Plasmonic Bubble Nucleation in Binary Liquids

Marvin Detert, Binglin Zeng, Yuliang Wang, Hai Le The, Harold J. W. Zandvliet, and Detlef Lohse

ABSTRACT: Metal nanoparticles under laser irradiation can produce enormous heat due to surface plasmon resonance. When submerged in a liquid, this can lead to the nucleation of plasmonic bubbles. In the very early stage, the nucleation of a giant vapor bubble was observed with an ultrahigh-speed camera. In this study, the formation of this giant bubble on gold nanoparticles in six binary liquid combinations has been investigated. We find that the time delay between the beginning of the laser heating and the bubble nucleation is determined by the absolute amount of dissolved gas in the liquid. Moreover, the bubble volume mainly depends on the vaporization energy of the liquid, consisting of the latent heat of vaporization and the energy needed to reach the boiling temperature. Our results contribute to controlling the initial giant bubble nucleation and have strong bearings on applications of such bubbles.

INTRODUCTION

When irradiated by a continuous-wave laser, gold nanoparticles (GNPs) immersed in a liquid can produce huge amounts of heat due to the surface plasmon resonance. The enormous heat can vaporize the surrounding liquid, leading to the nucleation of so-called plasmonic vapor bubbles. These bubbles have shown potential for various future applications. They range from medical ones, such as drug delivery to a single cell and cancer therapy, to devices on microfluidic chips like micropumps and microvalves. Another interesting approach is plasmon-assisted catalysis for steam reforming ethanol. It has been demonstrated that a microfluidic channel decorated with GNP s and irradiated by a laser can form the catalytic reaction products H2, CO, and CO2 using GNP s as a catalyst and heat source simultaneously. Understanding the nucleation and growth dynamics of the plasmonic bubbles in multicomponent liquids is thus essential to develop and further improve this multitude of applications.

In our recent study, the nucleation of an initial giant bubble in pure liquids was found in the very early stage of the plasmonic bubble generation via ultrahigh-speed imaging. This bubble shows extraordinary characteristics, such as a short lifetime and an explosive growth rate. In particular, the rapid growth is essential for applications, for example, for the aforementioned cell therapy, and might also be used in other future applications. However, the nucleation process is not well-understood yet. This is partially due to the complexity of the system and partially due to the short time scales on which the nucleation takes place. A preliminary study has shown that the delay between the beginning of the laser heating and the nucleation in water is affected by both the laser power and the relative gas concentration. Additionally, these bubbles have also been studied in n-alkanes. There, a decrease of the bubble volume has been observed for an increase in the carbon chain length of the n-alkane. Moreover, the nucleation takes place faster in all investigated n-alkanes than in water. Although water and six different pure n-alkanes have been investigated, a detailed understanding of the nucleation mechanism is still lacking.

In order to better understand the bubble nucleation, it is necessary to experimentally explore the effect of multiple parameters, such as the gas concentration, boiling point, thermal conductivity, heat capacity of the liquid, and the latent heat of vaporization. However, these parameters are hard to tune for pure liquids. This difficulty led us to binary liquids, as their parameters can easily be tuned via the mixing ratio and hence allow to explore a wider range of parameters. Therefore, we have systematically investigated six binary liquids, namely water and six diﬀering pure n-alkanes.
a photodiode power sensor (S130C, ThorLabs). An acoustic-controlled via a halfwave plate and a polarizer and measured by liquid and irradiated by a 300 mW, 532 nm continuous wave decorated sample is placed in a glass cuvette, submerged in a for the plasmonic microbubble imaging. The gold nanoparticle respectively.

