PLASMONIC MICROBUBBLES: NUCLEATION, GROWTH AND COLLAPSE

MIKHAIL ZAYTSEV

Plasmonic microbubbles: nucleation, growth and collapse

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Front cover: Schematic representation of the formation of bubbles on liquid-immersed gold nanoparticles under laser irradiation

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Chapter 1

Introduction

1.1 General

Bubbles are an integral part of everyday life. They are widely present in various media, systems, and applications. Bubbles are essential components of numerous natural phenomena, e.g. in magmas and rhyolites [1,2], in oceans [3-5], in breaking waves [6], oil reservoirs [7,8] and many others. For some animals, bubbles are even the crucial factor for survival, as they act as a tool to stun or kill prey animals [9,10]. We should also thank bubbles for making the flavor of beloved all over the world beverages such as beer, champagne, and fizzy drinks so delicious [11-16].

Bubbles formation can be both beneficial and detrimental. In biomedicine bubbles are essential, as they act as drug delivery tools [17-19], contrast agents during ultrasound scanning [20,21] and high-intensity focused surgery [22-24]. On the other hand, in the field of electrolysis bubbles formation is undesirable, as they stick to the reacting surfaces and inhibit the chemical reactions [25]. Moreover, bubbles may cause erosion of metals and, therefore, the destruction of propellers, pumps, hydraulic turbines, *etc.* [26-29]

In order to form a bubble, one has to overcome tensile strength within the liquid. It's more likely to occur at the so-called weaknesses in the liquid. Generally, two different types of bubble nucleation exist. First, homogeneous nucleation, related to thermal fluctuations within the liquid, that could create microscopic voids necessary for liquid rupture and bubble formation [27]. This type of nucleation is highly energetically-demanding. In practice, it is much more common to encounter the second type of nucleation - heterogeneous nucleation, when weaknesses occur due to the presence of gas pockets

at the liquid/wall boundary (microscopic cracks, pits, and cavities on the solid surface) or due to microparticles, gas clusters or other impurities suspended in liquid. A classic example is a glass of water. Right after pouring some water in the glass, no bubbles are observed. However, if the glass stays at the table for a couple of hours, many small bubbles appear, which typically are attached to the glass walls, where the nucleation barrier is low.

Bubbles can consist of vapor or gas or both. It is crucial to make a clear distinction between vapor bubbles and gas bubbles. The physics of vapor bubbles have little in common with gas bubbles. Vapor bubbles grow by overcoming latent heat required for liquid evaporation and are known to be fragile, due to the fast condensation of the vapor when in contact with cold surroundings [30,31]. Gas bubbles grow by the accumulation of gas molecules dissolved in the surrounding liquid. Those bubbles remain stable in the cold liquid. The reason for such difference is that vapor bubbles are controlled by heat diffusion, while gas bubbles by mass diffusion, which is typically 3 orders of magnitude smaller.

To sum up, the variety of processes and applications bubbles are involved, make them a vital subject to investigate. Amongst the crucial topics are bubbles nucleation, growth and collapse dynamics, and interaction with the surrounding.

1.2 Plasmonic nanoparticles

Noble metal nanoparticles (NPs) attract high interest during the last years, mainly due to their extraordinary optical properties. [32-35]. The basis for the unique spectral response is that specific wavelengths of light can drive the conduction electrons in the metal to collectively oscillate, a phenomenon known as a surface plasmon resonance (SPR), which is confined in a small volume around an isolated nanoparticle. [36,37]. These resonances remarkably enhance both electromagnetic scattering and absorption abilities of nanoparticles. The resonance condition strongly depends on the morphology of NP and the dielectric function of the medium.

The origin of SPR in metal nanoparticles can be derived for a sphere that is much smaller than the illumination wavelength and can be considered as an electromagnetic dipole. In this case, the sphere polarizability is given by [35]:

$$\alpha(w) = 4\pi R^3 \frac{\epsilon_1(w) - \epsilon_2}{\epsilon_1(w) + 2\epsilon_2}, \quad (1.1)$$

Figure 1.1: SEM images of various nanoparticles: a) spherical nanoparticles, b) nanorods, c) an array of nanodots and d) an array of nanocups

where R is the radius of the sphere, ϵ_1 is the wavelength-dependent dielectric function of the nanoparticle, and ϵ_2 is the dielectric function of the surrounding medium which remains roughly constant regardless of wavelength. From equation (1.1) it is clear that when $\epsilon_1(w) = -2\epsilon_2$, the resonance takes place resulting in a strong increase in the absorption and/or scattering intensity at that wavelength. For larger or non-spherical nanoparticles, the dipolar approximation is no longer valid, and more complex models should be used. [35, 38]. For any NP morphology, the efficiency of absorption and scattering is defined by cross-sections [35, 38]:

$$\sigma_{abs} = k \operatorname{Im}(\alpha) - \frac{k^4}{6\pi} |\alpha|^2 \quad (1.2)$$

$$\sigma_{scat} = \frac{k^4}{6\pi} |\alpha|^2 \quad (1.3)$$

$$\sigma_{ext} = \sigma_{abs} + \sigma_{scat} \quad (1.4)$$

Figure 1.2: Absorption and scattering cross-section spectra for a gold nanosphere in water with sizes a) 40 nm, b) 80 nm, c) 150 nm and for d) a silver nanoparticle of 80 nm in diameter calculated on the basis of Mie theory for homogeneous spheres [39]

By changing the nanoparticle size, shape, and composition, the optical response can be tuned in a broad spectrum from the ultraviolet through the visible to the infrared regions. (Figure 1.2) Thus, depending on the task, enhancement in absorption or/and scattering can be achieved, either by changing NPs morphology or match the resonance with the proper electromagnetic source.

The unique characteristics of plasmonics lead to a broad range of applications across many different fields, such as biomedicine and biotechnology [35, 40–43], sensing and imaging [43–46], enhanced chemical reactions [47–52] and surface-enhanced Raman scattering [45, 53, 54], solar energy conversion [55–57], among others [34, 43, 45, 58, 59].

1.3 Plasmonic bubbles

Plasmonic nanoparticles, as was discussed in the previous section, being highly efficient heat absorbers, can act as nanosources of heat. Suspended in liquid and irradiated by the energy source, those particles rapidly heat up and can vaporize the liquid in their vicinity, forming so-called plasmonic bubbles. It has been suggested that nanoparticles suspensions could act as a simple steam source for desalination and sterilization purposes by converting the incident sunlight into vapor [60–62]. When the bubble is formed, steam as a poor thermal conductor, at least partially, thermally decouples the liquid from the heated nanoparticles, therefore, inhibits heat transfer from the nanoparticle to

Figure 1.3: Schematic representation of the plasmonic bubble formed around hot gold nanoparticle under laser irradiation.

the bulk liquid. As the sunlight further heats the nanoparticle, the thickness of the steam shell gradually grows. Once the steam shell is thick enough, the bubble/nanoparticle system rises toward the surface. Finally, the steam is released from the water. The schematic representation of plasmonic bubble is shown in Figure 1.3.

Plasmonic bubbles are of high interest for many other potential applications and have been extensively studying at the nanoscale as well as microscale. It is essential to distinguish between those two. Plasmonic nanobubbles are formed by ultra-short highly focused laser pulses, with typical lifetimes and sizes in nanoscale [63–69]. If the pulse is short enough (typically less than 0.1 ns) and the NP is small enough (typically less than 100 nm) then the absorption of the laser pulse happens in three consecutive steps [70,71]. If so, then no heat diffuses from the NP to the bulk liquid before the absorption of the whole pulse, resulting in the maximal possible temperature of a nanoparticle. Using continuous wave (cw) laser leads to less confinement temperature profile; however, due to the collective effect of neighbouring nanoparticles, a significant temperature increase is also observed. In this case, bubbles might grow to microscale sizes with much longer lifetimes. [72–77] The exact origin and underlying mechanism for the formation, growth, and dissolution of the microbubbles remain, however, unresolved. In particular, the interplay of dissolved gas and water vapor in the dynamics of microbubbles had not been

clearly identified, and a quantitative understanding is lacking.

1.4 A guide through this thesis

In Chapter 2, the dynamics of steady plasmonic microbubble growth are discussed. Two different successive regimes have been observed. First, rapid evaporation-dominated growth during which the bubble dynamics can be approximated with the scaling law, which is identical for highly degassed water and gas-saturated water. During the second phase, the bubble growth is governed by gas diffusion from the surrounding liquid; therefore, the considerable difference in bubble dynamics in air-saturated water and degassed water has been observed.

In Chapter 3, the plasmonic bubble nucleation on water-immersed nanoparticle arrays is studied. We speculate on the superheating of water, vapor bubble nucleation, subsequent growth, and collapse. We show that two additional regimes preceding the regimes, described in Chapter 2, take place: giant vapor microbubble and unstable oscillating bubble.

In Chapter 4, we proceed with a quantitative investigation of the role of the dissolved gas in bubble nucleation and steady diffusive growth.

In Chapter 5, the plasmonic bubble formation in organic liquids, namely, *n*-alkanes, is discussed. The considerable difference in bubble dynamics in *n*-alkanes and water has been observed and studied in detail. Plasmonic bubbles in *n*-alkanes undergo only two regimes during their evolution. The first phase is similar to the one in water, namely the formation of an explosive vapor bubble. Surprisingly though, bubble size during this phase doesn't depend on alkanes chain length, despite the remarkable difference in boiling points. During the second phase, the bubble steadily grows; however, in contrast with water, this growth is defined by liquid evaporation, while the diffusion may even hinder this growth.

In Chapter 6, we consider the dynamics of plasmonic bubble shrinkage. The influence of gas/vapor ratio in bubble composition, along with other relevant parameters, on bubble shrinkage, has been studied. We show that the history of bubble formation defines the bubble dynamics during the first, condensation dominated phase, while the second, slow diffusion-controlled phase barely depends on the history of bubble formation, but rather on gas saturation level in the liquid.

Chapter 2

Vapor and gas bubble growth dynamics around laser irradiated, water immersed plasmonic nanoparticles ¹

Microbubbles produced by exposing water-immersed metallic nanoparticles to resonant light are of use in various novel applications. How do these bubbles form and what is their gas composition? In this chapter, the growth dynamics of nucleating plasmonic bubbles are studied to determine the exact origin of the occurrence and growth of these bubbles. The microbubbles parameters (radius, contact angle, and footprint diameter) were measured in air-equilibrated water (AEW) and degassed water (DGW). Our experimental data reveal that the growth dynamics can be divided into two regimes: an initial rapid growth phase (regime I, <10 ms) and a subsequent much slower growth phase (regime II). The explosive growth in regime I is identical for AEW and DGW, due to the vaporization of water. However, the slower growth in regime II is distinctly different for AEW and DGW, which is attributed to the uptake of dissolved gas expelled from the water around the hot nanoparticle. Our scaling analysis shows that the bubble radius scales with time as $R(t) \propto t^{1/6}$ in the initial regime I, whereas in the later regime II it scales as $R(t) \propto t^{1/3}$ for AEW and is constant for perfectly degassed water.

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2.1 Introduction

Microbubble formation induced by plasmonic effects of noble metal nanostructures under resonant illumination is of great importance for many plasmonic-enhanced processes, ranging from catalytic reactions [47–49, 78], solvothermal chemistry [51], solar energy harvesting [56, 62], to biomedical photothermal imaging and cancer therapeutics [35, 44, 79, 80]. The field of plasmonic bubbles had a boost in 2013, due to several reports on impressive efficiency in solar energy harvesting by plasmonic heating [60–62, 77]. The proposed mechanism was that steam was produced if gold nanoparticles immersed in water were illuminated by sunlight [60, 61]. In this process, the bulk water in the container was hardly heated up by the hot plasmonic nanoparticles. The estimated overall efficiency of this sunlight to steam conversion process was claimed to be as high as 80%, which would be a leap forward for solar energy harvesting.

The exact origin and underlying mechanism for the formation and growth of the microbubbles (hereafter referred to as MBs) remains, however, unknown. In particular, up to now the interplay of dissolved gas and water vapour in the growth of MBs had not been clearly identified, and a quantitative understanding is still lacking. The physics of vapor bubbles is rather different from that of gas bubbles [30, 31]. The former is controlled by diffusion of heat, whereas the latter by mass diffusion of the dissolved gas, which is typically three orders of magnitude slower than the diffusion of heat. In addition, the latent heat of the liquid-vapor phase transition results in an orders-of-magnitude smaller stiffness of vapor bubbles as compared to gas bubbles. Vapor bubbles are known to be very fragile due to the fast condensation of the vapor when they are in contact with a cold liquid [31, 81]. If the photothermal MBs were indeed vapor bubbles, as claimed [60, 62], the key scientific challenge would be to understand why the emerging vapor bubbles do not collapse, in spite of the surrounding cold liquid.

We conjecture that the dissolved gas must play a crucial role in the MB stabilization [73, 74]. During the intensive growth of the MBs around the heated nanoparticle, dissolved gas unavoidably diffuses into the emerging vapor bubble.

The above hypothesis on the relevance of dissolved gas is supported by two recent studies performed by Baffou *et al.* [73] and Liu *et al.* [74]. Baffou and coauthors [73] studied the shrinkage of MBs on a substrate uniformly covered with gold nanoparticles. They found that the lifetime of these MBs can be several hundreds of seconds. This is due to the fact that MBs are

actually not vapor bubbles, but comprised of dissolved air originating from the liquid. However, they only studied the shrinkage of MBs and not the growth. Later, Liu *et al.* [74] investigated the growth dynamics for MBs generated at highly-ordered plasmonic nanopillar arrays. These authors considered both air-equilibrated water (AEW) and degassed water (DGW). They found that MBs exhibited a much larger growth rate in AEW than in DGW. However, the role of dissolved air in MB growth was not studied quantitatively.

In this work, we focus on the dynamics of plasmonic MB growth on well-defined patterned gold nanoparticle (GNP) decorated surfaces under illumination of a continuous wave (CW) laser. Our study will disentangle the roles of vapour and dissolved air in the growth of plasmonic bubbles, and reveal that the growth of plasmonic MB can be divided into two regimes, namely an initial short phase of immediate and explosive growth of a vapor bubble and – but exclusively only for the AEW case – a much longer second phase governed by the influx of dissolved gas from the surrounding water. We will provide quantitative data for the growth processes and a scaling analysis whose results are consistent with these data. The understanding from this work on the regimes in plasmonic bubble growth may help to facilitate the design and control of bubble formation for more efficient energy conversion and many other plasmonic-enhanced processes.

2.2 Methods and materials

2.2.1 Sample preparation

A gold (Au) layer of approximately 45 nm was deposited on an amorphous fused-silica wafer by using an ion-beam sputtering system (home-built T’COathy machine, MESA+ NanoLab, Twente University). A bottom anti-reflection coating (BARC) layer (~ 186 nm) and a photoresist (PR) layer (~ 200 nm) were subsequently coated on the wafer. Periodic nanocolumns with diameters of approximately 110 nm were patterned in the PR layer using displacement Talbot lithography [82] (PhableR 100C, EULITHA, the Netherlands). These periodic PR nanocolumns were then at wafer level transferred to the underlying BARC layer, forming 110 nm BARC nanocolumns by using nitrogen plasma etching (home-built TEtske machine, NanoLab), at 10 mTorr, and 25 W for 8 min. Using these BARC nanocolumns as a mask, the Au layer was subsequently etched by using ion beam etching (Oxford i300, Oxford Instruments, United Kingdom) with 5 sccm Ar, and 50-55 mA at an inclined angle of 5° .

The inclined etching for 9 min resulted in periodic Au nanodots supported on cone-shaped fused-silica features. The remaining BARC was stripped with oxygen plasma (TePla 300E, PVA TePla AG, Germany). The fabricated array of Au nanodots was heated up at 1100° , and subsequently cooled down passively to room temperature. During the annealing process, these Au nanodots reformed into spherical-shaped Au nanoparticles (Fig. 2.1).

Figure 2.1: Patterned gold nanoparticle sample surface. (a) Schematic of a gold nanoparticle sitting on a fused SiO_2 island on glass substrate. (b) Right: SEM image of the patterned gold nanoparticle sample surface. Left: ESB image of the same area. The bright areas correspond to the actual nanoparticle areas.

2.2.2 Setup description

In order to observe microbubble formation and growth we put the sample of gold nanoparticles in a liquid cell made of quartz glass and filled with water. We used both air-equilibrated (AEW) and degassed water (DGW) in our experiments. To make DGW, the liquid cell was placed in a sealed chamber connected to an external pump that created vacuum inside the vessel. Most of gas dissolved in water was expelled after two hours and there were no visible bubbles in liquid. As soon as we took the liquid cell out from the vacuum chamber, gas inevitably started to re-dissolve in water, so we used a closed liquid cell to slow down this process.

The experimental setup to study dynamics of microbubbles is shown in Fig. 2.2. A continuous-wave laser (Cobolt Samba) with 532 nm wavelength and maximum power of 300 mW was used for nanoparticles irradiation. In our experiments, a variable attenuator was used to tune the laser power. We installed two long working distance objectives (Olympus SLMPLN 50x) in our

setup: first, to focus a laser beam on the sample surface and to observe the bubble dynamics from the top, and second, to monitor the bubble growth from one side. Two high-speed cameras (Photron Fastcam SA1 and Photron Fastcam SA7 for side-view and top-view respectively) recorded views of the generated bubble with various frame rates from 2000 to 10000 fps. A fiber lamp (Olympus ILP-1) and a light (Schott ACE I) provided an illumination for high-speed cameras. Later we mainly considered the side-view observations as in this case we obtained not only the bubble diameter dynamics, which could be recorded from top as well, but also variations of the contact line and the contact angle. In our experiments we figured out that nanoparticles illumination from the top is more efficient than the bottom one. If a laser shines from the top it goes through the liquid and directly hits the nanoparticles while in the bottom illumination case, a laser beam passes through glass substrate and silica support that causes power loss.

