Nanosecond plasmas in water: ignition, cavitation and plasma parameters

K Grosse, J Held, M Kai and A von Keudell

Experimental Physics II—Reactive Plasmas, Ruhr-Universität Bochum, D-44780, Bochum, Germany

E-mail: Katharina.Grosse@rub.de

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Abstract

Nanosecond plasmas in liquids play an important role in the field of decontamination, electrolysis or plasma medicine. The understanding of these very dynamic plasmas requires information about the temporal variation of species densities and temperatures. This is analyzed by monitoring nanosecond pulsed plasmas that are generated by high voltages (HV) between 14 and 26 kV and pulse lengths of 10 ns applied to a tungsten tip with 50 μm diameter immersed in water. Ignition of the plasma causes the formation of a cavitation bubble that is monitored by shadowgraphy to measure the dynamic of the created bubble and the sound speed of the emitted acoustic waves surrounding this tungsten tip. The temporal evolution of the bubble size is compared with cavitation theory yielding good agreement for an initial bubble radius of 25 μm with an initial pressure of 5 × 10⁸ Pa at a temperature of 1200 K for a HV of 20 kV. This yields an initial energy in the range of a few 10⁻⁵ J that varies with the applied HV. The dissipated energy by the plasma drives the adiabatic expansion of water vapor inside the bubble from its initial supercritical state to a low pressure, low temperature state at maximum bubble expansion reaching values of 10³ Pa and 50 K, respectively. These predictions from cavitation theory are corroborated by optical emission spectroscopy. After igniting the nanosecond plasma, the electrical power oscillates in the feed line between HV pulser and plasma chamber with a ring down time of the order of 60 ns. These reflected pulses re-ignite a plasma inside the expanding bubble periodically. Broadband emission due to recombination and Bremsstrahlung becomes visible within the first 30 ns. At later times, line emission dominates. Stark broadening of the spectral lines of Hα (656 nm) and OI (777 nm) is evaluated to determine both the electron density and the electron temperature in these re-ignited plasmas.

Keywords: electron density, electron temperature, cavitation, shadowgraphy, nanosecond, ignition, plasma in liquid

1. Introduction

Plasmas inside and in contact with liquids are used for the decontamination of water, for plasma medicine, and for the modification of metallic and organic surfaces which are in contact with the treated liquid. These plasmas are usually generated by applying a high voltage (HV) to a tip shaped electrode immersed in the liquid of interest. Especially, the ignition of a plasma inside a liquid has generated special interest due to the enhanced mass transfer of the reactive species inside the liquid. The properties of those short nanosecond pulsed plasmas inside a liquid medium has been studied by many groups [1–7].

In μs pulsed plasmas, An et al [8] observed two types of streamers in liquids called primary streamers (PS) and secondary streamers (SS). PS exhibit very weak light emission and the streamers occur in a bushlike structure right after ignition, whereas SS grow at the tip of PS in a treelike structure and exhibit rather bright light emission. Additionally, Marinov et al [1] observed similar bushlike or treelike streamer modes for low and HV pulses applied to a tip
immersed in a liquid in nanosecond pulsed discharges. The authors observed the formation of a micro cavity at the rising and/or falling edge for HV pulses close to the breakdown voltage. Bushlike streamers then ignite in this cavity. This stands in contrast to HV pulses at much higher voltages, where they observed treelike streamers that seem to be ignited directly inside the liquid. Finally, Dobrynin et al. [4] investigated a so-called ‘dark phase’ as a phase of no light emission during the plateau phase of a nanosecond pulse with short rising times of 3 ns leading to two intensity maxima during the rising and the falling edge of the HV pulse, respectively. This was also observed by Marinov et al. [9] but could not be verified by Pongrac et al. [6], although the pulse shapes and rising times were similar.