Sample Preparation. A gold layer of ~45 nm was deposited on an amorphous fused-silica wafer via an ion-beam sputtering system (home-built TCOathy machine, MESA+ NanoLab, University of Twente). Then, a bottom antirefection coating (BARC) layer (~186 nm) and a photo resist (PR) layer (~200 nm) were coated on the wafer surface. The PR layer waspatterned with periodic nanocolumns (diameter of ~110 nm) using displacement Talbot lithography (PhableR 100C, EULITHA). Subsequently, these periodic PR nanocolumns were transferred at the wafer level to the underlying BARC layer, forming 110 nm BARC nanocolumns via nitrogen plasma etching (home-built TETski machine, MESA+ NanoLab, University of Twente) at 10 mTorr and 25 W for 8 min. Taking these BARC nanocolumns as a mask, the Au layer was etched by ion-beam etching (Oxford i300, Oxford Instruments, United Kingdom) with 5 sccm Ar and 50–55 mA at an inclined angle of 5°. After 9 min of etching, periodic Au nanodots supported on cone-shaped fused-silica features formed. The remaining BARC was stripped using oxygen plasma for 10 min (TePla 300E, PVA TePla AG, Germany). To reform the Au nanodots, the wafer was heated slowly (within 90 min) to 1100 °C and subsequently cooled passively to room temperature. Via this annealing process, the Au nanodots transformed into spherical-shaped Au nanoparticles.

Table 1. Parameters of the Pure Liquids

| parameter          | water | ethanol | acetone | 1-propanol | 2-propanol | 1-butanol |
|--------------------|-------|---------|---------|------------|------------|----------|
| boiling point (°C) | 100   | 78      | 56      | 97         | 82         | 118      |
| heat capacity (J/(mol K)) | 75.9 | 146.6   | 129.4   | 192.7      | 205.2      | 249.8    |
| latent heat of vap. (kJ/mol) | 40.7 | 39.2    | 29.1    | 41.3       | 39.9       | 43.3     |
| surface tension (mN/m) | 72.8 | 22.4    | 23.7    | 23.7       | 21.4       | 24.5     |
| thermal cond. (W/(mK)) | 0.679 | 0.153   | 0.143   | 0.138      | 0.125      | 0.135    |
| nitrogen solubility (Vg/Vl) | 0.018 | 0.149   | 0.184   | 0.133      | 0.147      | 0.122    |
| oxygen solubility (Vg/Vl) | 0.035 | 0.244   | 0.267   | 0.221      | 0.246      | 0.190    |

“All values are given at ambient pressure. The surface tensions and solubilities are those at room temperature. All other parameters are those at the respective boiling points of the liquid.19–23

RESULTS

The nucleation and explosive growth of a giant bubble were captured in six binary liquids with a high-speed camera. We call the time between turning on the laser and bubble nucleation the delay time \( \tau_d \). In Figure 2 this delay time \( \tau_d \) is shown as a function of the mixing ratio for the six investigated binary liquids. As seen in Figure 2a–c, \( \tau_d \) decreases with the increasing amount of the organic component in the three aqueous binary liquids (water/ethanol, water/acetone, and water/1-propanol). Surprisingly, \( \tau_d \) is roughly an order of magnitude smaller for purely organic binaries, see Figure 2d–f. Moreover, for these, it exhibits a different behavior, namely, \( \tau_d \) varies only slightly with the mixing ratio for the ethanol/acetone and ethanol/2-propanol binary liquids, as shown in Figure 2d,e. In contrast, \( \tau_d \) increases with the amount of 1-butanol in the ethanol/1-butanol binary. Besides that, the laser optic modulator acts as a triggerable shutter. The laser spot diameter is 10 μm, and the intensity can be varied between 0 and 200 mW. Laser pulses of 400 μs were generated and controlled by a pulse/delay generator (BNC model 565) in order to study the short-term dynamics of the microbubbles. Two high-speed cameras were installed in the setup, one for the top view and another for the side view. The top view camera (SA7) is equipped with a SX long working distance objective (LMPLFLN, Olympus). The side view camera (Photron SAZ) can be equipped with two long working distance objectives, 10× (LMPLFLN, Olympus) or 20× (SLMPL, Olympus), and can be operated at frame rates up to 1200 kfps. Two light sources, a Sumita LS-M350 and a Schott ACE I, provided back light illumination for the high-speed cameras.
power $P_l$ affects $\tau_d$. For all binary liquids, $\tau_d$ decreases with increasing $P_l$, which has also been observed for pure water$^{17}$ and pure n-alkanes.$^{18}$