Figure 2.2: Schematic of the optical setup used for bubble generation and observation

2.3 Results and discussion

2.3.1 Characterization of microbubbles and their dynamics

In Fig. 2.3(a) a schematic diagram of a side-view image of a MB is shown. The key geometric parameters, such as the bubble radius R , the contact angle θ , the footprint diameter L , the height H , and the volume V of the MB can be extracted from a side-view image as depicted in Fig. 2.3(b). Only two of these parameters are independent. *E.g.*, from R and L all others follow, namely the contact angle $\sin \theta = L/2R$, the height $H = (1 - \cos \theta) L / (2 \sin \theta)$ and the volume $V = \pi H (3L^2 + 4H^2) / 24$. As in our case θ is close to 180° , the emerging bubbles are close to spherical; typically the volume of a MB is about 98% of a sphere with radius R .

Figure 2.3: Side view of a MB. (a) Illustration and parameters extracted through image processing. (b) An example of the obtained image, together with the image processing result.

The overall dynamical behavior of the MBs can be seen from the series of snapshots in Fig. 2.4. While on short-time scales up to about 100 ms after illumination there is hardly any difference in the bubble dynamics between the AEW and the DGW cases (Fig. 2.4a, b), on long-time scale between 0.5 s up to 5 s there are major differences: The microbubble in the AEW case (Fig. 2.4c) grows much faster and larger as compared to the DGW case (Fig. 2.4d), for which the growth nearly comes to a standstill.

In the next two subsections we will treat the short-time and the long-time behavior of the bubbles separately, and we will start with the long-time behavior.

Figure 2.4: The first two rows of snapshots show the short-term plasmonic bubble dynamics between 5 ms and 100 ms after laser illumination for a plasmonic bubble in air-equilibrated water ((a), AEW) and in degassed water ((b), DGW). The scale bar is $25\mu\text{m}$. Hardly any difference is seen. The second two rows of snapshots show the long-term plasmonic bubble dynamics between 0.5 s and 5 s after laser illumination for a plasmonic bubble in air-equilibrated water ((c), AEW) and in degassed water ((d), DGW). The scale bar is $50\mu\text{m}$.

2.3.2 Long-time dynamics of bubble growth

To reveal the long-term bubble dynamics, we followed the bubble growth for a period of several seconds with a frame rate of 2000 frames per second (fps). The results are shown in Fig. 2.5, where Fig. 2.5a and 2.5b show bubble volume V and bubble radius R as a function of time for five different laser powers. It

can be seen that, for all laser powers, the bubble volume V increases linearly with time t . Moreover, the pre-factor, $k = V/t$, increases with increasing laser power, as shown in the inset of Fig. 2.5a. The linear relation $V \propto t$ for larger times is also obtained from a double logarithmic plot of V vs. t , as shown in Fig. 2.5c. After 0.2 s the curve has a well-defined slope with a value of 1.

The linear relationship between V and t is consistent with the observed behavior for $R(t)$, see fig. 2.5b. Since V linearly increases with t and since the bubble is nearly spherical, R should scale as $t^{1/3}$. Indeed, a double logarithmic plot of $R/t^{1/3}$ versus t (Fig. 2.5d) reveals this: while in the early phase the slope of $R/t^{1/3}$ versus t gradually decreases with t , beyond $t > 0.2$ s the slope in this plot becomes zero, indicative of a $t^{1/3}$ dependence of $R(t)$.

This $R(t) \propto t^{1/3}$ dependence is quite intriguing. One could expect that for bubbles growing out of an oversaturated solution, transport-controlled (i.e. diffusion-limited) growth takes place [83]. In that case, the diffusive bubble dynamics is given by

$$\frac{dV}{dt} \propto R^2 \dot{R} \propto \frac{D}{\rho} R^2 \frac{\partial C}{\partial r} \bigg|_R \sim \frac{D}{\rho} R^2 \frac{C_\infty - C_s}{R}, \quad (2.1)$$

from which one immediately obtains $R(t) \propto t^{1/2}$. Here D is the diffusion coefficient, ρ the gas density, C_s the gas solubility, C_∞ the gas (over)saturation far away from the bubble, and $C(r)$ the concentration field around the bubble assumed to be spherical. However, as we do not observe such behavior, we suggest that our bubble is growing due to the gas oversaturation which is locally produced at the plasmonic nanoparticle due to heating. During laser illumination, the heat generated by the GNPs is transferred to the surrounding water, leading to an increase of the water temperature. Since the air solubility C_s in water decreases with increasing water temperature, the heating leads to a local oversaturation $\zeta = C_\infty/C_s - 1 > 0$. Originally, we have saturation, $C_\infty = C_s$ or $\zeta = 0$. The air is thus expelled from the water and the MB will grow. The key point is that all expelled gas is immediately taken up by the bubble. Therefore the distortion of the equilibrium remains local and the global oversaturation does not increase with time. For such production-limited growth process the growth rate is constant, $dV/dt = k$ and consequently

$$V(t) \propto t \text{ or } R(t) \propto t^{1/3}. \quad (2.2)$$

The volume growth rate $dV/dt = k$ can be correlated to the laser power P_l , which we assume to be constant during the laser illumination. We in addition

Figure 2.5: Long-term MB growth in air equilibrated water (AEW) with different laser power. (a) Bubble volume as function of time for different laser power illuminations. The volume linearly increases with time for different laser power exposure. The inset figure shows that the linear factor $k = V/t$ linearly increases with the laser power P_l . (b) Bubble radius as a function of time for the AEW case (upper lines). For comparison, also the degased water case (DGW) is shown (lower lines), which shows a much weaker growth. (c) Double-logarithmic plot of MB volume as a function of time for the AEW case. A linear relation (i.e., slope=1.0) between MB volume and time is observed for late times. (d) Double-logarithmic plot of $R/t^{1/3}$ as a function of time. As about 0.2 s, the slope of the curves decreases to zero, implying a $t^{1/3}$ dependence of the MB radius for late times.

assume that the heat conversion efficiency f (with $0 < f < 1$) from laser power to thermal energy (through nanoparticles heating) is constant in this regime. After a time period dt the water will be heated up by dT . This increase in temperature obeys

$$fP_l dt = c_w m_w dT, \quad (2.3)$$

where c_w is the specific heat capacity of water, m_w is the mass of the heated water (which will cancel out later), and dT the increase of the water temperature, leading to a gas oversaturation

$$d\zeta = -\frac{C_\infty}{C_s^2} \frac{dC_s}{dT} dT. \quad (2.4)$$

The mass influx of gas into the bubble due to the local oversaturation $d\zeta$ is

$$dm_g = C_s V_w d\zeta, \quad (2.5)$$

where $V_w = m_w/\rho_w$ is the volume of the heated water and ρ_w its density. The mass influx dm_g leads to a volume increase

$$dV = \frac{\mathcal{R}_g T dm_g}{M_g P_g}, \quad (2.6)$$

where M_g is the molecular mass of the gas, $\mathcal{R}_g$ the gas constant, and $P_g = P_\infty + 2\sigma/R$ the pressure inside the gas bubble, where P_∞ is the ambient pressure and σ the surface tension. Combining things together, we finally have

$$\frac{dV}{dt} = k = -\frac{\mathcal{R}_g T}{M_g (P_\infty + \frac{2\sigma}{R})} \frac{C_\infty}{C_s} \frac{dC_s}{dT} \frac{fP_l}{c_w \rho_w}, \quad (2.7)$$

i.e., for large $R \gg 2\sigma/P_\infty = 1.4\mu\text{m}$ linear growth of the bubble volume as obtained already above. We note that the volume of the heated water around the bubble cancels out, as it should. We also note that $k \propto P_l$, which is consistent with our findings in the inset of Fig. 2.5a (apart from an offset). Writing eq. (2.7) in terms of the radius, one has for large R

$$R(t) = \left(\frac{1}{4\pi} \frac{\mathcal{R}_g T}{M_g P_\infty} \frac{C_\infty}{C_s} \frac{dC_s}{dT} \frac{fP_l}{c_w \rho_w} \right)^{1/3} t^{1/3}. \quad (2.8)$$

The above analysis thus supports our hypothesis that the dissolved air plays a crucial role in the growth of MBs.

In order to further verify our conjecture, we replace the air-equilibrated water (AEW) by degassed water (DGW). The resulting long-term dynamics of the MB radius R is also shown in Fig. 2.5b, remaining way under the AEW case. Indeed, in the second phase the MB grows much slower in the DGW case as compared to the AEW case. In Fig. 2.6 a double logarithmic plot of

$R(t)$ is shown. The slope in the DGW case is only 0.07, which is substantially smaller than the slope $1/3$ for the AEW case. We anticipate that the much slower growth in the DGW case is due to the lack of dissolved gas, though the small remaining growth suggests that the degassing had not been complete.

Figure 2.6: Double-logarithmic plot of long-term bubble growth in degassed water with different laser powers as a function of time. An effective slope of 0.07 is obtained for late times.

2.3.3 Short-term dynamics: Rapid growth of bubbles in air-equilibrated and degassed water in the initial stage

From the experimental results shown in Fig. 2.5 and Fig. 2.6 we have a good impression of the long-term MB growth dynamics beyond 0.2 s. To obtain quantitative information of the initial phase of MB growth, we will now study the MB growth dynamics for the first 100 ms with a substantially higher frame rate of 10 kfps.

Fig. 2.7a and Fig. 2.7c show the short-term dynamics $R(t)$ in the AEW and DGW cases, respectively. Both plots show a rapid increase of the MB in the first 10 ms. After that, the MBs continue to grow at a relatively high rate in the AEW case, whereas the growth slows down in the DGW case. In Figs. 2.7b and 2.7d double logarithmic plots of $R(t)$ in the AEW case and DGW case, respectively, are shown. The results clearly reveal that for the first 10 ms (phase I), the slopes for the AEW and DGW cases are very similar (slope of about 0.15). The slopes in the DGW case start to gradually decrease after phase I, whereas they start to increase for AEW.

Figure 2.7: MB growth in the initial short period of time in air-equilibrated water and degassed water. Bubble radius as function of time in AEW (a) and DGW (c), respectively. Double-logarithmic plot of bubble radius as a function of time in AEW (b) and DGW (d), respectively. From 0.1 s on, $R(t)$ in the AEW case is already seen to take off as compared to the DGW case.

The strong similarity of phase I for AEW and DGW implies that dissolved gas is not decisive here. The only viable explanation for phase I is that the growth of the MBs is due to the evaporation of water. So initially we are dealing with vapor bubbles, but beyond 10 ms in the AEW case the bubbles grow because of the influx of dissolved gas from the surrounding water.

This explosive vapor formation scenario also suggests why the scaling exponent of the $R(t)$ relation in the initial regime I is so low, $R(t) \propto t^\alpha$, with $\alpha \approx 0.16$. In regime I, the laser energy (lhs of equation (2.3)) is mainly consumed by the evaporation of water. *I.e.*, in regime I we have

$$f(R)P_l dt = 4\pi\Lambda\rho_w R^2 dR, \quad (2.9)$$

where Λ is the latent heat of water. Note that for this early regime, in which the vapor bubble is in direct contact with the plasmonic nanoparticle, we have to assume that the laser efficiency depends on the bubble size, $f(R)$. It

will depend on the direct contact between the plasmonic nanoparticle and the growing vapor bubble and thus decrease with increasing R with $f(R) \propto R^{-3}$. Putting this into eq. (2.9), we obtain

$$R(t) \propto \left(\frac{P_l}{\rho_w \Lambda} \right)^{1/6} t^{1/6}, \quad (2.10)$$

close to our experimental finding $R(t) \propto t^{0.16}$ in this regime I.

2.3.4 Transition between the two regimes

What sets the transition from regime I to regime II? We suggest that while in the initial regime I the laser power and the resulting plasmonic heating is sufficient to provide the energy (*i.e.*, latent heat) for the evaporation of the water around the bubble, at some point this can no longer be the case, as the bubble surface (and thus the water mass around the bubble which must be evaporated) grows with R^2 . Then the supplied laser power only leads to a heating of the surrounding liquid, but not to evaporation, *i.e.*, regime II in which the heated water partly loses its dissolved gas into the bubble. We can also obtain a relation for the transition between regime I and II: comparing eq. (2.8) and eq. (2.10), we derive

$$t_{trans} \propto P_l^{-1}, \quad (2.11)$$

roughly consistent with our above reported findings from Fig. 2.5d: When extrapolating the small time and the large time behaviors, we estimate the transition time to be around $t_{trans} \approx 0.1s$ for $P_l = 130mW$, whereas it is $t_{trans} \approx 0.2s$ for $P_l = 240mW$.

2.4 Conclusion

In summary, the MB growth can be separated in two regimes, as summarized in Fig. 2.8. In regime I ($t < 0.1s$), the MB growth is governed by the evaporation of water, leading to $R(t) \propto t^{1/6}$. In this regime, the growth dynamics of the bubbles is the same in air-equilibrated and degassed water. In regime II ($t > 0.1s$) the bubble growth is dominated by the influx of dissolved gas from the surrounding water. Then $R(t) \propto t^{1/3}$ in air-equilibrated water, but in degassed water $R(t)$ is nearly constant. This work settles the controversy on the role of dissolved gas and water vapour in the formation of plasmonic

bubbles and provides important guideline for the design and control of the bubble formation in many plasmon enabled processes.

Figure 2.8: Illustration of the bubble dynamics $R(t)$ for air-equilibrated water and degassed water. The MB growth process can be divided into two phases, with a crossover in between.

We speculate that a two step growth process is not limited to plasmonic bubbles, but may also occur for bubble formation in other processes, for example, during the photoelectrochemical conversion [84] or electrolysis [25].

Chapter 3

Giant and explosive plasmonic bubbles by delayed nucleation ¹

When illuminated by a laser, plasmonic nanoparticles immersed in water can very quickly and strongly heat up, leading to the nucleation of so-called plasmonic vapor bubbles, which have huge application potential in e.g. solar light-harvesting, catalysis, and for medical applications. Whilst the long-time behavior of such bubbles has been well-studied, here, by employing ultra-high-speed imaging, we reveal the nucleation and early life phase of these bubbles. After some delay time τ_d after beginning of the illumination, a giant bubble explosively grows, up to a maximal radius of $80\text{ }\mu\text{m}$, and collapses again within $\approx 200\text{ }\mu\text{s}$ (bubble life phase 1). The maximal bubble volume V_{max} remarkably increases with decreasing laser power P_ℓ . To explain this behavior, we measure the delay time τ_d from the beginning of the illumination up to nucleation, which drastically increases with decreasing laser power, leading to less total dumped energy $E = P_\ell \tau_d$. This dumped energy E shows a universal linear scaling relation with V_{max} , irrespectively of the gas concentration of the surrounding water. This finding supports that the initial giant bubble is a pure vapor bubble. In contrast, the delay time does depend on the gas concentration of the water, as gas pockets in the water facilitate an earlier vapor bubble nucleation, which leads to smaller delay times and lower bubble nucleation temperatures. After

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the collapse of the initial giant bubbles, first much smaller oscillating bubbles form out of the remaining gas nuclei (bubble life phase 2, up to typically 10 ms). Subsequently the known vaporization dominated growth phase takes over and the bubble stabilizes (life phase 3). In the final life phase 4 the bubble slowly grows by gas expelling due to heating of the surrounding.

3.1 Introduction

Noble metal nanoparticles under resonant irradiation of continuous wave (cw) lasers can produce huge amount of heat due to the enhanced plasmonic effect, resulting in the evaporation of the surrounding water. This will cause the formation of micro-sized plasmonic bubbles [48,60,72,74,77,85]. These bubbles appear in numerous applications, including micro/nanomanipulation [86,87], biomedical therapy [35,79,80,88,89], and solar energy harvesting [60,61,77,85,90–92]. Understanding the nucleation mechanism and growth dynamics of these plasmonic bubbles is key to successfully take up the challenges connected to these applications. However, most studies up to now have not yet focused on the plasmonic microbubble *nucleation* and its early dynamics but, instead, are conducted on the long-term (milliseconds to seconds) timescale [73,74,85,93]. In a recent study, we revealed that the long-time growth of these plasmonic bubbles can be divided into two phases, namely a vaporization dominated phase for vapor bubbles (up to 10 ms) followed by a slow diffusion-dominated growth of vapor-gas mixture bubbles [94]. The later phase reflects the role of dissolved gas in the growth dynamics of the bubbles [94]. Note that the vaporization event for plasmonic bubbles is different than for normal vapor bubbles, which arise from simply locally heating the liquid with a laser [31,95–98].

Upon laser irradiation, water around plasmonic nanoparticles at solid-liquid interfaces experiences a rapid temperature increase, first proportional to the input laser intensity. The resulting temperature rise can exceed the boiling temperature (100 °C) within a few nanoseconds to microseconds [63,66,67,72,99]. This is several orders of magnitude faster than the millisecond time scale in which plasmonic bubbles are normally observed. At the ns to μ s time scales, the fate of the plasmonic nanoparticles under cw laser irradiation and that of the liquid in their vicinity has remained unexplored. The reason for this primarily lies in the difficulty to visualize the early stage of the vaporization dynamics around the plasmonic nanoparticles, due to the lack of imaging systems with sufficient temporal resolution.

