durante su crecimiento difusivo, el intensificado agotamiento producido dentro de un confinamiento, la coalescencia de dos burbujas cercanas, y la difusión rectificada y la eliminación de burbujas de una superficie como respuesta a la aplicación de ultrasonidos.

El conocimiento adquirido mediante estos experimentos nos permite avanzar un poco más hacia análisis más profundos dentro de las reacciones químicas, ya que podemos comparar los resultados conocidos con los menos conocidos en el caso de electrólisis. Descubrimos que, para las dos situaciones, la geometría de los sustratos en los que las burbujas crecen y se desarrollan es de extrema importancia en el tamaño final de la burbuja antes de desprenderse de los mismos. No obstante, la evolución de la capa límite de concentración en los alrededores de las burbujas se comporta de manera muy diferente en el caso de electrólisis, ya que las reacciones químicas mantienen la producción de gas de manera constante. Mediante la fabricación de microestructuras en sustratos, tales como micropilares, podemos ganar cierto control sobre la localización en la que las burbujas nuclean y crecen, liberando así las superficies reactantes de su perjudicial bloqueo. El hecho de que las burbujas bloqueen estas superficies es curiosamente útil si se quiere investigar y medir el ritmo de nucleación de dichas burbujas. El tiempo que éstas tardan en nuclear y crecer hasta bloquear los electrodos se puede medir entonces con precisión y provee información cuantitativa que puede utilizarse para el diseño de futuras aplicaciones.

Este libro deja la puerta abierta para continuar expandiendo los horizontes alrededor de la generación de burbujas en electrodos con el propósito de, en un futuro no muy lejano, conseguir mejorar la eficiencia de las reacciones químicas.

IV

List of publications

IV

- The history effect on bubble growth and dissolution. Part 2. Experiments and simulations of a spherical bubble attached to a horizontal flat plate, P. Peñas-López, Á. Moreno Soto, M. A. Parrales, D. van der Meer, D. Lohse and J. Rodríguez-Rodríguez, *J. Fluid Mech.* **820**, 479-510 (2017)
- Electrolysis-driven and pressure-controlled diffusive growth of successive bubbles on microstructured surfaces, P. van der Linde, Á. Moreno Soto, P. Peñas-López, J. Rodríguez-Rodríguez, D. Lohse, H. Gardeniers, D. van der Meer and D. Fernández Rivas, *Langmuir* **33**, 45, 12873-12886 (2017)
- Gas depletion through single gas bubble diffusive growth and its effect on subsequent bubbles, Á. Moreno Soto, A. Prosperetti, D. Lohse and D. van der Meer, *J. Fluid Mech.* **831**, 474-490 (2017)
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- The nucleation rate of single O₂ nanobubble on Pt nanoelectrodes, Á. Moreno Soto, S. R. German, H. Ren, D. van der Meer, D. Lohse, M. A. Edwards and H. S. White, *Langmuir* **34**, 25, 7309-7318 (2018)

- Gas evolution on microstructured silicon substrates, P. van der Linde, P. Peñas-López, Á. Moreno Soto, D. van der Meer, D. Lohse, H. Gardeniers and D. Fernández Rivas, *Energy Environ. Sci.* **11**, 12, 3452-3462 (2018)

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David, *Javi*, you are like supervisors to me, we had very long conversations about physics and science in general. As a result, there is barely an article in this thesis which does not have one of your names as a co-author. It is great to do science with you. In the personal aspect, specially with Javi, it is great visiting places with you, always a beer in hand. Always remember: venía yo de nazareno con mi padre después de salir en el Gran Poder cuando...

Henry, thank you very much for welcoming me in Salt Lake City. It was a great experience collaborating with a chemistry department, in which things are done so differently than in physics. Utah really surprised me and I have great memories about the time I spent there. *Sean*, *Hang*, *Martin*, *Shane* and *Julio*, thanks for making my stay in the Mormon country a wonderful experience

Joanita, I always said that without you, the full group will disappear within one week. You are the most effective person that I have met and you tackled

every single issue from the very first second. No paperwork was left behind with you. Thank you very much for that.