In order to understand how the mixing ratio affects $\tau_d$, the change in parameters must be taken into account. In Table 1, the parameters of the various pure liquids are listed. Only the surface tension, thermal conductivity and the amount of dissolved gas (implied by the combination of N$_2$ and O$_2$ solubilities) exhibit a large difference between water and the organic liquids. However, the thermal conductivity can be ruled out, because it would predict the same behavior in all organic binaries, which is not the case. While the surface tension varies drastically for small deviations from the pure liquids, the amount of dissolved gas changes almost linearly over the whole range of mixing ratios. This allows to distinguish between the effects of the two, and we find the surface tension insufficient to explain the behavior of $\tau_d$. Our reasoning is elaborated in the Supporting Information. Consequently, the amount of dissolved gas should play a major role, and we show $\tau_d$ as a function of it in Figure 3a. $\tau_d$ decreases with an increase in the dissolved gas for all shown liquids individually. Moreover, the global behavior also shows the decrease of $\tau_d$ with the increasing amount of dissolved gas, which can be fitted with the power law $\tau_d \propto (V_g/V_l)^{\gamma}$. We observe the same global behavior for all laser powers investigated, though the power law exponent $\gamma$ decreases with increasing $P_l$, see Figure 3b. Hence, the amount of dissolved gas is the most important parameter for $\tau_d$. This is supported further by prior investigations of Wang et al. for pure water that showed an increased $\tau_d$ for degassed water$^{17}$ and also fits to the results on n-alkanes.$^{18}$ One might wonder whether it is the total amount of dissolved gas or the saturation level that causes this effect.$^{17}$ However, our results demonstrate that it is the total amount of dissolved gas because all binary liquids are saturated and the effect appears nonetheless.

### DISCUSSION

In order to understand the mechanism by which the dissolved gas affects $\tau_d$, we study the nucleation temperature $T_n$. To determine $T_n$, we first study the temperature evolution around...
a single nanoparticle. We assume a spherical geometry and constant thermal properties and solve the spherical linear Fourier equation for heat conduction

\[
\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} = \frac{1}{\rho c_p} \frac{\partial^2 T}{\partial t^2} \quad \text{(1)}
\]

where \( \kappa \), \( \rho \), and \( c_p \) are thermal diffusivity, density, and heat capacity of the liquid, respectively, \( r \) is the distance to the GNP, and \( p(r,t) \) is the deposited power density (unit in W/m\(^3\)). Then, \( T_n \) and the corresponding \( \tau_d \) can be calculated by the superposition of GNP. Further information on this calculation can be found in Wang et al.\(^{17} \) We fit the calculated \( \tau_d \) with the experimental data in Figure 2 to determine the corresponding \( T_n \). This is exemplarily shown for pure water in Figure 4 a,b, where the blue curve is the fit. It is located between two restrictions, namely, the boiling temperature (\( T_{\text{boil}} \) orange curve) and the spinodal temperature (\( T_{\text{spin}} \) green curve). The boiling, nucleation, and spinodal temperatures for the binary liquids at different component ratios are shown in Figure 4d–i.

For aqueous binary liquids, the \( T_n \) continuously decreases from 285 to 180, 150, and 185 °C with an increasing amount of ethanol, acetone, and 1-propanol, respectively, see Figure 4d–f. In the ethanol/acetone and ethanol/2-propanol binary liquids, \( T_n \) remains constant at approximately 170 °C while varying the mixing ratio, as shown in Figure 4g,h. On the contrary, Figure 4i shows that \( T_n \) slightly increases with an increase in the amount of 1-butanol in the ethanol/1-butanol binary.