In this work, we overcome this bottleneck by means of the ultra-high-speed imaging facility Brandaris128 [100,101] and reveal the early dynamics of plasmonic bubbles nucleating on an immersed gold nanoparticle (GNP) decorated surface. Brandaris128 has a temporal resolution of 100 ns, which allowed us to reveal that a giant transient vapor bubble arises prior to the hitherto observed plasmonic microbubbles. The delay between the beginning of the laser heating and the bubble nucleation depends on the laser power and the concentration of the gas dissolved in water. We compare a gas-rich and a gas-poor case with the latter having about half of the gas concentration as the former. The measured relation between the delay and the laser power will be used to estimate the nucleation temperature of the vapor bubbles in water. Combined with the sub-microsecond cavitation dynamics, this nucleation delay provides information on the energy conversion efficiency. Our findings have strong bearings on the applications mentioned above, and affect their risk assessment.

3.2 Experimental details

In this study, two imaging setups were used to capture the growth dynamics of plasmonic microbubbles, both on short-term and long-term, as shown in Fig. 3.1. Short-term measurements were performed using the Brandaris 128 ultra-fast imaging system [100,101]. This system can capture 128 consecutive images with a frame rate of up to 25 Mfps. The schematics of the Brandaris 128 setup is shown in Fig. 3.1(a); an upright microscope was installed together with a water immersion objective (LUMPLFLN, Olympus) for bubble observation. In the Brandaris 128, 128 CCD cameras are sequentially installed along an arc. The images from the objective are redirected to the sequence of the CCD sensors by a rotating mirror-polished beryllium turbine. By adjusting the rotation speed of the turbine one can tune the recording speed. In our experiments the frame rates were around 7-8 MHz, which allowed to capture the detailed temporal evolution of the initial giant bubbles or 3 to 4 oscillation cycles of the subsequent oscillating bubbles. A xenon flash light was used as illumination source.

The gold nanoparticle decorated sample was immersed in a water tank and placed vertically to enable side view imaging of plasmonic bubbles. During measurement, the sample surface was irradiated with a continuous-wave laser (Cobolt Samba) of 532 nm wavelength and tuneable power up to 200 mW. An acousto-optic modulator (Opto-Electronic, AOTFncVIS) was used as a shutter to control on/off of laser irradiation on the sample surface. A 400

Figure 3.1: Schematic of the optical imaging facilities for plasmonic microbubble formation observation. (a) Brandaris 128 imaging system with frame rate up to 25 Mfps. (b) High-speed camera imaging system with frame rate up to 500 kfps.

μs laser pulse was generated and controlled by pulse/delay generator (BNC model 565). Additionally, an ultrasonic transducer was installed inside the water tank in order to obtain the acoustic signal of initial bubble nucleation. This facilitates the synchronization of the laser pulse and Brandaris 128 image capture.

The Brandaris 128 ultra-high-speed imaging facility can capture 128 consecutive frames, thus recording only for a limited period of time. Thus, for the longer times the setup described in Chapter 2.2 has been used. The high-speed camera operated at a frame rate of 500 Kfps, equipped with 5x (LMPLFLN, Olympus) and 20x (SLMPLN, Olympus) long working distance objectives.

In two sets of experiments, plasmonic microbubble formation in both gas-rich water and gas-poor water was studied. Water directly obtained from a Milli-Q machine was taken as gas-rich water. To get gas-poor water, the liquid cell filled with water and vacuumed. The total degassing time was about 3 hours. The relative gas concentration for both gas-rich and gas-poor water was measured with an oxygen meter (Fibox 3 Trace, PreSens) in the ambient environment (temperature: 22°C). During measurements, the fluid cell was

sealed to slow down re-gassing. The relative gas concentration in the gas-poor water is 34%. This is about a half of the value 71% measured in the gas-rich water.

Figure 3.2: Evolution of an initial giant bubble (a) and a subsequent oscillating bubble (b) along with their life cycles captured at 7.47 Mfps for the gas-rich case and $P_l = 185 \text{ mW}$. The two kinds of bubbles show different shapes and dynamics. The respective positions of the nanoparticles and the bubble is the same as in Fig. 2.3. (c) Radius of curvature R as a function of time for an initial giant bubble and for the subsequent oscillating bubbles. (d) Maximum volume V_{max} of the giant bubble as function of laser power P_l in gas-rich water and gas-poor water. Counter-intuitively, the bubble volume decrease with increasing laser power P_l .

3.3 Results and discussion

An array of GNPs with diameters of 80 nm was deposited on a fused silica substrate to induce plasmonic bubble nucleation. Experiments were first conducted with the Brandaris 128 ultra-high-speed imaging system at frame rates near 8 Mfps. The origin of time ($t = 0$ s) is the instant at which the laser beam hits the substrate. After a delay time τ_d , a bubble (Figure 3.2a) nucleates. During the violent subsequent growth, the cavitation bubble can reach a size exceeding $100\text{ }\mu\text{m}$ within $6\text{ }\mu\text{s}$, while retaining a hemi-spherical shape. Figure 3.2d shows that an increase of the laser power P_l counter-intuitively leads to a decrease in the maximum bubble volume V_{max} . Also counter-intuitively, the gas-poor case leads to larger bubbles as compared to the gas-rich case.

After the initial giant bubble has collapsed, smaller bubbles experience cycles of sustained oscillations (Figure 3.2b) before gradually stabilizing. These bubbles, referred to as oscillating bubbles, are about $100\times$ smaller in volume than the initial giant bubble (Figure 3.2c). Accordingly, the oscillation period of these bubbles is substantially shorter than the lifetime τ_c of the giant bubble.

These two life phases, *i.e.* the giant bubble growth and collapse (life phase 1) and the oscillating bubbles (life phase 2) precede the observed plasmonic bubble dynamics [73, 74, 78, 93, 94]. As revealed in [94], this later plasmonic bubble dynamics consists of two subsequent and slower phases, namely a vaporization-dominated growth (life phase 3) and a diffusion-driven growth that is dominated by the influx of gas dissolved from the water (life phase 4), and correspondingly depends on the dissolved gas concentration. Figure 3.3 summarizes all four life phases.

Figure 3.3: Time sequence of the bubble dynamics under continuous laser irradiation on the patterned GNP sample surface in gas-rich water and $P_l = 83\text{ mW}$. According to their nucleation and growth dynamics, the evolution of the plasmonic bubbles is divided into four phases. The scale bar is $25\text{ }\mu\text{m}$.

Figure 3.4a shows the volume V as a function of time t for an initial giant

Figure 3.4: (a) Bubble volume dynamics during growth for an initial giant bubble (life phase 1, black), a vaporization dominated bubble (life phase 3, red), and a diffusively growing bubble (life phase 4, blue) in gas-rich water. (b) Growth rates $\dot{R}$ of the same three bubbles. Both plots are in double logarithmic scale. Note: the origin of time for the diffusively growing bubble was aligned to that of vaporization dominated bubble to facilitate the comparison.

bubble (life phase 1), a vaporization dominated bubble (life phase 3), and a bubble growing slowly by gas diffusion (life phase 4) for the gas-rich case. The volume of the initial giant bubble rapidly exceeds that of the vaporization dominated bubble (phase 3) and that of the diffusively growing bubbles (phase 4). The growth rate of the giant bubble (see Figure 3.4b) reaches a maximum value of about 12.5 m/s, which is respectively about 2000 times and 10^5 times larger than the respective growth rates of the vaporization dominated and the diffusively growing bubbles.

In order to capture the dynamics on a longer timescale that encompasses

the nucleation delay, a second set of experiments was performed using a high speed camera operated at 300 kfps. The experiments were conducted with different laser powers P_l in both gas-rich water and gas-poor water. The observed decrease in maximum volume V_{max} of the initial giant bubble with increasing laser power P_l seems counter-intuitive and so does the observed larger bubble volume for the gas-poor case. The reason for this behavior is that nucleation of vapor bubbles in water requires the temperature to reach the nucleation temperature T_n . Under ideal conditions (pure water), this temperature is identical to the liquid spinodal decomposition temperature [102]. However, the presence of impurities, gases or interfaces, results in a lower T_n (see Figure 3.5a). The nucleation temperature T_n does not depend on the laser power P_l , which explains the increased delay time τ_d for lower P_l seen in Figure 3.5b.

Figure 3.5: (a) Phase diagram of water (schematics). The green solid line is the liquid spinodal line, the theoretical limit of superheat, while the blue and red dashed lines schematically depict the attainable superheat for gas-poor and gas-rich water. (b) Measured delay τ_d as function of P_l . The symbols represent the experimental data and the solid lines the fit curves using Eq. (5.1). (c) Double logarithmic plot of τ_d vs $P_l - P_l^{th}$. Both curves fall within the theoretical limits, namely the boiling temperature (black curve) and the spinodal curve ($T_s = 578.2$ K for a pressure of 1 atm, green curve). The shorter delay time τ_d for gas-rich water indicates that dissolved gas facilitates bubble nucleation.

We now go ahead and analytically quantify this behavior. The time-dependent temperature field $T(\vec{r}, t)$ around a single nanoparticle, assuming spherical geometry and constant thermal properties, is governed by the spherical linear Fourier equation for heat conduction:

$$\partial_t(T(r, t)) = \frac{p_l(r, t)}{\rho c_p} + \kappa \frac{1}{r^2} \partial_r(r^2 \partial_r T(r, t)), \quad (3.1)$$

where κ , ρ , and c_p are thermal diffusivity, density, and heat capacity of water, r is the spherical distance to the GNP, and $p_l(r, t)$ is the deposited power density (unit in W/m^3). Here p_l is a constant if r is smaller than that of the GNP, and 0 else.

This problem is solved analytically, in the Fourier domain, and subsequently reversed back to real space numerically. The temperature field generated by the nanoparticle array can then be computed by superposition, placing the nanoparticle sources on the liquid/substrate interface, within the Gaussian laser beam. A first order correction is applied to account for the presence of a substrate as detailed in the Appendix.

The resulting time-dependent temperature field is the linear superposition of the temperature fields of the N_{np} nanoparticles,

$$T(x, y, z, t) = \sum_{n=1}^{N_{np}} (T_i(d_{i,(x,y,z)}, t)), \quad (3.2)$$

with T_i the temperature field created by the particle i , $d_{i,(x,y,z)}$ the distance from the center of this nanoparticle to the point located at the coordinates (x, y, z) . The result, proportional to the input power, is given in the Appendix. From the computation, taking into account the laser input power, one directly obtains the time required to reach a given temperature for a given laser power. This approach was used to fit the experimental data in Figure 3.5b using a root-mean-square-minimization method, resulting in the solid curves in Figure 3.5b.

This fitting procedure directly provides values for the nucleation temperature, namely $T_n = 422$ K and $T_n = 498$ K for the gas-rich and gas-poor water, respectively, and for the vaporization power thresholds P_l^{th} , namely $P_l^{th} = 39$ mW and 62 mW, respectively. Figure 3.5c shows a double-logarithmic plot of τ_d versus $P_l - P_l^{th}$. As expected, both curves are located between the two limiting cases, namely the liquid-vapor equilibrium temperature $T_n = 373.2$ K (black curve) and the water spinodal temperature $T_s = 578.2$ K [102] (green curve). Moreover, above obtained values for the vaporization power thresholds are in reasonable agreement with the respective measured thresholds of 44 mW and 56 mW for the gas-rich and gas-poor case. Below this threshold, the steady-state regime for spherical heat diffusion has time to establish and the temperature stops rising before the system reaches the required nucleation temperature.

The experimental results also reveal that the dissolved gas plays a crucial role in the initial giant bubble nucleation. Numerous studies have shown that

Figure 3.6: (a) Maximal volume of the giant bubble V_{max} as function of the energy $E = P_l \tau_d$ in gas-rich and gas-poor water. Both cases show an identical linear relation between $V_{max} = kE$, regardless of τ_d and P_l . (b) Actual conversion efficiency of the GNPs for the energy converted from laser heat deposition to vaporization enthalpy contained in the vapor.

impurities in water can greatly reduce T_n from the liquid spinodal temperature [103–105]. As the concentration of dissolved gas in the gas-poor water is about half of that in gas-rich water, the probability of forming gas nuclei larger than the critical size is statistically reduced [106], resulting in a higher T_n , which leads to an increase in the delay time τ_d in gas-poor water.

Nonetheless, as shown Figure 3.6a, the maximum bubble volume V_{max} displays a universal linear relation $V_{max} = kE$ (with $k \approx 1.7 \times 10^4 \mu\text{m}^3/\mu\text{J}$) with the total dumped energy $E = P_l \tau_d$, the accumulated laser energy in the illumination spot on the substrate from the moment of laser on to the moment of bubble nucleation. This linear relation is independent of the gas concentration. It reflects that the energy stored in the vicinity of the nucleus determines the energy available for vaporization, and more energy results in larger vapor bubbles. The linear relation is a consequence of the short delay time observed in these experiments relatively to the thermal diffusion time $\tau_{diff} \approx R_l^2/\pi/\kappa \approx 400\mu\text{s}$, where R_l is the laser spot radius. Moreover, the linear relation further confirms that the initial giant bubbles are pure vapor ones, for both gas-poor and gas-rich water.

The major motivation for using plasmonic particles for applications such as solar to steam energy harvesting or plasmonic bubble photoacoustic therapy lies in their outstanding efficiency of light absorption. In such case, the limiting factor becomes the thermal processes occurring within the system, that convert thermal energy into vapor. It is therefore important to quantify the energy

conversion efficiency. For water, one can neglect the heat capacity compared to latent heat of vaporization. Thus, the energy contained in the giant initial bubble can be estimated using the ideal gas law:

$$E_{bub} = \Lambda_{vap} \frac{MP_{sat}V_{max}}{R_g T_{sat}}, \quad (3.3)$$

where P_{sat} and T_{sat} are water saturation pressure and temperature, respectively, M is the molar mass of water, Λ_{vap} its latent heat of vaporization and $R_g = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ the gas constant. Since the ratio P_{sat}/T_{sat} is independent of the laser power P_l (see Appendix), E_{bub} is proportional to the maximal bubble volume V_{max} . The ratio of the energy contained in the initial giant vapor bubble to the energy absorbed by the substrate, which is the effective energy conversion efficiency for this process, is displayed in Figure 3.6b and is equal to $(3.6 \pm 0.5) \%$. The conversion efficiency displays a slight decrease for larger energies, corresponding to an increase of τ_d . This is in agreement with the increasing (with time) losses by heat diffusion.

3.4 Conclusion

To summarize, we have shown that the nucleation of plasmonic bubble on water-immersed, laser-irradiated GNPs is initiated by a transient and explosively growing giant vapor bubble with a life time of about 10 μs . The maximum growth rate $\dot{R}$ of the initial giant bubbles exceeds 12.5 m/s , which is three orders of magnitude larger than that of the later and hitherto observed plasmonic bubbles that grow by steady vaporization. Whether and when a giant initial bubble nucleates is determined by the competition between laser heating and cooling through thermal diffusion. As a result, the delay time τ_d up to bubble nucleation decreases with increasing laser power P_l , leading to smaller bubbles. Both the nucleation temperature T_n and the laser power threshold value can be obtained from a simple heat diffusion model, and are consistent with the experimental values. Moreover, the experimental results show that the gas-poor water has a much larger delay time τ_d than the gas-rich water. This reflects that the dissolved gas facilitates vapor bubble nucleation and lowers the superheat temperature limit. After nucleation, the giant bubbles in both cases obey the same dynamics (life phase 1). The maximum bubble volume follows the same linear relation with the accumulated energy for both gas-rich and gas-poor water. In the later life stages, the plasmonic bubble displays small, sustained oscillations (life phase 2), followed by the known

vaporization dominated phase (life phase 3), and diffusive growth phase (life phase 4). Our findings on plasmonic bubble dynamics have strong bearings on various applications of plasmonic bubbles, notably on medical applications where large plasmonic bubbles can cause damage [27]. In the context of catalysis or triggering chemical reactions the energetic giant bubble collapse may be beneficial.

3.5 Appendix

3.5.1 Numerical solution of temperature rise around laser-irradiated gold nanoparticles on the substrate

The temperature evolution of a single heated sphere immersed in water can be computed by solving the heat diffusion equation in spherical coordinates:

$$\partial_t T(r, t) = \frac{p_l(r, t)}{\rho c_p} + \kappa \frac{1}{r^2} \partial_r (r^2 \partial_r T(r, t)), \quad (\text{S1})$$

with $T(r, t)$ the temperature rise with respect to the initial ambient temperature $T(r, 0) = 295.15$ K, κ , ρ , and c_p are thermal diffusivity, density, and heat capacity of water, and $p_l(r, t)$ is the deposited power density (unit in W/m^3). At short time and length scales, convection is neglected. After spatial Fourier transformation of $T(r, t)$ to $\hat{T}(k, t)$, the partial differential equation (S1) becomes a first order ordinary differential equation in time with the solution:

$$\hat{T}(k, t) = \frac{P_0}{\kappa k^4} \left\{ \left[\exp(-jkR_p)(1+jkR_p) - \exp(jkR_p)(1-jkR_p) \right] \left[1 - \exp(-\kappa k^2 t) \right] \right\} \quad (\text{S2})$$

Here, k is the wave vector and R_p is the radius of the nanoparticle. The temperature field $T(r, t)$ is obtained by inverse Fourier transformation of $\hat{T}(k, t)$ back to r -space. The temperature field generated by the array of nanoparticles is then computed using the superposition principle stating that the temperature field in the system equals the sum of the temperature fields generated by the individual sources within the Gaussian laser beam.

The system consists of two media assumed to be semi-infinite: the water and the fused silica substrate. In first approximation, the thermal interaction of these media is neglected. The temperature field can therefore be estimated by:

a) computing the full 3D field for both media,

b) matching the temperature of both media at the interface
c) scaling the temperature field to ensure energy conservation, *i.e.* that the total energy in the system is equal to the energy deposited by the laser.
These steps result in a first order correction for the presence of the substrate whose effect can be seen in Figure 3.7.