These studies in the literature illustrate that the full understanding of the physics of plasma ignition and sustaining the discharge is still in its infancy due to the complexity of the phenomenon. Plasma generation depends on the characteristics of the plasma electrode, the powering of the electrode by a HV and the properties of the liquid. For example, if the rise time of the HV is of the order of many microseconds, the Ohmic heating of the liquid by the dc current will locally cause water vapor bubbles to be formed until the ignition criterion inside that bubble is met [10, 11]. A plasma is then generated in the gas inside this bubble and the plasma pressure continues the bubble to grow. In contrast, if the rise time of the HV is of the order of nanoseconds or below, electrostriction may cause the rupture of the liquid by a negative pressure difference of at least 24 MPa [12–14]. Seepersad et al. [3] postulated that this liquid rupture could induce the formation of so-called ‘nanopores’. This electrostriction is induced by the strong electric field gradient surrounding the tip electrode for short voltage pulse rising times in the nanosecond scale [15]. It is important to mention that microbubbles from dissolved gas in the liquid may also be present at ambient pressure, which then serve as ignition sites for plasma generation. This illustrates that the postulated presence of microbubbles or nanopores prior to plasma ignition is still an open debate.

Plasma ignition converts the liquid spontaneously into the plasma state, which then drives the formation and expansion of a plasma or hot gas filled bubble. The initial pressures after plasma ignition can be derived from the velocities of the emitted acoustic waves in liquids, yielding values in the range of 10s of GPa depending on the voltage [1, 5]. At the same time, the plasma or hot gas pressure expands the initial bubble until a specific size is reached before the counteracting force due to surface tension and the pressure in the ambient liquid causes this bubble to collapse. This sequence of plasma ignition followed by the expansion of a cavitation bubble has been analyzed by cavitation theory by Tereshonok et al. [16, 17].

The properties of ns plasmas inside liquids are difficult to assess, because optical and electrical diagnostics have to cope with the fast time scales and the inherent small size of the plasmas. Spectroscopic analysis reveals a broad continuum emission upon plasma ignition, which then converts into line emission after the HV pulse ends [6, 9]. The most commonly observed emission lines are the hydrogen Balmer $H_\alpha$ line ($3d^2D \rightarrow 2p^2P^0$) at 656 nm and the atomic oxygen line ($3p^4P \rightarrow 3s^2S^0$) at 777 nm. Line widths of $H_\alpha$ of several 10s of nanometers have been observed and utilized to determine electron densities up to $10^{26}$ m$^{-3}$ using the Stark effect [4, 6, 8, 9]. However, reliable values for electron densities from Stark broadening can only be determined, if the Stark effect can be separated from the pressure sensitive van der Waals broadening. This is especially important due to the very high pressures during the initial phase of bubble expansion. This is addressed in the literature by several authors. Dobrynin et al. found in time-averaged measurements the line shape to consist of the sum of two Lorentzian profiles [4]. They argued, that one of the profiles should represent van der Waals broadening and the other one Stark broadening. However, the interaction of these two line broadening mechanisms requires a convolution of both line profiles rather than its sum [18–20]. Therefore, it seems more likely that the two line profiles in the time-averaged data of Dobrynin et al. [4] represent different points in time instead of the overlap of different broadening mechanisms. More recently, Marinov et al. argued that the van der Waals contribution can be calculated using the red-shift of optical emission lines [9] and stated that such shifts are absent in Stark broadening of the $H_\alpha$ line. However, such a shift of the $H_\alpha$ line caused by electron impact cannot be neglected at very high electron densities [21, 22]. For example, an electron density of $10^{25}$ m$^{-3}$ induces a shift of the $H_\alpha$ line by 6 nm [21]. Consequently, line widths and line shifts have to be analyzed both to separate van der Waals broadening from Stark broadening. Nevertheless, several authors reported their results using Stark broadening only [6, 8]. Therefore, additional information about gas densities and pressures during and after the HV pulse are very much needed to interpret optical emission spectra without ambiguities.