Now, we can explain how the dissolved gas affects \( \tau_d \). The nucleation temperature \( T_n \) changes with the amount of dissolved gas, because dissolved gas molecules can act as nucleation sites.\(^{24–26} \) Hence, an increase in the amount of dissolved gas reduces \( T_n \). Therefore, the decreased \( T_n \) in in the aqueous binaries with an increase of the organic component (see Figure 4d–f) is a result of the increase in dissolved gas. Moreover, this decrease in \( T_n \) leads to faster nucleation and thereby explains the reduction in \( \tau_d \) with the increasing amount of dissolved gas (see Figure 3a). The same holds true for the organic binaries. For the ethanol/1-butanol, the amount of dissolved gas is slightly decreasing with increasing amount of 1-butanol, and consequently, a rise in \( T_n \) and thereby also in \( \tau_d \) is observed. The changes are not as large as for the aqueous binaries because the change in the amount of dissolved gas is smaller. The change is even smaller for the ethanol/acetone and ethanol/2-propanol binaries, and therefore \( T_n \) and \( \tau_d \) remain almost constant.

What remains to be explained is how the laser power \( P_l \) affects the behavior of \( \tau_d \). The nucleation temperature \( T_n \) is
independent of \( P_l \). Therefore, a higher \( P_l \) only increases the heating rate and thereby reduces the time to reach \( T_{n} \). Consequently, the nucleation happens earlier, and \( \tau_d \) decreases for higher laser powers as seen in Figure 2. Moreover, this is also a possible explanation for the reduction of the exponent \( \gamma \) for higher laser powers. If the temperature rises faster, the time difference between different \( T_n \) decreases. Hence, the effect of the change in \( T_n \) due to the dissolved gas on \( \tau_d \) decreases and thereby also the exponent.

Besides the delay time, it is also important to understand how the volume of the bubble is determined. To compare the different binary liquids, we define the accumulated energy before nucleation as the deposited energy \( E_d = \tau_d \cdot P_l \). In Figure 5, the first column shows the bubble volume versus \( E_d \) for various mixing ratios and exemplarily for the binaries water/ethanol (a), ethanol/acetone (d), and ethanol/1-butanol (g). For all cases, we can identify a linear behavior between the volume and \( E_d \) at low energies. However, the slope of this linear behavior varies with the mixing ratio, as shown in the second column of Figure 5. While for the water/ethanol binary, the slope remains constant at approximately 6 \( \mu \text{m}^3/\mu\text{J} \), and for the ethanol/acetone binary, it increases with the increasing amount of acetone from 5.3 to 8.7 \( \mu \text{m}^3/\mu\text{J} \). Moreover, for the ethanol/1-butanol binary, the slope decreases from 5.3 to 2.0 \( \mu \text{m}^3/\mu\text{J} \) with the increasing amount of 1-butanol in the binary.

In order to explain this difference in behavior, we have to look at the energy balance. We assume that the vaporization energy per mole \( E_{l-v} \) (kJ/mol) can be approximated by the energy needed to heat the liquid to the boiling temperature \( T_{b01} \) and the latent heat of vaporization.

\[
E_{l-v} = \int_{T_0}^{T_{b01}} c_p,m (T) \, dT + \Lambda_{vap}(T_{b01})
\]

(2)

The first term is the energy needed for the heating described as the integral over the molar heat capacity at a constant pressure \( c_p,m \) from the ambient temperature \( T_0 \) to the boiling temperature \( T_{b01} \). While this is easily calculated for pure liquids, mixtures are more complicated. Therefore, we estimate \( E_{l-v} \) for the mixtures by the pure liquid values weighted by their mole fraction in the vapor. This is similar to how we estimated the liquid mixture parameters; however, the gas-phase mole fractions are used instead to take into account that preferential evaporation of one species can occur. The mole fraction in the vapor can be determined by the mole fraction in the liquid using vapor−liquid equilibrium data. Hence, we use for the mixtures

\[
E_{l-v} = \alpha \cdot E_{l-v,1} + (1 - \alpha) \cdot E_{l-v,2}
\]

(3)

where \( \alpha \) is the mole fraction in the vapor of the first binary component, and \( E_{l-v,1} \) and \( E_{l-v,2} \) are the pure liquid values of components 1 and 2, respectively. If we assume that all the deposited energy is used to create vapor and the ideal gas law can be applied, we find the following relation between the deposited energy and the volume.