3.5.2 Heat diffusion model and associated errors

Figure 3.7: Maximum temperature versus time for four idealised systems: a single sphere (blue), a layer of nanoparticles immersed in water (yellow), a layer of nanoparticles at the interface of 2 media (purple), and an infinitely large heated plane (orange). The former three cases are computed for the same total power deposited, and the latter three ones are computed for the same power density the grey area represent the range of times in which the onset of vaporization was observed.

On small length and time scales, the heat first diffuses out spherically from each nanoparticle (sub-microsecond timescale). As the temperature fields generated by the nanoparticles aligned on the interface start to superpose, the various individual spherical heat fronts undergo a transition towards one 1D planar diffusing heat front. Finally, owing to the finite size of the laser spot, heat diffusion becomes roughly spherical again after a typical time $\tau = R_l^2/(\pi\kappa)$, with R_l the radius of the Gaussian laser beam, see Figure 3.7. There, the temperature converges toward a steady state value. If the steady state temperature is below the nucleation temperature of water, vaporization cannot occur. This leads to the existence a laser power threshold for vapor bubble nucleation.

Table 3.1: Thermal properties used for water and fused silica at 20°C and 200°C

		$\lambda(W/m/K)$	$\rho(kg/m^3)$	$C_p(J/K/kg)$	$D_h(m^2/s)$
water	20°	0.61	997	4170	$1.47 \cdot 10^{-7}$
	200°	0.65	835	4636	$1.68 \cdot 10^{-7}$
fused silica	20°	1.38	2196	742	$8.47 \cdot 10^{-7}$
	200°	1.55	2196	992	$7.12 \cdot 10^{-7}$

In reality, most thermal properties depend on temperature (Table 3.1), making the thermal diffusion equation nonlinear and thus incompatible with the superposition principle. However, the assumption of constant thermal properties in the numerical calculation only induces a marginal error. Figure 3.8 displays the temperature versus time curves for two extreme cases (20°C and 200°C), demonstrating that the difference in predicted temperature rise in the system is only about 10%. The thermal properties at 200°C are chosen, as this temperature is close to the expected superheat.

Figure 3.8: Temperature rise in the system constituted of gold nanoparticles on a substrate immersed in water for a unity laser power, and the properties of water and fused silica at 20°C and 200°C, respectively. The temperature difference is within 10% between the two cases.

The temperature evolution in the system (Figure 3.8) is computed for a unity laser power (1 W). Due to the linearity of the model, the temperature rise in our system can be predicted by multiplying this curve (Figure 3.8) by the applied laser power. The time delay to reach any arbitrary temperature as

a function of the laser power is then obtained by simple spline interpolation, performed using Matlab. Finally, the nucleation temperature in water in our experiment is estimated by minimization of the root-mean-square error between the experimentally measured delays and the modeled delays, computed for a range of temperatures varying from 293 K (room temperature) to 578 K (spinodal temperature) by increments of 1 K.

Figure 3.9: Compensated plot of the delay time and laser power difference. For various temperature increments P_c is the minimum laser power required for bubble nucleation and P is the real laser power. The plateau reveals that $\tau_d \propto (P - P_c)^{1.55}$ consistently describes the data over a large regime of large enough laser power differences.

Figure 3.9 depicts a compensated double logarithmic plot of the delay time necessary to achieve five temperature increments in the system. It reveals an apparent scaling law of $\tau_d \propto (P - P_c)^{1.55}$ for the delay time, for large enough powers and for all temperature increments between 75 K and 475 K.

3.5.3 Point-by-point superheat limit estimate

The root-mean-square minimization procedure described in the previous section was performed for each data point depicted in Figure 3.5b. The result is displayed in Figure 3.10. The dashed lines represent the nucleation temperatures estimates resulting from the fit of the complete dataset. The small scatter in the data demonstrates the robustness of the method and the good

agreement between our simplified model and the experimental data across the whole range of laser powers investigated here.

Figure 3.10: Superheat limit as a function of the laser power obtained by root-mean-square minimization method on each data point of Figure 3.5b. The dashed line represents the critical temperature obtained by fitting the full experimental dataset.

3.5.4 Minimum bubble pressure

At maximum radial expansion, the velocity of the bubble wall is zero. At this instant, the pressure inside the cavitation bubble is minimum and can be estimated using the Rayleigh-Plesset equation:

$$P_{min} \approx P_{at} - \rho R_M \ddot{R}, \quad (S3)$$

where P_{at} is the atmospheric pressure and R_M is the maximum bubble radius. Here, the Laplace pressure is neglected. The acceleration of the water/vapor interface at maximum bubble expansion is on the order of $\ddot{R} = R_M / (4\tau_c^2)$, where τ_c is the bubble lifetime. Therefore,

$$P_{min} \approx P_{at} - \rho \frac{R_M^2}{4\tau_c^2}. \quad (S4)$$

The results are shown in Figure 3.11. The minimum pressure in the bubble appears to be constant across all experiments. Since in the early stage the bubbles are almost exclusively composed of vapor, this pressure is also the

Figure 3.11: Estimated pressure in the bubble at maximum expansion as a function of deposited energy.

saturation pressure of water, and corresponds to a saturation temperature T_{sat} of about 371 K. As a consequence, the latent heat of vaporization stored in the bubble at maximum expansion is directly proportional to the bubble volume.

3.5.5 Gold nanoparticle image after exposure to laser

Figure 3.12: SEM images of the gold nanoparticle sample surface after laser irradiation. No damage is observed on the sample surface.

During irradiation of laser beams on gold nanoparticles, there is a possibility that they might be melted by the heat generated from the plasmonic effect and hence cause damages to sample surfaces. After laser irradiation on a gold nanoparticle sample surface under the same experimental conditions as

reported in the experimental section, we conducted SEM (scanning electron microscope) scanning on the sample surface. The obtained images with different length scales are shown in Figure [3.12](#). From the images, it is obvious that the gold nanoparticles remain intact after laser irradiation.

Chapter 4

Plasmonic Bubble Nucleation and Growth in Water: Effect of Dissolved Air ¹

Fully understanding the dynamics of plasmonic bubbles is essential if one wants to obtain full control over the formation and size of these bubbles. In this work, we quantitatively study the effect of the amount of air dissolved in water on the two phases of plasmonic bubble growth observed before, first - the explosively growing vapor bubble and second - steady growing bubble by the diffusion of gas expelled from the liquid. In the first case, higher gas concentrations lead to lower bubble nucleation temperatures, while in the second case, water undersaturation leads to the deviation of bubble growth from $R(t) \propto t^{1/3}$ law for air equilibrated water to lower scaling exponents.

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4.1 Introduction

When noble nanoparticles immersed in water are irradiated by a laser at their resonant frequency, a huge amount of heat is explosively produced, which leads to the vaporization of the surrounding water, resulting in the formation of bubbles. In these processes, many factors are relevant, such as particles arrangement [107], laser power [108], liquid type [109], and gas concentration [73, 74, 94, 110]. To fully exploit microbubbles potential applications, it is of key importance to understand the nucleation mechanism and explore the growth dynamics of these bubbles.

In Chapters 2 and 3, the plasmonic bubble nucleation mechanism and growth dynamics have been discussed. We found that plasmonic microbubble nucleation and evolution in water can be divided into four phases: an initial giant vapor bubble (phase 1), oscillating bubbles (phase 2), a vaporization dominated growth phase (phase 3), and finally a gas diffusion dominated growth phase (phase 4). Under laser irradiation water surrounding gold nanoparticles becomes superheated [63, 66, 67, 72, 73, 94, 99, 109, 110]. Consequently, vapor bubble nucleates and grows reaching microscale. In partially degassed water, lower gas concentration leads to fewer nucleation sites, thus suppressing the bubble formation. As a result, the superheat temperature in degassed water is higher than in air-equilibrated water. In phase 4, the bubble grows due to the influx of dissolved gas from the surrounding water. Experimental results show that the bubble radius scales as $R(t) \propto t^\alpha$, where $\alpha = f(c_\infty/c_s)$ is a function of dissolved gas concentration.

In spite of the above-mentioned studies, a quantitative investigation for systematically varying gas saturation is still lacking. In this work, such a systematic study is performed at six different concentrations c_∞/c_s of dissolved gas, ranging from highly degassed to oversaturated water. Here, c_∞ is the actual gas concentration, and c_s is saturation concentration. This allows us to further explore the dependence of the dynamic parameters of bubble formation and growth on the gas concentration.

4.2 Experimental details

The experimental setup for plasmonic microbubbles imaging is described in Chapter 2.2 and shown in Figure 2.2. The gold nanoparticle covered sample was placed in a quartz glass cuvette and filled with deionized water. Two high-speed cameras were installed in the setup, one (Photron SA7) equipped

with 5x long working distance objective (LMPLFLN, Olympus) and the other (Photron SA1) equipped with various long working distance objectives: 10x (LMPLFLN, Olympus) and 20x (SLMPLN, Olympus) and operated at various framerates from 5 kfps up to 540 kfps.

The oversaturated water was prepared by keeping the water at 4°C for 12 h and then warming up to the room temperature of 25°C. The measured gas saturation c_∞/c_s was 1.2 (by oxygen meter, Fibox 3 Trace, PreSens). For the air-equilibrated water, a sample bottle was kept open in air for 10 hours; the measured gas saturation level was 1.0. To prepare partially degassed water with different gas concentrations $c_\infty/c_s=0.55, 0.65, 0.75, 0.85, 0.96$, the water was degassed, and then the required values were obtained by tuning the time exposed in air for the highly degassed water.

4.3 Results and discussion

The influence of gas concentration on the nucleation of plasmonic bubbles was investigated with a high-speed camera at a frame rate of 500 kfps. The dependence of the delay time τ_d on the laser power P_l at each gas concentration is shown in Figure 4.1a. It further confirms findings in Chapter 3: at each gas concentration c_∞/c_s , the delay time decreases with increasing laser power P_l , while for a given laser power value, the delay time decreases with an increasing gas concentration in water. Due to the limited spatial resolution of the optical imaging system and the temporal resolution of the high-speed camera, the estimated error in the determination of the delay time is about 2 μ s.

To determine the nucleation temperature for each combination of laser power P_l and gas concentration c_∞/c_s , we followed the procedure described in Chapter 3.3. The fitted curves for the three concentration cases are shown in the double logarithmic scale in Figure 4.1b. The liquid-vapor equilibrium line and the spinodal curve were determined by numerically calculating τ_d required to reach 100 °C and 305 °C, respectively, for given laser power. The estimated nucleation temperatures from the fitting process $T_1 = 190^\circ\text{C}$ for $c_\infty/c_s = 1.2$, $T_n = 212^\circ\text{C}$ for $c_\infty/c_s = 0.8$, and $T_n = 245^\circ\text{C}$ for $c_\infty/c_s = 0.1$ are shown in Figure 4.1c. Indeed, gas molecules aggregations act as nucleation sites and, therefore, facilitate bubble nucleation and reduce the nucleation temperature, T_n , to a value substantially lower than the liquid spinodal temperature.

After the initial giant bubble collapses, it sequentially passes the unstable oscillating phase and vaporization dominated growth, followed by the diffusive growth. This final phase was observed to take place at $t \propto 0.2s$ [94]. We now

Figure 4.1: (a) Measured delay time τ_d as a function of laser power P_l at different gas concentration. At a given laser power, the higher the gas concentration, the shorter the delay time. (b) Double logarithmic plot of τ_d versus P_l . Solid lines are fitted to the measured τ_d following the procedure described in Chapter 3.3. (c) The calculated nucleation temperature T_n for gas concentration $c_\infty/c_s = 0.1, 0.8$ and 1.2 .

focus on this long-term growth dynamics of the bubbles to investigate the role of the dissolved gas on this steady growth phase, varying the gas concentration levels from undersaturation to oversaturation ($c_\infty/c_s = 0.55 - 1.2$).

Figure 4.2 shows the long-term growth dynamics of plasmonic bubbles at six concentration levels $c_\infty/c_s = 1.2, 0.95, 0.85, 0.75, 0.65$, and 0.55 . For the oversaturated water ($c_\infty/c_s = 1.2$), the bubble volume V as a function of time is shown for several laser powers in Figure 4.2a. The bubble volume V increases linearly with time t for all laser powers. The corresponding bubble radius $R(t)$ is shown in Figure 4.2b in double-logarithmic scale. After 0.2 s, R follows an $R(t) \sim t^{1/3}$ scaling law. Figure 4.2c and d show the corresponding results in nearly gas equilibrated case with $c_\infty/c_s = 0.95$. The bubble growth has similar behavior with that in the oversaturated water: the linear relationship of bubble volume versus time and the $1/3$ effective power scaling law of $R(t)$.

The results for less saturated water are displayed in Figures 4.2(e-l). In the water with $c_\infty/c_s = 0.85$ (Figure 4.2e and f), we again observe a similar bubble growth dynamics as in previous cases, *i.e.* almost linear relationship of bubble volume versus time (Figure 4.2e), and α close to $1/3$ (Figure 4.2f). With further degassing the growth dynamics starts to significantly deviate from $1/3$ scaling law. Figure 4.2g shows the bubble volume versus time in water with $c_\infty/c_s = 0.75$. In this case there is no longer linear dependence of V and t . The radius scales as $R(t) \propto t^{0.27}$ (Figure 4.2h). For even lower gas concentrations, namely, $c_\infty/c_s = 0.65$ and 0.55 , α reduces to 0.22 and 0.07 , respectively.

In Chapter 2 it was shown that in the water close to fully saturation

Figure 4.2: Long-term bubble growth dynamics at different gas concentrations and laser powers. Linear plots of bubble volume V (a, c, e, g, i, and k) and double logarithmic plots of bubble radius R (b, d, f, h, j, and l) as functions of time t for gas concentrations $c_\infty/c_s=1.2, 0.95, 0.85, 0.75, 0.65$, and 0.55 , respectively. In oversaturated and nearly air-equilibrated water V linearly increases with time for different laser powers and $R(t)$ follows the $t^{1/3}$ scaling law. At lower gas saturation levels the volume no longer linearly increases with t and the scaling exponent α $R(t) \propto t^\alpha$ deviates from $1/3$ decreasing till 0.07 for degassed liquid with $c_\infty/c_s=0.55$.

Figure 4.3: (a) Effective exponent α as a function of laser power for various gas concentrations c_∞/c_s . (b) Effective exponent α as a function of gas concentration for different laser powers P_l . (c) 3D plot of α as a function of c_∞/c_s and P_l . Approximately, α monotonously increases with both P_l and c_∞/c_s .

the bubble growth is dominated by the influx of gas, which is locally produced around the plasmonic nanoparticles due to heating, as the solubility c_s decreases with increasing temperature, creating local oversaturation. For a production-limited growth (all the expelled gas is taken up by the bubble) the growth rate is constant, $dV/dt = \kappa$ and can be written as [94]:

$$\kappa = -\frac{R_g T}{M_g (P_\infty + \frac{2\sigma}{R})} \frac{c_\infty}{c_s} \frac{dc_s}{dT} \frac{f P_l}{C_w \rho_w} = k_{P_l} \cdot P_l, \quad (4.1)$$

where M_g is the molecular mass of the gas, R_g the gas constant, P_∞ is the ambient pressure and σ the surface tension, ρ_w is water density, and C_w is the specific heat capacity of water, dT is the increase of water temperature. For large bubbles ($R \gg 2\sigma/P_\infty$), κ is proportional to both the relative gas concentration c_∞/c_s and the laser power P_l .

The effective scaling exponent α is used to further investigate the role of the dissolved gas on the bubble steady growth dynamics (Figure 4.3). As shown in Figure 4.3a, the effective exponent α is close to 1/3 for all laser powers if c_∞/c_s exceeds 0.85. For lower gas concentrations, $c_\infty/c_s = 0.55 - 0.75$, the effective exponents are smaller than 1/3 and tend to increase with increasing laser power P_l . Figure 4.3b shows the effective exponent as a function of c_∞/c_s . As seen before, for given laser power, the exponent increases with increasing gas concentration. The dependence of α on both c_∞/c_s and P_l is summarized in the three-dimensional Figure 4.3c.

The above results demonstrate how the dissolved gas influences the steady bubble growth dynamics. For high gas concentrations $c_\infty/c_s \geq 0.85$, there is

a constant influx of gas into the bubble, leading to $R(t) \propto t^{1/3}$, which is the limiting value for the current diffusive growth. For undersaturated water, the exponent is smaller than $1/3$, as water first has to be locally heated up to a temperature where it becomes oversaturated. However, the bubble surface grows with R^2 , which means that the thermal energy transferred per unit area to the bubble/water interface will rapidly decrease. As a result, the amount of oversaturated water in the vicinity of the bubble will decrease too. At some point, the energy transferred to the bubble/water interface from nanoparticles only can maintain equilibrium conditions, and the bubble growth terminates.

It is worth noting that at higher laser powers, α for $c_\infty/c_s=0.65$ and 0.75 in figure 4.3a becomes approximately equal. The relative gas oversaturation, which determines the steady growth of microbubbles, depends on the original amount of dissolved gas (at initial conditions) as well as the instant temperature (and thus the laser power). While for lower laser powers, *i.e.* lower instant temperatures, the initial gas concentration determines the exponent, higher laser powers lead to larger oversaturations, and, therefore, the effect of initial gas concentration becomes weaker. We found a similar behavior for $c_\infty/c_s=0.85, 0.96$, and 1.2 : the scaling exponents are comparable at high laser powers.