In this paper, we use cavitation theory to examine the evolution of the expanding gas bubble that is monitored with shadowgraphy imaging. The predictions from cavitation theory are then fitted to the temporal evolution of the bubble sizes. Since the gas bubble is only clearly visible at 10 $\mu$s after the HV pulse, the conditions are extrapolated to the earlier phase of the ns discharge in order to gain information about gas densities and temperatures during the discharge evolution. These extrapolated predictions from cavitation theory are then compared to time-resolved optical emission spectroscopy (OES) to assess the temporal evolution of the initial continuum emission and subsequent line emission. Finally, these emission lines are then evaluated to determine electron density and electron temperature during the later stages of the discharge.

2. Experiment

2.1. Plasma setup and HV supply

Figure 1 shows a schematic of the experimental setup. The plasma is ignited inside a chamber made out of PMMA with
Additional, the setup was optimized by a HV pulser and to the plasma chamber, respectively, are denoted as \(a\) and \(b\) in figure 1. Additionally, the setup was optimized by a HV pulser that is synchronized with two ICCD cameras (ICCD1 and ICCD2) attached to a spectrograph that samples the plasma light via an optical fiber with a collimator. (b) Close up of the plasma in liquid chamber housing a pin-to-pin geometry with a 50 \(\mu\)m tungsten wire as plasma electrode. Shadowgraphy images are taken by using a Xe short arc lamp for illumination. The dimensions of the HV cable, the cannula and the tungsten wire are to scale.

Figure 1. (a) Experimental setup for spectroscopic analysis of plasma. Two transmission lines were used with total lengths of \(L_a = 3.4\) m (‘short’ cable) and \(L_b = 8.65\) m (‘long’ cable), respectively, including a back current shunt (BCS). The sections before and after the BCS are either \(a = 2.44\) m and \(b = 0.96\) m for the short cable and \(a = 4.33\) m and \(b = 4.32\) m for the long cable, respectively. The plasma is powered by a FID pulser that is connected to the plasma chamber by either a 3.4 m (‘short’) or 8.65 m (‘long’) cable of the type RG217. These two cable lengths are used to separate the initial pulse from the reflected pulses that oscillate between pulser and plasma chamber. Both, the initial and all reflected pulses are monitored via a custom made back current shunt (BCS) which is mounted into the cables. A detailed description of the BCS can be found in [23]. An exemplary BCS signal for the long cable is shown in figure 2.

The distance between the BCS to the pulser and to the plasma chamber, respectively, are denoted as \(a\) and \(b\) in figure 1. Additionally, the setup was optimized by a HV connector between the transmission line and the electrodes for the long cable. This connector allows easier exchanges of cables while keeping the same electrode distance within the chamber. Such connector was not used in the experiments using the short cable.

2.2. Shadowgraphy measurement

Shadowgraphy images are taken to monitor plasma ignition and bubble expansion. A Xe short arc lamp is used to illuminate the electrode tip. An optical system of different lenses was used to focus the light onto the electrode tip and to enlarge the image onto an Andor iStar DH734-18U-03 camera. The camera has a spectral sensitivity in the range of 180–850 nm and was triggered by the sync-output of the HV pulse generator. The jitter of the triggering signal is in the low ps range and can, therefore, be neglected. The gate width of the camera had to be adjusted to the different phases: \(t_{\text{gate}} = 2\) ns (ignition and re-ignition from 0 to 30 ns), \(t_{\text{gate}} = 50–70\) ns (gas channel and bubble formation from 38 ns to 1 \(\mu\)s) and \(t_{\text{gate}} = 100\) ns (bubble expansion and collapse from 1 \(\mu\)s to 1 ms). The single-shot shadowgraphy images show the propagation of plasma, gas channel and bubble behavior for different pulses. The overall temporal development of plasma ignition, formation of gas channels and their propagation, and bubble growth and collapse appears very reproducible in the shadowgraphy imaging.
2.3. Optical emission spectroscopy

Time-resolved OES was performed with a triple-grating SpectraPro 750 spectrograph from Acton Research. The light emission of the plasma was coupled into an optical fiber bundle using a collimator and transported directly to the spectrograph. A 50 g mm\(^{-1}\) grating, blazed at 600 nm, was used and the spectrum was recorded by a PI-MAX 1K Princeton Instruments camera (Gen II RB Slow Gate Intensifier). The time-resolved spectra were accumulated over 10,000 cycles with a triggering frequency of 15 Hz. The gate width of the camera was 30 ns with time steps of 15 ns. Therefore, a time span of approximately 300 ns was recorded, monitoring both the ignition and the afterglow in a phase-resolved manner. An intensity calibration was not performed.