Gert-Wim, we have spent a lot of time designing updates for our set-up. Your friendliness characterises you. You have made so many reparations of the set-up that I even feel bad that you are not a co-author in any of my publications. You have my full respect and my most sincere gratitude. I want to thank *Martin* also for helping in fabricating the pieces to the puzzle. *Bas*, I still apologise for annoying and spamming you so much with ordering material. Let's not order any more from Canada, right? They take tooooooooo long. I hope you miss me coming to double-check if we received any packages. *Stefan*, without you, half of my papers will not have seen the light because I would not have been able to perform my experiments. No black silicon, no bubbles. Half of the thesis is yours.

My officemates... I really miss my first colleague when I arrived to the office, *Minori*. Even though you went back to Japan, your spirit was still here when I played anime songs, the ones you love, remember? *Liz*, we zijn vanaf het begin samen. Ook was ik bij je huwelijk aanwezig en ik heb probeerd mijn Nederlands met jou te oefenen. We hebben niet veel in het Nederlands gesproken, maar ik heb wel van jou geleerd. Dank je wel. En dank je wel voor het genieten van mijn muziek, ik weet dat je er van houdt. *Maxime*, why did you have to leave before my defence? You know what? The best thing that I will remember from you is your famous sentence: 'putain, I hate french people!' And your bow tie, nobody wears it better than you do. A late incorporation to the office, *Michiel*, thank you very much for standing my music. But I know you love it, especially when I play Disney songs. And Schlager...

I want to apologise and thank the patience of the people in the neighbouring offices, *Guillaume*, *Tim*, *Misha*, *Myrthe*, *Peter* and *Carola*. You could hear my conversations all the time, I know. If I could hear you from time to time, I guess you could hear me all the time. Misha and Carola, I could also hear you laughing, great time, it made me laugh as well (even though I didn't know what you were talking about). Hola, Peter. ¿cómo estás? Carola, please, tell your hair never to go straight again, curls rule! Misha, you Russian beast. Myrthe, we need to sing again. And bake a cheesecake, this time for us. Guillaume, five minutes in-between your meetings is not enough, take a rest, man! My thesis is in the end 0.73 Guillaume number, I guess it is pretty ok.

I cannot forget to congratulate the people of our football team, *PoF-United*: *Ivan*, *Ruben*, *Pieter*, *Yaxing*, *Alex*, *Vamsi*, *Jelle*, *Utkarsh*, *Steven*, *Srinath*, *Mathijs*, *Walter*... and many others who left the group. When I joined, we used to lose every single match (Ivan remembers that). Then we became champions and now... well, we don't lose too often. Alex, I will keep trying

to score goals from outside the area, don't worry. Shoot to the goal!

What about those lunches with very atypical conversations? From the Japanese toilets to politics and topics that I would rather not mention here. *Rodrigo, Mazi*, both *Dennis, Ricardo, Biljana, Jessica, Martin, Dominik, Anja, Chong*, and many others, you made lunch something special. Rodrigo, we should invite people more often to our holidays, always through the pof-all email. Jessica, we never watched Sakura together, too bad! Anja, I can always teach some more Oktoberfest songs if you like. Mazi, you need to show me around Iran. Sports were also extremely important in our group, and I will remember participating in the Batavierenrace and the Warrior Race with *Sander, Pim, Pallav, Maaïke* and many others. Ricardo, your final sprint in the Bata left me astonished. Reminder in case Dennis didn't tell you: you should join CrossFit. And learn Python.

In general, thanks to all of my colleagues who contributed in a way or another to create a very friendly group environment. That is essential and extremely important to achieve good results. Sorry if I forgot to mention your name. You can come to me and I will acknowledge you in person. Or punch me in the face, as you prefer... please, don't punch me in the face...

Special mention to the people who collaborated in this thesis. *Piedad*, mi MariPi, gracias por tu biografía, has reflejado exactamente lo que quería para acabar mi libro. Te conozco desde los 13 años, y a pesar de las discusiones y nuestras idas de pinza, siempre hemos sido grandes amigos. Y siempre lo seremos. Me encantan nuestros debates políticos y nuestros cotilleos de viejas. *Pilar*, muchísimas gracias por el diseño de la portada de la tesis, has hecho un grandioso trabajo.