4.4 Conclusion

To sum up, the effect of the dissolved gas on the plasmonic bubble nucleation and the steady growth has been systematically studied. In the initial phase, lower gas concentrations lead to longer delay times τ_d , larger bubbles, and higher nucleation temperatures, which implies that the dissolved gas molecules act as nucleation sites. Regarding the long-term growth dynamics, we have shown that the growth rate κ of the bubble volume monotonically increases with gas concentration c_∞/c_s and laser power P_l . Our experimental results show that plasmonic microbubble growth can be approximated by the power law dependence $R(t) \propto t^\alpha$, where $\alpha = f(c_\infty/c_s)$. The effective exponent α is close to $1/3$ in oversaturated and nearly saturated water ($c_\infty/c_s = 1.2, 0.95, 0.85$) despite the laser power. For lower saturation levels ($c_\infty/c_s = 0.75, 0.65, 0.55$), the effective exponent deviates from $1/3$ and monotonously decreases with decreasing P_l and c_∞/c_s , reaching 0.07 for the lowest laser power and lowest gas saturation level.

Chapter 5

Plasmonic bubbles in n-alkanes

1

In this section we study the formation of microbubbles upon the irradiation of an array of plasmonic Au nanoparticles with a laser in n-alkanes (C_nH_{2n+2} , with $n = 5-10$). Two different phases in the evolution of the bubbles can be distinguished. In the first phase, which occurs after a delay time τ_d of about 100 μs , an explosive microbubble, reaching a diameter in the range from 10 μm to 100 μm , is formed. The exact size of this explosive microbubble barely depends on the carbon chain length of the alkane, but only on the laser power P_l . With increasing laser power, the delay time prior to bubble nucleation as well as the size of the microbubble both decrease. In the second phase, which sets in right after the collapse of the explosive microbubble, a new bubble forms and starts growing due to the vaporization of the surrounding liquid, which is highly gas rich. The final bubble size in this second phase strongly depends on the alkane chain length, namely it increases with decreasing number of carbon atoms. Our results have important implications for using plasmonic heating to control chemical reactions in organic solvents.

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5.1 Introduction

Microbubbles generated around plasmonic gold nanoparticles by resonant laser irradiation are relevant to various applications in biomedical diagnosis and cancer therapy [35, 79, 80, 88, 89, 111], solar energy harvesting [60, 61, 77, 85, 90–92], micromanipulation of nano-objects [86, 107, 112–114] and locally enhanced chemical reactions [48, 78]. Controlled and highly tunable plasmonic bubble formation is in particular suitable for colloidal nanoparticles deposition and clusters formation on a substrate to enhance the signal for Raman spectroscopy in ultrasensitive analysis and sensing [87]. Moreover, the plasmonic effect may locally facilitate and enhance catalytic conversion while the entire system still remains at ambient temperature, which allows to utilize the conversion process in miniaturized systems suitable for lab-on-a-chip applications [78].

Owing to the technological relevance of these microbubbles, the dynamics of their growth and shrinkage has been scrutinized in several investigations [60, 72–74, 77, 85, 94, 110]. Plasmonic bubble generation is a complex phenomenon, which involves numerous physical processes, such as heat transfer from the nanoparticle to the liquid, supersaturation of the liquid, phase transitions, bubble nucleation, diffusion of gas dissolved in the liquid, evaporation of the liquid and many others. The irradiation of metal nanoparticles immersed in liquid with a continuous laser at resonant wavelength results in plasmonic excitation of the nanoparticles and thereby, in a rapid increase of the temperature of the nanoparticles. Consequently, the liquid surrounding the nanoparticles also exhibits an increase in the temperature, albeit much slower than the nanoparticles. In the absence of any nuclei, the surrounding liquid can become superheated, i.e., reach a temperature that exceeds the boiling temperature. Eventually, however, nucleation will occur, resulting in the explosive growth of a vapor microbubble. In a recent study we have found that the dynamics of plasmonic microbubble nucleation and evolution *in water* can be divided into 4 subsequent phases, namely, an initial explosive vapor bubble phase (life phase 1), an oscillating bubble phase (life phase 2), a vaporization dominated growth phase (life phase 3), and a gas diffusion dominated growth phase (life phase 4) [94, 110].

Up to now, the studies have focused on the formation of plasmonic bubbles in pure water and aqueous solutions or suspensions. However, many plasmonic assisted processes take place in presence of an organic phase. In order to better understand the physics of the formation and growth of these microbubbles in different liquid media, it is essential to vary the relevant physical

properties of the liquid host, such as the boiling point, the enthalpy of vaporization, the heat capacity, the surface tension, the thermal conductivity, and the gas solubility of the host liquid. In this study, our liquids of choice are n-alkanes. These are simple hydrocarbons, which consist of a carbon backbone and their general formula is C_nH_{2n+2} . In Table 5.1 various physical properties of the n-alkanes and water are summarized. Their properties depend on the carbon chain length, which make them ideally suited for investigating bubble formation in an organic phase. Here we will systematically study the dynamics of plasmonic microbubbles formed on the substrate with an array of gold nanoparticles (GNP) with a diameter of about 100 nm immersed in n-alkane under a continuous laser irradiation ($\lambda=532$ nm).

We found that, as compared to water as host medium, the dynamics of plasmonic microbubbles in n-alkanes differs significantly. The bubbles in n-alkanes exhibit only two consecutive phases during their evolution, rather than four, as in the water case. In the first phase, which occurs after a delay time τ_d after turning on the laser, still an explosive vapor microbubble is formed. In the second phase, after the collapse of the initial microbubble, a new bubble forms and starts growing due to the vaporization of the surrounding liquid. The life phases 2 and 4 found in the water case are however absent. These results bear important implications for using plasmonic heating to control chemical reactions in organic solvents.

Table 5.1: Physical properties of water and n-alkanes at 20° C [115].

	H_2O	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
Boiling point (K)	373.2	309.2	341.9	371.5	398.8	423.9	447.2
Molar mass (g/mol)	18.01	72.15	86.18	100.21	114.23	128.76	142.29
Density (kg/m^3)	998	626	659	684	702	718	730
Heat capacity (kJ/kgK)	4.184	2.293	2.231	2.222	2.209	2.189	2.174
Enthalpy of vap. (kJ/kg)	2193.2	360.2	337.8	316.6	304.4	288.5	281.3
Surface tension (mN/m)	72.74	16.01	18.49	20.55	21.64	22.90	23.82
Viscosity ($mPas$)	1.002	0.227	0.312	0.411	0.541	0.697	0.912
Thermal cond. (W/mK)	0.598	0.113	0.128	0.132	0.126	0.128	0.131
N_2 solubility (mol/mol)	0.017	0.559	0.449	0.374	0.324	0.281	0.252

5.2 Methods

The experimental setup for plasmonic microbubbles imaging is shown in Figure 2.2 and was described in Chapter 2.2. The gold nanoparticle covered sample was placed in a quartz glass cuvette and filled with liquid. 400 μs and 4s laser pulses were generated and controlled by pulse/delay generator in order to study the short-term and the long-term dynamics of microbubbles, respectively. Two high-speed cameras were installed in the setup, one (Photron SA7) equipped with 5x long working distance objective (LMPLFLN, Olympus) and the other (Photron SA1) equipped with various long working distance objectives: 5x (LMPLFLN, Olympus), 10x (LMPLFLN, Olympus) and 20x (SLMPLN, Olympus) and 50x (SLMPLN, Olympus) and operated at various framerates from 5 kfps up to 500 kfps. The first camera was used for a top-view and the second one for side-view. Two light sources Olympus ILP-1 provided illumination for the two high-speed cameras. In our experiments n-alkanes from Sigma-Aldrich and MiliQ water were used.

5.3 Results and discussion

The initial stages of the explosive growth of plasmonic microbubbles in n-alkanes has been monitored with a high-speed camera operated at a frame rate of up to 500 kfps. Figure 5.1 depicts examples of these vapor microbubbles at their maximum expansion for water, pentane, hexane, heptane, octane and nonane, respectively. Decane is not considered here, as the life cycle of an explosive bubble in decane is too short to be characterized with available frame rates. Figures 5.2(a) and 5.2(b) show the bubble radius R_b and the delay time before nucleation of the bubble τ_d , respectively. With increasing laser power P_l , the bubble radius as well as the delay time decrease, similarly to what has been observed for water [110]. The delay time increases with increasing alkane chain length, whereas the maximum microbubble size mainly depends on the laser power.

Figure 5.1: Examples of initial explosive bubble at maximum expansion in a) water and n-alkanes: b) pentane, c) hexane, d) heptane, e) octane and f) nonane at the same laser power $P_l = 60$ mW.

For a given laser power of 60 mW, the microbubbles formed in water have a radius of about 50 μm and are by far the largest, followed by pentane, hexane, heptane, octane and finally nonane. It is worth noting that only a slight difference in bubble size of the various n-alkanes was observed. On first sight this seems counterintuitive, considering the significant variation in boiling temperatures of the alkanes, from 36 °C for C_5H_{12} to 151 °C for C_9H_{20} , but we will explain this later.

Figure 5.2: a) Maximum bubble radius R_{max} versus laser power P_ℓ . b) Delay time τ_d prior to bubble nucleation versus laser power P_ℓ . c) Maximum bubble volume V_{max} versus the deposited energy $E_d = P_\ell \tau_d$. C5, C6, C7, C8 and C9 refer to pentane, hexane, heptane, octane and nonane, respectively.

Figure 5.2(c) shows the volume of the microbubble versus the cumulative energy before nucleation, hereafter referred to as the deposited energy, $E_d = P_\ell \tau_d$. For all liquids the volume of the microbubble scales linearly with the deposited energy. The curve for water in Fig. 5.2(c) is located in between the curves of heptane and octane, which is consistent with the boiling temperatures of these liquids, i.e. 98 °C for heptane and 126 °C for octane, respectively.

Prior to bubble nucleation, the liquid has to be heated up to a temperature that exceeds its boiling temperature. Particularly, the nucleation temperature of very pure liquids can be much higher than their boiling temperature [102, 103]. There is, however, a limit to this superheating. For a given pressure, the maximum attainable temperature is the so-called spinodal temperature. At the spinodal temperature the evaporation enthalpy vanishes, resulting in spontaneous homogeneous nucleation. However, in most cases nucleation occurs at a temperature substantially lower than the spinodal tem-

perature, owing to the presence of tiny cracks, cavities or pits filled with gas, impurities or aggregations of gas molecules that can act as centers of nucleation [103–105]. The latter nucleation process is referred to as heterogeneous nucleation. A schematic phase diagram is shown in figure 5.3 (a).

Figure 5.3: a) Schematic phase diagram. (b-f) Double logarithmic plot of delay time τ_d as function of laser power P_l for (b) pentane, (c) hexane, (d) heptane, (e) octane and (f) nonane. P_{th} is the threshold laser power below which no nucleation can occur. The symbols represent the experimental data and the solid lines are the spinodal lines (bronze), the equilibrium lines (black), and the fitted curves using Eq. 5.1. All fitted lines are within the metastable region, i.e. between the equilibrium and spinodal boundaries.

In order to determine the nucleation temperature, just as done in our previous study for water [110], we numerically calculate the temperature evolution around a nanoparticle, assuming spherical geometry, by solving the heat conduction equation,

$$\partial_t(T(r, t)) = \frac{p_l(r, t)}{\rho c_p} + \kappa \frac{1}{r^2} \partial_r(r^2 \partial_r T(r, t)), \quad (5.1)$$

where κ , ρ , and c_p are thermal diffusivity, density, and heat capacity of n-alkanes, r is the distance to the GNP, and $p_l(r, t)$ is the deposited power density (unit in W/m^3), which is assumed to be constant for a radius r within the GNP,

and 0 elsewhere. The temperature field generated by the nanoparticles array has been calculated by superposition, within a Gaussian beam profile. The resulting time-dependent temperature field is given by

$$T(x, y, z, t) = \sum_{i=1}^N (T_i(d_{i,(x,y,z)}, t)) , \quad (5.2)$$

where T_i the temperature field created by the nanoparticle i , d_i the distance from the center of the i th nanoparticle. Using the above equations, one directly obtains the time required to reach a given temperature for a given laser power. This approach was used for every alkane to fit the experimental data using a root-mean-square-minimization method, resulting in the solid curves in Fig. 5.3 (b-f). The nucleation temperatures for the alkanes are 79°C, 102°C, 123°C, 139°C and 160°C for C_5H_{12} , C_6H_{14} , C_7H_{16} , C_8H_{18} and C_9H_{20} , respectively. In Figure 5.4, the boiling, nucleation, and spinodal temperatures as well as the superheating temperature (nucleation temperature – boiling temperature) are shown. Boiling, nucleation and spinodal temperatures all increase with the length of the alkane chain. Notably, the degree of superheat decreases with increasing number of carbon atoms in alkanes from 63 K for pentane to 29 K for nonane.

Figure 5.4: Boiling, nucleation, spinodal and superheating (difference between average nucleation and boiling temperatures) temperatures for pentane, hexane, heptane, octane, and nonane. The nucleation temperatures from repeating experiments have been plotted to show the reproducibility in the different runs. All error bars lie within the size of the markers.

The bubble nucleation mechanism in alkanes appears to differ from the one

in water. Air solubility in water decreases with increasing temperature and, therefore, the heated liquid becomes supersaturated and, therefore, expelled gas molecules facilitate bubble nucleation. However, in n-alkanes the solubility of air *increases* with increasing temperature [116,117], causing undersaturation in the heated zone. However, it is important to point out (see Table 5.1) that the amount of dissolved gas in alkanes is 15-30 times more than in water, so the gas level in the surrounding liquid may still play a role in bubble nucleation.

From the above mentioned numerical calculations the threshold values of laser power P_{th} for all alkanes have been extracted, namely $P_{\ell}^{th} = 18$ mW, 24 mW, 28 mW, 34 mW, 37 mW for pentane, hexane, heptane, octane and nonane, respectively. The laser powers are consistent with the experimental results (see Figure 5.2), which confirms the robustness of our method. Below these threshold values, heat diffusion prevents the system from reaching the required nucleation temperature and, therefore, a bubble cannot be generated.

The conversion efficiency of light energy absorbed by the NP to vapour generation is crucial for various applications. The efficiency can be estimated as a ratio of the energy stored in the bubble and the deposited energy. Using the ideal gas law and Antoine's equation we obtain:

$$ef = \frac{E_{bubble}}{E_{deposited}} = \Lambda_{vap} \frac{MP_{sat}V_{max}}{R_g \left(\frac{B}{A - \lg P_{sat}} - C \right) \xi P_l \tau_d}, \quad (5.3)$$

where P_{sat} is saturation pressure, M is the molar mass, Λ_{vap} is the latent heat of vaporization, $R_g = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, A , B and C are component-specific constants, and ξ is the nanoparticle absorption coefficient. The estimated efficiencies for all alkanes as functions of the deposited energy are shown in Figure 5.5. The efficiency decreases with increasing chain length, which means that for longer chains more energy is lost for bulk liquid heating. All curves in Fig. 5.5 follow the same trend: starting from a low deposited energy, which corresponds to short delay times and high laser powers, the efficiency goes up, reaches a maximum, and then rapidly decrease with increasing deposited energy, i.e. longer delay times and lower laser powers. The initial efficiency increase is caused by the heat diffusion dynamics (see Chapter 3.5.2 and Figure 3.7). At the time scale of tens of μs the heat diffusion is close to the 1D planar case, while later on the transition from planar heat diffusion to spherical heat diffusion occurs. Further increase of the deposited energy reflects long delays prior to nucleation, consequently, there is enough time for heat to diffuse deep into the bulk liquid. Therefore, the energy losses increase and the conversion efficiency quickly drops.

Figure 5.5: Conversion efficiency of the GNPs for the energy converted from laser heat deposition to vaporization enthalpy contained in the vapor bubble.

As already mentioned in the introduction, in water, there are four distinctly different phases of plasmonic microbubbles evolution [94, 110]. Up to now we only discussed the first one. For water, this first bubble phase is analogous to the here discussed first phase of alkanes and involves the formation of an explosive vapor bubble [110].

However, in the case of water, the first phase is followed by a second oscillating bubble phase. In the case of alkanes this second phase is completely absent, which we ascribe to the fact that air solubility in alkanes is 15-30 times higher than in water (see Table 5.1). Therefore, the bubble, which is generated by liquid evaporation right after the collapse of the first explosive bubble, already contains some gas and has more chances to survive and stabilize.

Evidence for the existence of gas in the bubble for the n-alkane case comes from the peculiar bubble behavior during the bubble collapse, which is especially pronounced for n-pentane. Instead of complete shrinkage, the bubble exhibits some sort of rebound, retains a certain size with a wavy interface and then detaches from the substrate, rising in the cool liquid medium. This dynamics is quite intriguing by itself but falls out of the scope of this paper. However, it is remarkable that the bubble does not vanish or condense immediately in this environment. Also the phenomenon of a stable rising bubble clearly suggests that the bubble formed after the collapse (or partial collapse in the case of n-pentane) of the initial explosive bubble is indeed partially filled with gas.

During the second phase the bubble steadily grows. In Figure 5.6 (a) the

Figure 5.6: a) Radius versus time during plasmonic bubble growth in n-alkanes at 100 mW laser power. The inset shows the same data as double logarithmic plot with two slopes given as orientation; (b-g) Snapshots of the steadily growing bubble in n-alkanes: b) C_5H_{12} , c) C_6H_{14} , d) C_7H_{16} , e) C_8H_{18} , f) C_9H_{20} , g) $C_{10}H_{22}$, all after 20 ms of laser irradiation.

bubble radius versus time is shown for the first 4 seconds of laser irradiation at a laser power of 100 mW. The inset shows a double logarithmic plot of the bubble radius versus time. It is immediately clear from Figure 5.6 that the longer the carbon chain of the alkane, the smaller the bubble. Whilst in C_5H_{14} , C_6H_{14} , C_7H_{16} and C_8H_{18} , the bubble grows steadily with time, the growth of C_9H_{20} and $C_{10}H_{22}$ bubbles quickly saturates. From the data presented in Fig. 5.6, one can calculate the energy stored in the vapor bubble $E_{required} = \rho_v V_v (C_p \Delta T + \Lambda_{vap})$ for any alkane at any given time, for a laser power of 100 mW. The energy stored in the pentane bubble is an order of magnitude larger than that stored in the decane bubble. Remarkably, this result for the second phase of the bubble evolution mirrors the efficiency calculated in Fig. 5.5 for the first phase. Power losses through the bubble interface might be estimated as $\mathcal{P} = 4\pi R^2 \lambda \frac{T_{boil} - T_0}{\delta}$, where δ is thermal boundary layer thickness, and T_0 is room temperature (20°C). Given the similar heat diffusion coefficients and

thermal boundary layer thicknesses, for the same bubble size the decane bubble experiences a much larger energy loss than the pentane one $\frac{\mathcal{P}^{C10}}{\mathcal{P}^{C5}} \approx \frac{T_{boil}^{C10} - T_0}{T_{boil}^{C5} - T_0} \approx 10$.