Figure 5. First column: maximal bubble volume as a function of the deposited energy in the binaries (a) ethanol/water, (d) ethanol/acetone, and (g) ethanol/1-butanol. Second column: slope of the volume growth as a function of the mixing ratio for the binaries (b) ethanol/water, (e) ethanol/acetone, and (h) ethanol/1-butanol. Third column: \( E_{l-v} \) of the liquid as a function of its mixing ratio for the binaries (c) ethanol/water, (f) ethanol/acetone, and (i) ethanol/1-butanol.
Here, \( R \) is the universal gas constant, \( T \) is the temperature, \( P_{\text{sat}} \) is the saturation pressure, \( n \) is the amount of vapor in mole, and \( V \) is the bubble volume at maximal expansion. Consequently, we expect \( V/E_d \) to be inversely proportional to \( E_{l-v} \); see eq 5.

\[
\frac{V}{E_d} = \frac{RT}{P_{\text{sat}}} \frac{1}{E_{l-v}}
\]

In the last column of Figure 5, the behavior of \( E_{l-v} \) as a function of the mixing ratio is shown. While the slope remains constant for the ethanol/water binary, the same holds true for \( E_{l-v} \) that stays at approximately 46.75 kJ/mol. For the increasing slope of the acetone/ethanol binary, \( E_{l-v} \) decreases from 47 to 33 kJ/mol. Finally, for the decreasing slope of the 1-butanol/ethanol binary, \( E_{l-v} \) increases from 47 to 64 kJ/mol. In comparison to the slope in the second column, the behavior is indeed inversely proportional to \( E_{l-v} \) as eq 5 suggests.

To show the global behavior, the slopes are extracted from all liquids and plotted against the right term of eq 5 in Figure 6.

![Figure 6](image-url) Maximal bubble volume per deposited energy as a function of \( RT/P_{\text{sat}}E_{l-v} \). The dashed line is a linear fit.

As expected from eq 5, we observe a linear increase for all liquids individually as well as globally, indicated by the dashed orange line. The only exception is the binary ethanol/2-propanol, which will be explained later. If we further analyze the global behavior, we find that the increase by an order of magnitude in \( V/E_d \) cannot be explained by the change in \( RT/P_{\text{sat}} \) since it only varies within 16% of the maximal value. Hence, the volume per energy is dominated by \( E_{l-v} \).

The reason why the global behavior and the ethanol/2-propanol case are not perfectly linear is probably related to the efficiency (slope of Figure 6). We assumed that the efficiency of the energy conversion from the absorbed light to the vapor bubble is the same for all liquids. In fact, this is not the case, and the efficiency varies between 5 and 12%. Therefore, the slope in Figure 6 varies slightly for each liquid, which leads to the deviation from the ideal case. In which way and why the efficiency changes will be the subject of another study.

**CONCLUSIONS**

In summary, we have shown how the volume and delay time of the initial giant bubble are controlled by the liquid parameters. This delay time between the start of the laser heating and the bubble nucleation \( t_2 \) is determined by the absolute amount of dissolved gas. The gas molecules act as nucleation sites, reducing the necessary nucleation temperature and thereby facilitate faster nucleation. The delay time can be tuned further by changing the laser power and consequently, the heating ratio. Furthermore, we revealed that the volume of the bubble at a given energy is determined by the liquid energy needed for vaporization \( E_{l-v} \). These results allow to tune the delay time and size of a vapor bubble by varying the corresponding liquid parameters. We envision that our findings will allow finer bubble control in applications, which is particularly promising for medical applications.

**ASSOCIATED CONTENT**

1. Supporting Information

   The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b10064.

   Detailed reasoning to prefer dissolved gas to surface tension as the dominant parameter (PDF)

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**Notes**

The authors declare no competing financial interest.

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