I cannot close this section without mentioning other special people in my life. *Antonio y Ángel*, habéis venido muchas veces a verme y hemos estado en muchísimos viajes juntos. Espero seguir contando con vosotros para futuros viajes y para nuestras conversaciones épicas y nuestras fiestas. Antonio, espero que hayas dejado de llorar ya... ¿te acuerdas de lo que hiciste hace 15 segundos? Ángel, tú y yo siempre podemos llegar a ese sitio andando. Siempre estás cuando vuelvo a casa, y siempre agradezco estar contigo. Y recuerda, para bailar, bajando, bajando... y menos mal que no grabaste una caída épica asegurada. *Ignacio, Javi, Gonzalo, Alejandro, Laura, Cristian, Ici*, nunca falláis cuando regreso a Sevilla. Siempre os echo en falta. Mi familia de Múnich, *Raúl, Cristina, Natalia, Pedro y Ana*, aunque algunos ya os habéis marchado, marcasteis mi vida en Múnich y os considero mi familia, sobre todo cuando vuelvo a mi segunda casa en Alemania. Siempre hemos intentado reencontrarnos, y espero que siempre siga así. Y por último, mi más reciente familia, mi familia enschediana, *Dani, Kiko, Elena, Javi, Blanca, Anna, Aleix, Iris*,

Zaida, Miguel, Matteo, Rainer, Pilar, Andrés, Pablo, Federica, Guido y gente que he conocido durante mi etapa aquí como *Patri, Marta, Irene, Valentina* (¡hola, bebé!), *Luuk* y *Bea*, de los que me llevo maravillosos recuerdos. Mención adicional para Dani y Kiko, porque son especiales, mis compañeros de kebabs y locuras hasta las tantas de la mañana, de viajes express a Murcia y de vacaciones unidos. Qué romántico todo. ¡Cómo os ha cambiado la vida el conocerme! Y Elena, que fue la primera persona que me conoció mientras le gritaba a una televisión apoyando a España en el bar belga. Sus m@z?!#%. ¡Que soy yo!

A todos vosotros, all of you, muchísimas gracias, thank you very much, vielen dank and dank je wel!

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Sobre el autor / About the author

Álvaro Moreno Soto eligió la primavera para nacer en Sevilla un 15 de mayo de 1990. Tenía que ser en primavera, cuando el atardecer abraza la ciudad con un cielo dorado y rosado que hace despertar a la dama de noche por los callejones. Creció en una familia que siempre le apoyó y fue coleccionando buenos amigos allá donde llegaba mientras pasaban los años, las primeras ilusiones, las aventuras de los viernes por la tarde en la que llegar al corazón de la ciudad podía ser toda una odisea cargada de anécdotas. Así se agolpaban los recuerdos hasta que se despojó del

pantalón gris y el chaleco burdeos en busca de la mayor de las aventuras: convertirse en lo que de verdad soñaba ser.

En el 2008 empezó a estudiar **Ingeniería Aeronáutica** en la **Universidad de Sevilla**. La ilusión de alcanzar una meta que empezaba a dibujarse en el ideario y que ahora, vemos materializada.

Dejar la tierra que uno ama nunca fue fácil, y más si la llevas tatuada en

la piel. Pero se hizo la promesa de volver en la primera luna llena de cada primavera, justo cuando la ciudad se viste de raso, púrpura y esparto, el azahar se mezcla con el incienso en el aire y ríos de cera riegan las calles por las que transitan nuevas y antiguas pasiones. Y con esa promesa aterrizó en Múnich, ciudad que lo acogió durante dos años y medio mientras acabó su titulación y el máster en la **Technische Universität München**.