The effective growth exponent α of the bubble radius dynamics $R \propto t^\alpha$ for the n-alkanes versus laser power is plotted in Figure 5.7. Interestingly, the effective growth exponent of pentane, hexane, heptane, octane slightly varies from 0.25 to 0.30 for all laser powers, whereas for nonane and decane it is substantially smaller (< 0.1). In the case of water the effective growth exponent is close to 0.33 and bubble growth is dominated by gas that is expelled from the liquid in the vicinity of the bubble, due to the decrease of gas solubility in water with increasing temperature [94]. In the case of n-alkanes, however, the solubility of gas increases with increasing temperature and therefore, the influx of dissolved gas is not the contributor to the second and final bubble life phase of alkanes. So the main source of the growth of the bubble is evaporation of the liquid and therefore, we conclude that the second life phase of plasmonic bubbles in n-alkanes is vaporization dominated.

Figure 5.7: The effective growth exponent α of the bubble radius ($R \propto t^\alpha$) for pentane, hexane, heptane, octane, nonane and decane at different laser powers.

In the second phase, the growth of the bubble is governed by a competition between heating from the nanoparticles and heat loss through the bubble interface as sketched in Figure 5.8. Owing to the large diffusivity of the gas ($D_{dif} \approx 10^{-5} \text{ m}^2/\text{s}$) and to the slow dynamics at hands (seconds), the temperature in the gas is homogeneous. Additionally, the thermal boundary layer around the bubble is given sufficient time to fully develop ($\delta_{th} = R_b$). In first approximation, heat loss is therefore proportional to the bubble radius. As a result, the bubble will grow until the heat loss through the interface bal-

ances the thermal energy provided by the nanoparticles. Solving two heat conduction equations corresponding to this steady state for the gaseous and liquid phase results in an estimated bubble size $R_{stable} = \frac{\xi P_i}{4\pi\lambda_l(T_{boil}-T_0)}$, where ξ is the nanoparticles absorption coefficient, P_i is provided power, λ_l is liquid conductivity and T_0 is room temperature (20 °C).

For light alkanes with low boiling temperatures, the delivered thermal energy is sufficient to heat up and vaporize a large volume of liquid. This growth, however, is severely hindered for higher boiling temperatures as can be seen from Fig. 5.6(a) for C_9H_{20} and $C_{10}H_{22}$. It is worth to mention that despite a vaporization dominated growth during the second phase, in n-alkanes the bubbles are effectively composed of a gas/vapor mixture. Due to the high amount of dissolved gas in alkanes (15 to 30 times more than in water), a lot of gas is collected by the bubble during the vaporization process.

Figure 5.8: Schematic of the mechanism of bubble growth in n-alkanes on the long timescale.

5.4 Conclusion

Plasmonic microbubbles in n-alkanes from C_5H_{12} to $C_{10}H_{22}$ display two different phases in their evolution. The first phase occurs after a delay time τ_d after illumination of about 100 μs , when an explosive vapor microbubble is formed. The size of this bubble barely depends on the alkane chain length. The achievable local superheat of the alkane as well as light to vapor conversion efficiency decrease with elongating carbon chains. The second phase, which is also vaporization dominated, is characterized by a steadily growing bubble. The effective scaling law exponent α in $R(t) \propto t^\alpha$ is 0.25 - 0.30 for pentane,

hexane, heptane and octane, whereas for nonane and decane it is substantially smaller (<0.1). Significant differences between plasmonic bubble dynamics in water and n-alkanes thus have been demonstrated, which is important for the design and regulation of the systems based on plasmonic bubble formation.

Chapter 6

Gas-vapor interplay in plasmonic bubble shrinkage ¹

The understanding of the shrinkage dynamics of plasmonic bubbles formed around metallic nanoparticles immersed in liquid and irradiated by a resonant light source is crucial for the usage of these bubbles in numerous applications. In this paper we experimentally show and theoretically explain that a plasmonic bubble during its shrinkage undergoes two different phases: first, a rapid partial bubble shrinkage governed by vapor condensation and, second, a slow diffusion-controlled bubble dissolution. The history of the bubble formation plays an important role in the shrinkage dynamics during the first phase, as it determines the gas-vapor ratio in the bubble composition. Higher laser powers lead to more vaporous bubbles, while longer pulses and higher dissolved gas concentrations lead to more gaseous bubbles. The dynamics of the second phase barely depends on the history of bubble formation, i.e. laser power and pulse duration, but strongly on the dissolved gas concentration, which defines the concentration gradient at the bubble interface. Finally, for the bubble dissolution in the second phase, with decreasing dissolved gas concentration, we observe a gradual transition from a $R(t) \propto (t_0 - t)^{1/3}$ scaling law to a $R(t) \propto (t_0 - t)^{1/2}$ scaling law, where t_0 is the lifetime of the bubble and theoretically explain this transition.

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6.1 Introduction

Plasmonic nanoparticles immersed in a liquid and irradiated by a resonant laser can rapidly heat up to high temperatures, due to their peculiar absorption ability, and transfer the heat to the surrounding liquid, causing its heating and subsequent evaporation. The dynamics of these plasmonic bubbles has been extensively studied at the nanoscale [63, 64, 66, 67, 118–122] as well as at the microscale [73–75, 85, 93, 109, 123], due to numerous important implications in biomedical therapy [35, 79, 80, 88, 89, 111], nano/micro manipulation [86, 107, 112–114], and enhancement of chemical reactions [48, 78]. Recently, it has been shown that plasmonic microbubbles forming on the water-immersed gold nanoparticle arrays under resonant cw-laser irradiation undergo four different phases: first – nucleation, growth and collapse of a giant vapor bubble, second – an oscillating bubble phase, third – bubble growth, which is mainly governed by water vaporization and fourth – slow bubble growth due to gas diffusion from the bulk liquid [94, 110]. So, the interplay between gas and vapor is crucial for the dynamics of plasmonic microbubbles.

After switching off the laser a plasmonic microbubble formed in water does not collapse immediately, but remains present on the substrate for minutes or even hours [73, 74]. That implies that the plasmonic bubble initially partially consists of gas and, therefore the bubble is quite stable in the liquid. The process of this slow bubble dissolution is governed by gas diffusion from highly-saturated areas in the vicinity of the bubble to the less saturated bulk liquid. Right before the process of slow bubble dissolution, rapid partial bubble shrinkage occurs, during the first milliseconds after switching off the laser, due to the fast vapor condensation. The pure vapor bubble collapse has been thoroughly scrutinized in numerous studies [27, 30, 31, 124–128], while the collapse of the bubble, which consists of gas/vapor mixture is still a topic of current research [31, 129–131]. A typical, experimentally obtained, dependence of the plasmonic bubble radius on time during shrinkage is shown in Figure 6.1.

In our experiments the influence of various parameters, such as dissolved gas concentration, which can be expressed in terms of gas saturation level c_g/c_{sat} , where c_g is the gas concentration and c_{sat} the saturation gas concentration, laser power P_l , and laser pulse duration τ_p during bubble growth on the subsequent bubble shrinkage is studied. The dynamics of the first phase (condensation-dominated) strongly depends both on the history of bubble formation, *i.e.* laser power and laser pulse length, and on dissolved gas concentration in the water, as they determine the bubble composition right be-

fore stopping of the laser irradiation. The second phase (diffusion-dominated) barely depends on the history of bubble formation, but strongly depends on the dissolved gas concentration. The dissolved gas concentration determines the effective scaling exponent for the bubble radius evolution in time. Our results bear important implications for the design and control of plasmonic microbubbles for various applications.

Figure 6.1: The two different regimes are clearly distinguishable during plasmonic bubble shrinkage: phase 1 – rapid bubble shrinkage governed by vapour condensation and phase 2 – slow bubble dissolution due to gas diffusion from the bubble to the bulk liquid.

6.2 Experimental details

The experimental setup for plasmonic microbubbles imaging is shown in Figure 2.2 and was described in Chapter 2.2. The gold nanoparticle covered sample was placed in a quartz glass cuvette and filled with deionized water. Various pulses lengths were generated and controlled by pulse/delay generator. Two high-speed cameras were installed in the setup, one (Photron SA7) equipped with 5x long working distance objective (LMPLFLN, Olympus) and the other (Photron SA1) equipped with the long working distance objective 50x (SLM-PLN, Olympus) and operated at various framerates from 50 fps up to 500 kfps. The optical images have been processed with an image segmentation algorithm in Python for the extraction of the bubble parameters. Gas concentration levels have been measured by an oxygen meter (Fibox 3 Trace, PreSens). For obtaining the air-equilibrated water, a sample bottle containing deionized water was kept open in air for 10 hours, the measured gas concentration level

is $c_g/c_{sat} = 0.99$. Partially degassed water with different gas saturation levels was prepared by tuning the time of deionized water degassing in a vacuum chamber and exposing in air.

6.3 Results and discussion

6.3.1 Condensation-dominated shrinkage

As was already mentioned, right after turning off the laser, the bubble quickly partially shrinks, due to vapor condensation. To illustrate this process, the bubble volume V as well as the normalized volume V/V_0 , where V_0 is bubble volume at the moment we switched the laser off, as a function of time during the first 100 ms after 0.1 s of laser irradiation in water with gas saturation level $c_g/c_{sat} = 0.99$ for different laser powers are shown in Figures 6.2a and 6.2b, respectively. One can see that for all laser powers rapid bubble shrinkage occurs during the first milliseconds but then slows down, followed by much slower volume reduction. The snapshots of the process in various moments of time are shown in Figure 6.2d. From Figure 6.2a, it is clear that at the specified parameters $\tau_p = 0.1$ s and $c_g/c_{sat} = 0.99$ higher laser powers lead to larger bubbles before switching off the laser. At the same time, the initial volume drop is much larger for big bubbles than for the small ones: for the lowest laser power used in the experiments $P_l = 50$ mW, the normalized bubble volume drops to 0.75 during first 100 ms after turning off the laser (Figure 6.2b), while it reduces to 0.52 for the highest laser power $P_l = 200$ mW during the same time period. This finding implies that in the second case there is relatively more vapor in the bubble than in the first case. Indeed, with higher laser powers, more energy can be provided to the system to evaporate the liquid in the vicinity of the bubble.

In a nutshell, for specified parameters (τ_p and c_g/c_{sat}) higher laser powers lead to larger bubbles with larger vapor portion in the total bubble composition and, therefore, a greater volume drop during the first milliseconds of bubble shrinkage has been observed. It is clear that the bubble behaviour during this phase is defined by the bubble composition right before turning off the laser irradiation. The previously fixed parameters τ_p and c_g/c_{sat} certainly influence the initial bubble composition as well. In order to thoroughly study these dependences we have considered a broad range of parameters: laser powers, P_l : 50, 80, 110, 140, 170 and 200 mW, pulse lengths τ_p : 0.03, 0.05, 0.1, 0.2, 0.5 s and gas saturation levels, c_g/c_{sat} : 0.99, 0.79, 0.64, 0.50 and 0.32.

Figure 6.2: a) Bubble volume, b) normalized bubble volume and c) normalized bubble volume in double-logarithmic scale as a function of time right after switching off the laser after 0.1 s of irradiation for various laser powers in water with $c_g/c_{sat} = 0.99$, d) snapshots of plasmonic bubble shrinkage in air-equilibrated water during the first 90 ms after switching off the laser after a 0.1 s laser pulse with a laser power of $P_l = 200$ mW. The first frame (0 ms) corresponds to the moment when the laser was switched off.

The gas-vapor ratio in the total bubble composition can be estimated, assuming that after the initial rapid partial shrinkage all the vapor has already condensed and considering the bubble as a pure gas bubble. This assumption is reasonable, as the complete vapor bubble condensation occurs in order of milliseconds [31]. Therefore, the slow shrinkage part (almost horizontal part of the lines at Figure 6.2b) can be linearly fitted and extrapolated to estimate, directly from Figure 6.2b, the part of the bubble that has been condensed, in other words, what was the vapor portion in the initial bubble composition.

Following the above method vapor portions in total bubble volume as a function of P_l at various gas concentrations for $\tau_l = 0.5, 0.2, 0.1, 0.05$ and 0.03 s have been estimated and presented in figures 6.3 (a)-(e), respectively. First of all, as expected, for all dissolved gas concentrations c_g/c_{sat} and laser pulse lengths τ_p , the vapor fraction V_{vapor}/V_{total} increases with increasing laser power. For example, in water with $c_g/c_{sat} = 0.79$ after 0.5 s of laser irradiation (Figure 6.3a) the vapor portion in the bubble composition gradually increases from 0.14 to 0.24 with increasing laser power from 50 mW to 200 mW, re-

Figure 6.3: $V_{\text{vapor}}/V_{\text{total}}$ as a function of P_l for a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s, e) 0.03 s used for bubble formation and various water saturation levels c_g/c_{sat} : 0.99 (blue), 0.79 (orange), 0.64 (green), 0.50 (red), 0.32 (purple); $V_{\text{gas}}/V_{\text{total}}$ as a function of P_l and τ_l for saturation levels c_g/c_{sat} : f) 0.99, g) 0.79, h) 0.64, i) 0.50, j) 0.32.

spectively. When more power is provided, there is more energy available in the system to evaporate the liquid during bubble growth. One can also notice that, for all pulse lengths and laser powers, bubbles, which have been formed in less saturated liquid, contain relatively more vapor than the ones generated in water with a higher dissolved gas concentration. For example, for $\tau_l = 0.5$ s, bubbles in water with 99% of air concentration consist of only 0.13...0.21 vapor, whilst, approximately, half of the bubble's volume in water with 32% of dissolved gas concentration is vapor. For less saturated water, there is lack of gas to diffuse into the bubble; therefore, the bubbles are more vaporous.

The gas volume portion in the initial total bubble volume as a function of P_l and τ_p for gas saturation levels $c_g/c_{sat} = 0.99, 0.79, 0.64, 0.50$ and 0.32 , respectively, is shown in figures 6.3 (f)-(j). The gas fraction in the bubble rapidly decreases with shortening of the laser pulse, which means that bubbles become more vaporous. A similar trend was observed for all water saturation levels. For example, in water with gas concentration of 99% (Figure 6.3f) the gas portion in the bubble composition, under the lowest laser power in our experiments - $P_l = 50$ mW, decreases from 0.87 to 0.59 with decreasing laser pulse duration from 0.5 s to 0.03 s, and decreases from 0.79 to 0.31 for the highest laser power $P_l = 200$ mW. The plasmonic microbubble during its steady growth undergoes two consecutive phases: an initial phase, governed by liquid evaporation ($\sim 10...20$ ms) and a second phase, governed by gas diffusion from the bulk liquid (>0.1 s) [94]. Therefore, for short laser pulses bubble growth is mainly in the evaporation-controlled regime and there is insufficient time for the gas to diffuse into the bubble. Therefore, these plasmonic bubbles are more vaporous. With increasing pulse duration, the transition to the diffusive-controlled regime occurs and, therefore, these bubbles turn into more gaseous bubbles. It is worth while to mention that even for the short laser pulses ($\tau_p = 0.03$), during which bubble growth is mainly governed by liquid evaporation, a considerable amount of gas is still present in the bubble, reaching more than a half of the bubble volume for low laser powers.

In order to estimate the influence of the initial bubble composition on the first shrinkage phase, one can extract the effective scaling exponent α from $V(t) \propto t^\alpha$ for the first 5 milliseconds after the end of laser irradiation. The effective scaling exponent as a function of P_l and τ_p is shown in Figure 6.4a with its projections to the $\alpha - P_l$ plane and $\alpha - \tau_p$ plane in Figures 6.4b and 6.4c, respectively. No clear dependence can be figured out from these plots. However, it turned out that α strongly depends on the vapor portion in the initial bubble composition (Figure 6.4d). The more gas is contained in the

bubble, the smaller the absolute value of α is. The behaviour is universal for all considered P_l , τ_p and c_g/c_{sat} .

6.3.2 Comparison with Rayleigh-Plesset type model and the diffusion equation

For a more quantitative description of the process, we compare our experimental results with a model developed for bubble growth/shrinkage, which takes into account temperature and gas diffusion in the liquid and temperature and gas-vapor diffusion in the bubble. [131] The model approximates the bubble as a complete sphere. Both the gas and the vapor are assumed to behave like ideal gases. The radial motion of the bubble is described by the Rayleigh-Plesset equation corrected for compressibility effects of the liquid. The pressure inside the bubble is assumed to be spatially uniform and is determined from a combination of the continuity and energy equations. The temperature field in the gas-vapor mixture is obtained from the enthalpy equation, including the effect of gas-vapor diffusion. Conservation of the gas, liquid/vapor and energy across the bubble interface is imposed. The model is solved numerically by a spectral method, which reduces the problem to a system of ordinary differential equations. For a more detailed description, the reader is referred to our recent prior publication. [131]

The calculation starts at the instant in which the laser is turned off. The measured bubble radius is used as the initial radius. The initial temperature of the liquid surrounding the bubble is used as a fitting parameter. Given a provisional value for this quantity, with the assumption of thermodynamic equilibrium, the partial pressure of the vapor is known, and the partial pressure of the gas follows from the assumption of mechanical equilibrium. The gas-vapor mixture is assumed to be initially homogeneous at the initial temperature. The initial surface temperature and gas concentration at the bubble surface are assumed to connect smoothly with the ambient values. The results are somewhat dependent on this initial distribution, which cannot be accurately determined from the experiment.

In spite of this uncertainty, it can be seen from Figure 6.5 that the model is able to reproduce the bubble evolution reasonably well after the laser has been switched off for as long the data were recorded. The error is noticeable during the time in which the bubble shrinkage switches from condensation dominated to gas-diffusion dominated, which is when the influence of the unknown initial temperature distribution in the liquid is particularly significant. Indeed, in Figure 6c, for which the laser power is small and the liquid is nearly saturated

Figure 6.4: a) The effective scaling exponent α in the $V(t) \propto t^\alpha$ during the first 5 ms of bubble shrinkage as a function of the pulse length τ_p and laser power P_l , b) projection to the $\alpha - P_l$ plane, c) projection to the $\alpha - \tau_p$ plane, d) the effective scaling exponent α as a function of vapour portion in initial total bubble composition for various gas saturations c_g/c_{sat} : 0.99 (red cross), 0.79 (blue square), 0.64 (green circle), 0.50 (yellow triangle) and 0.32 (purple cross). For all concentrations the same dependence of decreasing α with increasing vapour ratio is observed.

Figure 6.5: Comparison of the experimental results (blue) and model predictions (orange) of the bubble radius change with time during first 100 ms after switching off the laser for various initial conditions: a) $P_l = 170$ mW, $\tau_p = 0.05$ and $c_g/c_{sat} = 0.5$, $V_{vapor}/V_{total} = 0.79$; b) $P_l = 140$ mW, $\tau_p = 0.1$ and $c_g/c_{sat} = 0.99$, $V_{vapor}/V_{total} = 0.38$; c) $P_l = 50$ mW, $\tau_p = 0.5$ and $c_g/c_{sat} = 0.99$, $V_{vapor}/V_{total} = 0.19$

with gas so that the initial amount of vapor in the bubble is small, the agreement is significantly better than in the other cases. We have found a similar level of agreement for all the dissolved gas concentrations that we have tested.

To summarize, the bubble dynamics during the first phase depends on the initial bubble composition, which is defined by the conditions (P_l , τ_p , c_g/c_{sat}) during the bubble growth, i.e. on the history of bubble formation, which we can quantitatively describe with the model of ref. [131].

6.3.3 Diffusion-dominated shrinkage

After the rapid bubble shrinkage, a much slower process takes over. During this phase the bubble dissolves due to gas diffusion from the bubble to the bulk liquid. Our experimental results for laser powers $P_l = 50$ mW, 80 mW, 110 mW, 140 mW, 170 mW and 200 mW, pulse durations $\tau_p = 0.5$ s and 0.05 s and water with gas saturation levels $c_g/c_{sat} = 0.99$ and 0.50 are summarized in Figure 6.6. In Figure 6.6a the bubble radii R as function of time t for $c_g/c_{sat} = 0.99$ and $\tau_p = 0.5$ s along with a double logarithmic plot and a double logarithmic plot of R compensated with $(t_0 - t)^{1/3}$ are shown, where t_0 is the lifetime of the bubble. Figures 6.6(b)-(d) represent the same set of figures, but for different experimental conditions: $c_g/c_{sat} = 0.99$ and $\tau_p = 0.05$ s, $c_g/c_{sat} = 0.50$ and $\tau_p = 0.5$ s, $c_g/c_{sat} = 0.50$ and $\tau_p = 0.05$ s, respectively.

As was already mentioned, higher laser powers and longer laser pulses lead to larger bubbles and, therefore, at the same ambient conditions, it takes longer

for them to completely dissolve. For example, in water with 99% of dissolved air concentration it takes around 100 s for the bubble, which was formed after laser pulse with $\tau_p = 0.5$ s and $P_l = 50$ mW, and initial radius $R_0 = 23 \mu\text{m}$ to dissolve, while it takes around 550 s for the one, formed with $P_l = 200$ mW, and with $R_0 = 36 \mu\text{m}$. Bubbles of comparable size dissolve much faster in degassed water than in saturated water, *e.g.* the bubble with $R = 15 \mu\text{m}$ completely dissolves in water with $c_g/c_{sat} = 0.99$ in around 33 s (Figure 6.6b), while in water with $c_g/c_{sat} = 0.50$ in 10 s (Figure 6.6c), due to the larger concentration gradients between the bubble and the bulk liquid.

The solid black lines in the double logarithmic plots correspond to the effective scaling exponent of $1/3$ (Figures 6.6a, 6.6b) and $1/2$ (Figures 6.6c, 6.6d) in $R(t) \propto (t_0 - t)^\alpha$, and are shown for clearer indication of the slope. One can see that not only for all laser powers, but also for all pulse durations bubbles follow similar dynamics. The double logarithmic plots of R compensated by $(t_0 - t)^{1/3}$ (Figures 6.6a, 6.6b) and $(t_0 - t)^{1/2}$ (Figures 6.6c, 6.6d) further confirm the value of the effective scaling exponent. Despite the slight variations, the scaling exponent remains close to $1/3$ for $c_g/c_{sat} = 0.99$ and close to $1/2$ for $c_g/c_{sat} = 0.50$ for all experimental parameters with fixed gas concentration.

In order to further investigate how the concentration of gas dissolved in liquid influences the long-term bubble dissolution dynamics, we performed a series of experiments with various c_g/c_{sat} , namely, $c_g/c_{sat} = 0.99, 0.79, 0.64, 0.50$ and 0.32 and $\tau_p = 0.5$ s, 0.2 s, 0.1 s, 0.05 s, 0.03 s. Performing the same analysis as discussed above for all data sets, the effective scaling exponents α in $R(t) \propto (t_0 - t)^\alpha$ for various saturation levels have been extracted (see Figures S1, S2, S3, and S4 in Appendix). Remarkably, α only slightly varies with P_l and τ_p , however it strongly depends on the concentration of dissolved gas in the liquid. For water with $c_g/c_{sat} = 0.99$ almost irrespective of P_l and τ_p the average effective scaling exponent is always around 0.34 . For water degassed till 79% of the saturation gas concentration α increases to 0.41 . Further liquid degassing leads to larger scaling exponents, namely, for $f_g = 0.64$ it increases to $\alpha = 0.45$, for $c_g/c_{sat} = 0.50$ to $\alpha = 0.48$ and for $c_g/c_{sat} = 0.32$ to $\alpha = 0.50$ (Figure 6.8). So what defines the scaling exponent?

We consider a spherical purely gas bubble, resting in the surrounding liquid [132]. Assuming the gas inside the bubble as ideal, *i.e.* $PV = N\Re T$, and taking into account that the bubble inner pressure is given as a sum of ambient pressure and the Laplace pressure, the loss rate of the number N of molecules in the bubble can be derived:

Figure 6.6: Bubble radius R as a function of time t for various experimental conditions: a) $c_g/c_{sat} = 0.99$, $\tau_p = 0.5$ s, b) $c_g/c_{sat} = 0.99$, $\tau_p = 0.05$ s, c) $c_g/c_{sat} = 0.50$, $\tau_p = 0.5$ s, d) $c_g/c_{sat} = 0.99$, $\tau_p = 0.05$ s and various laser powers P_l : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red), 170 mW (purple) and 200 mW (brown). The second and third columns represent R as a function of t in double logarithmic scale and compensated plots $R/(t_0 - t)^{1/3}$ (a,b) and $R/(t_0 - t)^{1/2}$ (c,d) as functions of time in double logarithmic scale, respectively. Black dashed lines are theoretical curves obtained from the direct solution of the purely diffusive bubble dissolution problem, see text.

Figure 6.7: a) Normalized bubble radius R/R_0 as a function of time t , derived from the solution of equations (6.7), where $R_0 = 30\mu\text{m}$, b) Normalized bubble radius R/R_0 as a function of time t in double logarithmic scale and c) compensated plots $(R/R_0)/(t_0 - t)^\alpha$ in double logarithmic scale, where α is an effective scaling exponent, for various gas saturation levels c_g/c_{sat} : 0.99 (blue), 0.79 (orange), 0.64 (green), 0.50 (red) and 0.32 (purple).

Figure 6.8: Effective scaling exponent α in $R(t) \propto (t_0 - t)^\alpha$ as a function of the gas concentration level for various laser powers P_l : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red), 170 mW (purple) and 200 mW (brown). The dashed black line is the theoretical curve obtained from a complete solution of equation (6.7) for various gas concentrations, showing good agreement with our data.

$$\dot{N} = \frac{4\pi\dot{R}R^2}{\Re T} \left(P_\infty + \frac{4}{3} \frac{\sigma}{R} \right), \quad (6.1)$$

where R is the bubble radius, $\Re$ the ideal gas constant, T the bubble temperature, P_∞ the ambient pressure, and σ the surface tension of the gas-liquid interface.

On the side of the liquid the molecular flux of gas molecules due to the diffusion through the bubble interface is determined by the gas concentration gradient,

$$\dot{N} = 4\pi R^2 D \left. \frac{\partial c}{\partial r} \right|_{r=R}, \quad (6.2)$$

where D is the mass diffusion coefficient and $c(r, t)$ is gas concentration. Combining equations (6.1) and (6.2) we have

$$\dot{R} \left(1 + \frac{4}{3} \frac{\sigma}{R P_\infty} \right) \frac{P_\infty}{\Re T} = D \left. \frac{\partial c}{\partial r} \right|_{r=R}. \quad (6.3)$$

The gas concentration field within the liquid is given by the convection-diffusion equation

$$\partial_t(c(r, t)) = \frac{D}{r^2} \partial_r(r^2 \partial_r c(r, t)) + \frac{a^2 \dot{a}}{r^2} \partial_r c(r, t). \quad (6.4)$$

For the majority of the diffusion process, we can make a quasi-steady approximation to the gradient of the dissolved gas concentration at the bubble surface and neglect the time-dependent terms to write

$$\partial_r c_g|_{r=R} \simeq \frac{c_\infty - c_g|_{r=R}}{R}. \quad (6.5)$$

The dissolved gas concentration at the bubble interface c_g will be related to the saturated gas concentration under a plane interface c_{sat} according to Henry's law as

$$c_g|_{r=R} = c_{sat}(P_\infty) \left(1 + \frac{2\sigma}{R P_\infty} \right). \quad (6.6)$$

Combining (6.3), (6.5) and (6.6) and introducing $\zeta = 1 - c_\infty/c_{sat}(P_\infty)$ and $\xi = c_{sat}(P_\infty)\Re T/P_\infty$ one can finally obtain:

$$\left(1 + \frac{4}{3} \frac{\sigma}{R P_\infty} \right) R \dot{R} = -D \xi \left(\zeta + \frac{2\sigma}{R P_\infty} \right). \quad (6.7)$$

If one neglects surface tension effects, the equation reduces to

$$R\dot{R} = -D\xi\zeta, \quad (6.8)$$

and can be easily integrated to find $R(t) \propto (t_0 - t)^{1/2}$. In our experiments the effective scaling exponent α was found to be close to $1/2$ for degassed water with $c_g/c_{sat} \leq 0.5$.

The other limiting case is fully saturated liquid, so no concentration gradient exists in the system, *i.e.* $\zeta = 0$. Omitting the second term in the sum on the left in equation 6.7, which is generally a small number for bubbles larger than $5\mu m$, and setting $\zeta = 0$ we have

$$R\dot{R} = -D\xi \frac{2\sigma}{RP_\infty}, \quad (6.9)$$

from which after integration one immediately finds the scaling law $R(t) \propto (t_0 - t)^{1/3}$, which is consistent with our experiments for water with $c_g/c_{sat} = 0.99$. The complete solution of equation 6.7 can also be readily find by integration:

$$1 - \frac{R^2}{R_0^2} - 2\left(1 - \frac{2}{3}\zeta\right)\frac{\Sigma}{\zeta}\left[1 - \frac{R}{R_0} + \frac{\Sigma}{\zeta}\ln\left(\frac{\Sigma/\zeta + R/R_0}{\Sigma/\zeta + 1}\right)\right] = 2\zeta\xi\frac{Dt}{R_0^2}, \quad (6.10)$$

where $\Sigma = 2\sigma/R_0P_\infty$.

It is reasonable to assume an effective scaling law for the bubble radius $R(t) \propto (t_0 - t)^{\alpha(c_g/c_{sat})}$, where the effective exponent $\alpha = f(c_g/c_{sat})$ is a function of the dissolved gas concentration. The normalized bubble radius R/R_0 , where $R_0 = 30\mu m$ as a function of time t , derived from the analytical solution (6.10) is shown in Figure 6.7. One can then extract α from the double logarithmic plot (Figure 6.7b) using a linear fit. The derived effective exponents are confirmed by the double logarithmic plot compensated by $(t_0 - t)^\alpha$ (Figure 6.7c), where $\alpha=0.34, 0.44, 0.46, 0.47$ and 0.48 for $c_g/c_{sat}=0.99, 0.79, 0.64, 0.50$ and 0.32 , respectively.

The dependence of α on c_g/c_{sat} , resulting from the complete solution (6.10) for various gas saturation levels, is shown as dashed black line in Figure 6.8. Just as in our experiments with decreasing gas concentration, one can see the gradual transition from the limiting regime, where water is almost fully saturated with gas and the effective scaling exponent is $1/3$, to the regime where we are dealing with large concentration gradients due to water degassing, and the $1/2$ effective scaling law shows up.

6.4 Conclusion

The dynamics of plasmonic microbubble shrinkage has been studied. During the dissolution a bubble undergoes two different phases. First, rapid bubble shrinkage due to vapor condensation occurs in the first milliseconds after switching off the laser irradiation. The dynamics of this phase highly depends on the history of bubble formation, which defines the initial bubble composition. The bubble contains more vapor in its composition and, therefore, shrinks faster for shorter laser pulse durations, lower dissolved gas concentrations and higher laser powers. Afterwards, the second phase of slow bubble dissolution takes over, which is governed by gas diffusion from the bubble to the bulk liquid and may last up to minutes or even hours. The dynamics of the plasmonic bubble during this phase barely depends on the laser power and laser pulse duration, used to form the bubble, but strongly depends on the gas saturation level in the bulk water, as it defines the concentration field in the liquid. The gradual transition from the effective scaling exponent $\alpha = 1/3$ for almost fully saturated water with $c_g/c_{sat} = 0.99$ to $\alpha \approx 1/2$ for degassed water ($c_g/c_{sat} \leq 0.5$) has been demonstrated both experimentally and theoretically.

6.5 Appendix

Our experimental results on the diffusion-dominated phase are summarized in Figures [6.9](#), [6.10](#), [6.11](#), [6.12](#) and [6.13](#). In Figure [6.9](#) the bubble radii R as function of time t for water with $c_g/c_{sat} = 0.99$ and pulse length a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s, and e) 0.03 s and for laser powers $P_l = 50$ mW, 80 mW, 110 mW, 140 mW, 170 mW and 200 mW, along with a double logarithmic plot and a double logarithmic plot of R compensated with $(t_0 - t)^{0.33}$ are shown, where t_0 is the lifetime of the bubble.

In Figure [6.10](#) the bubble radii R as function of time t for water with $c_g/c_{sat} = 0.79$ and pulse length a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s, and e) 0.03 s and for laser powers $P_l = 50$ mW, 80 mW, 110 mW, 140 mW, 170 mW and 200 mW, along with a double logarithmic plot and a double logarithmic plot of R compensated with $(t_0 - t)^{0.41}$ are shown, where t_0 is the lifetime of the bubble.

In Figure [6.11](#) the bubble radii R as function of time t for water with $c_g/c_{sat} = 0.64$ and pulse length a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, and d) 0.05 s and for laser powers $P_l = 50$ mW, 80 mW, 110 mW, 140 mW, 170 mW and 200 mW, along with a double logarithmic plot and a double logarithmic plot of R

compensated with $(t_0 - t)^{0.45}$ are shown, where t_0 is the lifetime of the bubble.

In Figure 6.12 the bubble radii R as function of time t for water with $c_g/c_{sat} = 0.50$ and pulse length a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, and d) 0.05 s and for laser powers $P_l = 50$ mW, 80 mW, 110 mW, 140 mW, 170 mW and 200 mW, along with a double logarithmic plot and a double logarithmic plot of R compensated with $(t_0 - t)^{0.50}$ are shown, where t_0 is the lifetime of the bubble.

In Figure 6.13 the bubble radii R as function of time t for water with $c_g/c_{sat} = 0.32$ and pulse length a) $\tau_p = 0.5$ s, b) 0.2 s, and c) 0.1 s and for laser powers $P_l = 50$ mW, 80 mW, 110 mW, and 140 mW, along with a double logarithmic plot and a double logarithmic plot of R compensated with $(t_0 - t)^{0.50}$ are shown, where t_0 is the lifetime of the bubble.

Figure 6.9: Bubble radius R as a function of time t in water with $c_g/c_{sat} = 0.79$ for various pulse length: a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s, e) 0.03 s and various laser powers P_l : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red), 170 mW (purple) and 200 mW (brown). The second and third columns represent R as a function of t in double logarithmic scale and compensated plots $R/(t_0 - t)^{0.33}$ as functions of time in double logarithmic scale, respectively. Black dashed lines are theoretical curves obtained from the direct solution of the purely diffusive bubble dissolution problem, see text.