En estos dos años y medio culminó sus estudios y empezó a dar pasos en su trayectoria profesional. No sin que eso le impidiese saciar su curiosidad ávida de más conocimiento. Múnich no sólo le abrió puertas profesionales. Esta experiencia le transformó, abrió sus miras, entabló lazos con personas de distintas culturas y siguió llevándose amigos en el corazón que le enseñaron que todos somos hermanos del mundo. El sabor a cerveza en el paladar y los paseos por Olympiapark, incluso cuando el frío calaba los huesos y la nieve llegaba a los tobillos, son la estampa de esos dos años que supusieron un paso muy importante en su vida a todos los niveles.

Aterrizaría tras esta vivencia en la **Universiteit Twente** y en el pintoresco Enschede, que lo acogió durante cuatro años que culminan en este libro, sintiéndose enseguida acogido y querido, aumentando su cartera de buenos amigos a los que acostumbraría a la música en el laboratorio, desde Michael Jackson a las sevillanas añoradas de su tierra en Abril, las revueltas de pasillo o los juegos y la camaradería con el grupo de trabajo. Decidió paralelamente y por puro placer, ya que le atrapaban sobremanera todas las publicaciones referentes a la historia – tan necesaria para entender nuestro presente – comenzar a estudiar **Historia** en la **UNED**.

Sería en este rincón holandés donde empezó este exhaustivo trabajo, *Bubbles on surfaces*. Un hito en su carrera que siempre estuvo enfocada a la aeronáutica espacial pero que le ha permitido enriquecerse en los terrenos de la física, no sólo en su perfil investigador, también en la docencia.

Alcanzar el doctorado es una carrera de fondo, que dicho sea de paso, ha cumplido en el sentido más literal corriendo en la carrera tradicional con sus compañeros de trabajo, ya que es un amante del deporte. Esta carrera hasta alcanzar el objetivo tiene paradas en el camino que enriquecen aún más el trayecto antes de llegar a la meta. Una de estas paradas fue Salt Lake City, en Estados Unidos, ciudad que habitó durante los seis meses que duró su acuerdo de colaboración entre la **Universiteit Twente** y la **University of Utah**.

Las imágenes y los recuerdos se funden con esos colores rojizos y verdes, casi imposibles, que ofrece el lago salado atravesado por una arteria de alquitrán por la que los coches circulan. Sus avances científicos fueron recogiendo en un blog que narraría sus experiencias en América, estancia que calmaría sus ansias viajeras, ya que es un aventurero irremediable que ama recorrer el

mundo. No hay desierto que no se disponga a cruzar durante seis horas en carretera, así como no hay objetivo que no esté dispuesto a cumplir. Y esos seis meses le traerían no sólo avances profesionales, también el bullicio, las luces de neón, la intimidación de la barra de los bares, y más vivencias enriquecedoras.

Ahora culmina su etapa con esta tesis que tienen en sus manos, que no deja de ser el principio para una nueva aventura a la que se dispone a embarcarse con miras a la investigación y con el bagaje adquirido de estos años. No es un final, más bien es un nuevo comienzo en una carrera que despunta. Que me perdone Bowie, pero: *There's a Starman waiting 'for' the sky.*

M^a Piedad Bejarano Fernández
Periodista

(English version)

Álvaro Moreno Soto, born in Sevilla (1990), graduated in **Aerospace Engineering** at the **Universidad de Sevilla** and the **Technische Universität München**. He lived for two years in the german city which widened his professional perspectives and enriched his personal life with people from different places and cultures. After this life milestone, he landed in the **Universiteit Twente**. During four years, he has been writing his thesis, which compiles different articles published in prestigious journals in the field of Fluid Mechanics. This period as a doctoral researcher has given him also the opportunity to assist in different teaching duties, as well as the chance to collaborate with other institutions, such as the **University of Utah**.

At the same time, as he declares himself a lover of history, he has started to study a bachelor degree in **History** at the **UNED**, just for the sake of quenching his thirst of knowledge. His future purposes lead him back to the aerospace field. In the more personal area, he loves travelling the world, a hobby that his professional career allows him, as well as practising different sports. With his heart back in his beloved Sevilla, but with his mind willing to meet new people and different cultures, he is looking forward to starting his new project in life.