Figure 6.10: Bubble radius R as a function of time t in water with $c_g/c_{sat} = 0.79$ for various pulse length: a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s, e) 0.03 s and various laser powers P_l : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red), 170 mW (purple) and 200 mW (brown). The second and third columns represent R as a function of t in double logarithmic scale and compensated plots $R/(t_0 - t)^{0.41}$ as functions of time in double logarithmic scale, respectively. Black dashed lines are theoretical curves obtained from the direct solution of the purely diffusive bubble dissolution problem, see text.

Figure 6.11: Bubble radius R as a function of time t in water with $c_g/c_{sat} = 0.64$ for various pulse length: a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s and various laser powers P_l : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red), 170 mW (purple) and 200 mW (brown). The second and third columns represent R as a function of t in double logarithmic scale and compensated plots $R/(t_0 - t)^{0.45}$ as functions of time in double logarithmic scale, respectively. Black dashed lines are theoretical curves obtained from the direct solution of the purely diffusive bubble dissolution problem, see text.

Figure 6.12: Bubble radius R as a function of time t in water with $c_g/c_{sat} = 0.50$ for various pulse length: a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s, d) 0.05 s and various laser powers P_l : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red), 170 mW (purple) and 200 mW (brown). The second and third columns represent R as a function of t in double logarithmic scale and compensated plots $R/(t_0 - t)^{0.50}$ as functions of time in double logarithmic scale, respectively. Black dashed lines are theoretical curves obtained from the direct solution of the purely diffusive bubble dissolution problem, see text.

Figure 6.13: Bubble radius R as a function of time t in water with $c_g/c_{sat} = 0.32$ for various pulse length: a) $\tau_p = 0.5$ s, b) 0.2 s, c) 0.1 s and various laser powers P_i : 50 mW (blue), 80 mW (orange), 110 mW (green), 140 mW (red). The second and third columns represent R as a function of t in double logarithmic scale and compensated plots $R/(t_0 - t)^{0.50}$ as functions of time in double logarithmic scale, respectively. Black dashed lines are theoretical curves obtained from the direct solution of the purely diffusive bubble dissolution problem, see text.

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Summary

Noble metal nanoparticles immersed in water and irradiated by a resonant laser rapidly and strongly heat, vaporizing the surrounding liquid, leading to the formation of so-called plasmonic bubbles, which have broad application potential in plasmonic-enhanced processes. How exactly do these bubbles form? What is their composition? Which parameters are crucial in bubble dynamics?

In Chapter 2, our results reveal that the steady growth dynamics of a plasmonic microbubble can be divided into two regimes: bubble growth controlled by water evaporation (regime I, <10 ms) and a subsequent diffusive growth phase (regime II, >0.2 s). The rapid growth in regime I is similar for saturated and undersaturated water, which implies that during this regime, the water evaporation dominates. The steady growth in regime II is distinctly different for air-equilibrated and degassed water, which is attributed to the influx of dissolved gas expelled from the water around the hot nanoparticles. Our analysis shows that the bubble radius scales with time as $R(t) \propto t^{1/6}$ for both cases in the initial regime I, whereas in the regime II it scales as $R(t) \propto t^{1/3}$ for gas saturated water and $R(t)$ barely changes with time in highly degassed water.

The nucleation and early life phase of these bubbles have been discussed in Chapter 3. After some delay time after the beginning of the illumination, a giant bubble explosively grows, up to a maximal radius of tens μm , and collapses again typically within 10-20 μs (bubble life phase 1). The maximal bubble volume V_{max} remarkably increases with decreasing laser power. The same holds for the delay time, which drastically increases with decreasing laser power, leading to higher energy provided to the system. This dumped energy E shows a linear scaling relation with V_{max} , irrespectively of the gas concentration of the surrounding water, which confirms that the initial giant bubble is a pure vapor bubble. In contrast, delay time does depend on the gas concentration, as gas pockets and molecules clusters facilitate bubble formation, which leads to shorter delay times and lower nucleation temperatures. Right after the collapse of the initial bubble, much smaller unstable oscillating bubbles appear (bubble

life phase 2) and maintain continuous cycles up to typically several ms. Only after the bubble stabilization the processes discussed in Chapter 2 take place (bubble life phases 3 and 4).

In Chapter 4, we continue with the quantitative study of the effect of the amount of air dissolved in water on the two phases observed before: the explosively growing vapor bubble (phase 1) and steady growing bubble by diffusion (phase 4). In the first case, lower gas concentrations lead to longer delay times, larger bubbles, and higher nucleation temperatures. In the second case, water undersaturation leads to the deviation of steady $R(t) \propto t^{1/3}$ growth behavior in air equilibrated water to lower scaling exponents.

Then the behavior of plasmonic bubbles in organic liquids, namely, n-alkanes (C_nH_{2n+2} , with $n = 5-10$), has been investigated in Chapter 5. Two different phases in the evolution of the bubbles can be distinguished. The first phase is similar to the one in water, when, after a short delay explosive microbubble forms. Despite the significant difference in boiling points, the exact size of this explosive microbubble barely depends on the carbon chain length of the alkane, but only on the laser power. In the second phase, right after the collapse of the explosive microbubble, a new bubble forms and starts steadily growing due to the vaporization of the surrounding liquid (contrary to water), which is highly saturated with gas. The bubble size in the second phase strongly depends on the alkane chain length and increases with a decreasing number of carbon atoms.

In chapter 6, we consider the shrinkage dynamics of plasmonic bubbles. We show that a plasmonic bubble during its shrinkage undergoes two different phases, first – a rapid partial bubble shrinkage due to vapor condensation and second – a slow diffusion-controlled bubble dissolution. The history of bubble formation plays an essential role in shrinkage dynamics during the first phase, as it determines the initial bubble composition. Higher laser powers lead to more vaporous bubbles, while longer pulses and higher dissolved gas concentrations lead to more gaseous bubbles. The dynamics of the second phase barely depends on the history of bubble formation, but strongly on the dissolved gas concentration, which defines the gradient at the bubble interface. We observe a gradual transition from a $R(t) \propto (t_0 - t)^{1/3}$ scaling law to a $R(t) \propto (t_0 - t)^{1/2}$ scaling law with decreasing dissolved gas concentration and theoretically explain this transition.

To sum up, liquid evaporation due to extensive heat transfer from submerged nanoparticles that efficiently absorb incident light and convert it into

heat is of interest for the last fifteen years; however, all aspects of physics related to this phenomenon are still not fully understood. In this thesis, bubble formation due to the collective effect from nanoparticles immersed in liquid under relatively low-intensity cw-laser irradiation has been extensively studied. All phases of the bubble life cycle have been investigated: from nucleation to growth and subsequent collapse with a broad set of variable parameters. Particularly, it worth emphasizing the role of the dissolved gas, which significantly modifies bubble behaviour in all of the above-mentioned life stages.

For further implementation of these systems into potential applications, many intriguing challenges are still arising on both microscale and nanoscale. How do plasmonic microbubbles form in various binary and ternary liquids and under various ambient conditions? Can we observe the coalescence of nanobubbles into microbubbles? How can we further improve light to vapor conversion efficiency and reduce heat losses? What is the optimal structure and distribution of nanoparticles for enhanced heat transfer and controllable bubble formation? These and many other questions still need to be answered to realise the full potential of these systems.

Samenvatting

Edelmetalen nanodeeltjes, ondergedompeld in water en bestraald door een resonerende laser, warmen snel en sterk op. Hierdoor verdampt de omringende vloeistof, hetgeen leidt tot de vorming van zogenaamde plasmonische bellen, die een breed toepassingspotentieel hebben. Hoe vormen deze bellen zich precies? Wat is hun samenstelling? Welke parameters zijn cruciaal in de dynamiek van deze bellen?

In hoofdstuk 2 laten onze resultaten zien dat de gestage groeidynamiek van een plasmonische microbel kan worden verdeeld in twee regimes: bellengroei geregeld door waterverdamping (regime I, < 10 ms) en een daaropvolgende diffusieve groeifase (regime II, $> 0,2$ s). De snelle groei in regime I is vergelijkbaar voor verzadigd en onverzadigd water, hetgeen inhoudt dat tijdens dit regime de waterverdamping domineert. De gestage groei in regime II is duidelijk anders voor met lucht geëquilibreerd en ontgast water, wat wordt toegeschreven aan de instroom van opgelost gas, dat uit het water rond de hete nanodeeltjes vrijkomt. Onze analyse laat zien dat de bellenradius met de tijd schaalt als $R(t) \propto t^{1/6}$ voor beide typen water in het oorspronkelijke regime I, terwijl in regime II het schaalt als $R(t) \propto t^{1/3}$ voor met gas verzadigd water en $R(t)$ verandert nauwelijks met de tijd in sterk ontgast water.

De nucleatie en de vroege levensfase van deze bellen zijn besproken in hoofdstuk 3. Enige vertragingstijd na het begin van de belichting, groeit er explosief een gigantische bel, met een maximale straal van tientallen μm , en stort weer in, meestal binnen $10\text{--}20\ \mu\text{s}$ (bellevensfase 1). Opmerkelijk gezien, neemt het maximale belvolume V_{max} toe met een afnemend laservermogen. Hetzelfde geldt voor de vertragingstijd, die drastisch toeneemt met een afnemend laservermogen, hetgeen leidt tot een hogere energie die aan het systeem wordt geleverd. Deze gedumpte energie E schaalt lineair met V_{max} , ongeacht de gasconcentratie van het omringende water, wat bevestigt dat de initiële gigantische bel een zuivere dampbel is. De vertragingstijd is daarentegen wel afhankelijk van de gasconcentratie, omdat gas en molecuulclusters de belvorm-

ing vergemakkelijken, wat leidt tot kortere vertragingstijden en lagere nucleatietemperaturen. Direct na het instorten van de initiële bel, verschijnen er veel kleinere onstabiele oscillerende bellen (bellevensfase 2). Deze bellen handhaven zich continue in cycli, gedurende typisch enkele ms. Pas na de belstabilisatie vinden de in hoofdstuk 2 besproken processen plaats (bellevensfasen 3 en 4).

In hoofdstuk 4 gaan we verder met een kwantitatieve studie aangaande het effect van de hoeveelheid lucht opgelost in water op de twee eerder waargenomen fasen: de explosief groeiende dampbel (fase 1) en de door diffusie gestaag groeiende luchtbel (fase 4). In het eerste geval leiden lagere gasconcentraties tot langere vertragingstijden, grotere bellen en hogere nucleatietemperaturen. In het tweede geval leidt onderverzadiging van water tot de afwijking van het $R(t) \propto t^{1/3}$ groeiedrag in lucht geëquilibreerd water, naar lagere exponenten.

Vervolgens is het gedrag van plasmonische bellen in organische vloeistoffen, namelijk n-alkanen (C_nH_{2n+2} , met $n = 5-10$) onderzocht in hoofdstuk 5. Twee verschillende fasen in de evolutie van de bellen kunnen worden onderscheiden. De eerste fase is vergelijkbaar met die in water, wanneer er na een korte vertraging een explosieve microbel vormt. Ondanks het grote verschil in kookpunt, hangt de exacte grootte van deze explosieve microbel nauwelijks af van de lengte van de koolstofketen, maar hangt alleen af van het laservermogen. In de tweede fase, direct na het instorten van de explosieve microbel, vormt zich een nieuwe bel die gestaag groeit door de verdamping van de omringende vloeistof (in tegenstelling tot water) dat sterk verzadigd is met gas. De belgrootte in de tweede fase hangt sterk af van de alkaanketenlengte en neemt toe met een afnemend aantal koolstofatomen.

In hoofdstuk 6 beschouwen we de dynamiek van het krimpen van plasmonische bellen. We laten zien dat een plasmonische bel tijdens zijn krimp twee verschillende fasen ondergaat, ten eerste – een snelle gedeeltelijke belkrimp als gevolg van dampcondensatie, en ten tweede – het langzame, diffusie-gecontroleerde, oplossen van bellen. De geschiedenis van bellenvorming speelt een essentiële rol in de dynamiek tijdens het krimpen in de eerste fase, omdat het de oorspronkelijke samenstelling van de bellen bepaalt. Een hoger laservermogen leidt tot meer dampvormige bellen, terwijl langere pulsen en een hogere concentratie van het opgelost gas leiden tot meer gasvormige bellen. De dynamiek van de tweede fase hangt nauwelijks af van de geschiedenis van de bellenvorming, maar sterk van de concentratie opgelost gas, die de gradiënt aan het bellenoppervlak bepaalt. We nemen een geleidelijke overgang waar van een $R(t) \propto (t_0 - t)^{1/3}$ schaling naar een $R(t) \propto (t_0 - t)^{1/2}$ schaling met afnemende opgeloste gasconcentratie, en we kunnen deze overgang theoretisch verklaren.

Заключение

Наночастицы из благородных металлов, погруженные в воду и облучаемые лазером с определенной длиной волны, быстро и сильно нагреваются, испаряя окружающую их жидкость, что приводит к образованию так называемых плазмонных пузырьков, которые имеют широкий потенциал применения в процессах, стимулируемых эффектом плазмонного резонанса. Но как именно образуются эти пузырьки? Какой их состав? Какие параметры являются ключевыми в динамике таких пузырьков?

В главе 2 наши результаты показывают, что динамику устойчивого роста плазмонного микропузырька можно разделить на два режима: рост пузырьков, контролируемый испарением воды (режим I, < 10 мс), и последующий диффузионный рост (режим II, $> 0,2$ с). Рост пузырьков в режиме I аналогичен для насыщенной газом жидкости и дегазированной жидкости, что означает, что в этом режиме пузырек растет, только за счет испарения воды. Устойчивый рост в режиме II значительно различается в насыщенной и ненасыщенной газом воде, что объясняется диффузией растворенного газа, выделяемого из воды вокруг нагретых наночастиц. Наш анализ показывает, что закон изменения радиуса пузырька со временем может быть аппроксимирован, как $R(t) \propto t^{1/6}$ для обоих случаев в режиме I, тогда как в режиме II для газонасыщенной воды $R(t) \propto t^{1/3}$, а для сильно дегазированной воды $R(t)$ практически не изменяются со временем, т.е. $R(t) \propto const$.

Нуклеация и ранняя фаза жизни плазмонных пузырьков обсуждаются в главе 3. Через некоторое время после начала облучения лазером (обычно $10^2 \dots 10^3$ мкс) образуется пузырь, который взрывно растет, достигая максимального радиуса в десятки мкм, и быстро схлопывается, как правило, в течение 10-20 микросекунд (фаза жизни пузыря 1). Максимальный объем пузырька V_{max} заметно увеличивается с уменьшением мощности лазера. Время задержки (промежуток времени от момента включения лазера до момента нуклеации пузырька) также резко увеличивается с уменьшением

мощности лазера, что и приводит к увеличению энергии E_d , подведенной к системе. Эта энергия линейно коррелирует с V_{max} независимо от концентрации газа, растворенного в воде, что подтверждает, что первоначальный пузырь представляет собой паровой пузырь. Время задержки также зависит от концентрации газа, поскольку газовые карманы и кластеры молекул могут являться гетерогенным центрами нуклеации и снижать энергетический барьер для образования пузырьков, что приводит к более коротким временам задержки и более низким температурам нуклеации. Сразу после схлопывания исходного пузырька появляются значительно меньшие по размерам осциллирующие пузырьки (фаза жизни пузырька 2), которые циклически растут и схлопываются на протяжении нескольких мс. Только после стабилизации пузыря происходят процессы, обсуждаемые в главе 2 (фазы жизни пузыря 3 и 4).

В главе 4 детально обсуждается вопрос влияния количества воздуха, растворенного в воде, на две фазы, которые наблюдались ранее: взрывно растущий паровой пузырь (фаза 1) и устойчиво растущий пузырь, вследствие диффузии газа из окружающей жидкости (фаза 4). В первом случае более низкие концентрации газа приводят к более длительным временам задержки, большим пузырькам и более высоким температурам нуклеации. Во втором случае дегазация воды приводит к отклонению динамики устойчивого роста от закона $R(t) \propto t^{1/3}$ в газонасыщенной воде.

Поведение плазмонных пузырьков в органических жидкостях, а именно n -алканах (C_nH_{2n+2} , при $n = 5-10$), было исследовано в главе 5. Можно выделить две последовательные фазы в эволюции пузырьков. Первая фаза схожа с фазой в воде, когда после небольшой задержки образуется взрывнорастущий микропузырек. Несмотря на существенную разницу в температурах кипения, максимальный размер такого микропузырька практически не зависит от длины углеродной цепи алкана, а зависит только от мощности лазера. На втором этапе, сразу после схлопывания взрывного микропузырька, образуется новый микропузырь и начинает устойчиво расти из-за испарения окружающей жидкости (в отличие от воды), которая сильно насыщена газом. Размер пузырьков во второй фазе сильно зависит от длины алкановой цепи и увеличивается с уменьшением числа атомов углерода.

В главе 6 рассмотрена динамика схлопывания плазмонных пузырьков. Мы показываем, что плазмонный пузырь во время схлопывания проходит через две различные фазы: первая - быстрое частичное сжатие пузыря из-за конденсации пара, и вторая - медленное растворение пузырька, кон-

тролируемое диффузией. История образования пузырьков играет существенную роль в динамике схлопывания в течение первой фазы, поскольку она определяет исходный состав пузырьков. Более высокая мощность лазера приводит к образованию более парообразных пузырьков, в то время как более длинные лазерные импульсы и более высокие концентрации растворенного газа приводят к образованию более газообразных пузырьков. Динамика второй фазы практически не зависит от истории образования пузырьков, а только от концентрации растворенного газа, которая определяет градиент концентрации в системе пузырь/жидкость. Мы экспериментально показали постепенный переход от закона $R(t) \propto (t_0 - t)^{1/3}$ к закону $R(t) \propto (t_0 - t)^{1/2}$ с уменьшением концентрации растворенного газа и теоретически объяснили этот переход.

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