The instrumental profile of the spectrograph was determined using a helium–neon laser that is known to produce a narrow emission line. The instrumental profile was approximated by a pseudo-Voigt profile, which was found to be mostly Gaussian in shape with a width of about 2.5 nm.

To determine the electron density and the electron temperature at the same time, two lines are mostly Gaussian in shape with a width of about 2.5 nm.

To determine the electron density and the electron temperature at the same time, two lines are fitted simultaneously: (i) hydrogen Balmer \(\text{H}_n\) (3d\(^f\)D \rightarrow 2p\(^p\)P\(^0\)) at 656 nm (\(\text{H}_n\)) and (ii) atomic oxygen (3p\(^p\)P \rightarrow 3s\(^s\)S\(^0\)) at 777 nm (\(\text{O}\text{777}\)).

While the shape of \(\text{H}_n\) is nearly independent from the electron temperature, the width of \(\text{O}\text{777}\) depends about equally on both electron density and temperature. By regarding both lines together, it is, therefore, possible to determine both parameters at the same time as long as other broadening mechanisms can be neglected.

The analysis of the bubble expansion by cavitation theory predicts a gas temperature of 1200 K at most during the expansion phase when line emission is visible. This corresponds to a Doppler broadening (full width at half maximum) of about 16 pm and 5 pm for \(\text{H}_n\) and \(\text{O}\text{777}\), respectively [20]. Doppler broadening may thus be neglected.

Van der Waals broadening, on the other hand, might make an important contribution to the overall line shape. The initial pressure during plasma ignition is expected to be in the range of GPa yielding van der Waals widths of more than 100 nm [24]. This pressure then strongly decreases during bubble expansion, but may still be high enough to influence the line widths at later times after the HV pulse. This influence of van der Waals broadening is evaluated according to [24, 25] assuming water as the neutral particle perturber with a polarizability of \(\alpha = 1.45 \times 10^{24} \text{cm}^3\) [26]. This calculation is straightforward for the analysis of the \(\text{O}\text{777}\) line. \(\text{H}_n\), however, exhibits multiple fine structure components with different orbital quantum numbers \(l\) which are thus broadened differently.

The calculation of van der Waals broadening was performed according to Griem [18, 24]. For \(\text{H}_n\), the computer simulations of Gigosos et al were utilized [27]. Two different approaches were combined: (i) for electron densities between \(10^{20}\) and \(10^{25} \text{m}^{-3}\), we used the complete line profiles provided by the authors for discrete electron densities in that range and interpolated those for other electron density values in between; (ii) for electron densities above \(10^{25} \text{m}^{-3}\) or below \(10^{20} \text{m}^{-3}\), we used the approximation formula provided by the authors although these results should be taken with caution, because the underlying theory begins to lose its validity at densities above \(10^{25} \text{m}^{-3}\) [27].

The line profile \(\epsilon\) is given by the convolution (*) of instrumental profile \((P)\), Stark profile \((S)\) and the van der Waals profile \((W)\) if necessary:

\[
\epsilon(n_e, T_g, n_e, T_e) = P * S(n_e, T_e) * W(n_e, T_g)
\]

with gas density and temperature \(n_e, T_g\) and electron density and temperature \(n_e, T_e\), respectively. The complete fit function \(I(A_{\text{H}_n}, A_{\text{O}\text{777}}, n_e, n_0)\) is the sum of the profiles of both lines \(\epsilon_{\text{H}_n}\) and \(\epsilon_{\text{O}\text{777}}\) weighted with their intensities \(A_{\text{H}_n}\) and \(A_{\text{O}\text{777}}\) according to:

\[
I(A_{\text{H}_n}, A_{\text{O}\text{777}}, \lambda_{0,\text{H}_n}, \lambda_{0,\text{O}\text{777}}, n_e, n_e, n_e, T_g) = A_{\text{H}_n} \cdot \epsilon_{\text{H}_n}(\lambda_{0,\text{H}_n}, n_e, n_e, T_g) + A_{\text{O}\text{777}} \cdot \epsilon_{\text{O}\text{777}}(\lambda_{0,\text{O}\text{777}}, n_e, n_e, T_g)
\]

with the line wavelength positions \(\lambda_{0,\text{H}_n}\) and \(\lambda_{0,\text{O}\text{777}}\). The parameters \(n_e, T_g\) and the line intensities and positions are fitted. In the case of a possible contribution of van der Waals broadening, \(n_e\) and \(T_g\) will be used as fixed constants. The choice of these constants will be motivated by cavitation theory and our experimental observations.

Figure 3 shows a typical emission spectrum at \(t = 90\ \text{ns}\) together with the best fit omitting van der Waals broadening. The fit parameters are: \(n_e = 8 \times 10^{24} \text{m}^{-3}\) and \(T_e = 0.5 \text{eV}\). Figure 3 also shows the continuum emission originating from the discharge afterglow before line emission emerges. To fit the line emission, this continuum has to be subtracted. This background subtraction is performed self-consistently as follows: in each optimization step the fit algorithm (Levenberg–Marquardt) subtracts the best guess of the line profiles from the data, smooths the resulting background spectrum with a
rolling average (over 100 pixel, about 70 nm) and then returns the sum of this smoothed background spectrum and the line emission as the result of the optimization step. In this way, the fit algorithm approximates the data as a combination of line emission and an arbitrary continuum background. The line emission cannot be erroneously included in this continuum function, since the rolling average acts as a low-pass filter. All fitted spectra were examined one by one to ensure that this approach did not introduce any systematic errors.

3. Results

3.1. Plasma phases

The FID nanosecond pulser generates voltages between 14 and 26 kV at a pulse length of 10 ns and a rise time of the order of 1 ns. These pulses propagate along the HV cable towards the plasma chamber. A part of a traveling HV pulse is reflected at the interface between cable and electrode assembly and between electrode assembly and liquid, as can be seen in figure 1. The efficiency of this reflection can be deduced for example from the Fresnel coefficient of the interface between electrode and liquid $r_{\text{electrode}}$: if we assume a dielectric constant of water of $\varepsilon_{\text{water}} = 80$, which is still valid at the GHz frequency range [28], and a dielectric constant of the dielectric inside the HV cable (the RG217 cable contains a dielectric from polyethylene (LDPE) as a shielding material with $\varepsilon_{\text{LDPE}} = 2.4$), one can deduce a value of the Fresnel coefficient $r_{\text{electrode}} = \sqrt{\varepsilon_{\text{water}} - \varepsilon_{\text{LDPE}}} / \sqrt{\varepsilon_{\text{water}} + \varepsilon_{\text{LDPE}}} = 0.7$. This yields a reflectivity $R_{\text{electrode}} = r^2 = 0.5$ indicating that a significant fraction of the HV power is reflected due to the large change of the refractive index at the interface between electrode and liquid. This reflected HV pulse is propagating back the transmission line towards the pulser, becomes reflected at the pulsar again, is recorded as a returning pulse by the BCS, and ignites finally the discharge a second time. The temporal distance $\Delta t$ between the different reflections depends on the length of the HV cable $[6, 29, 30]$. The velocity of the pulse $v_{\text{pulse}}$ within the coaxial cable is calculated by $v_{\text{pulse}} = c / \sqrt{\varepsilon_{\text{LDPE}}}$ with $c$ as the speed of light and $\varepsilon_{\text{LDPE}}$ the relative permittivity of the dielectric in the cable yielding $v = 1.94 \times 10^8$ km s$^{-1}$. The temporal distances between these pulses can be calculated by dividing the travel distance, equal to two times the cable lengths by $v_{\text{pulse}}$ yielding $\Delta t_{\text{short}} = 35$ ns for the short cable and $\Delta t_{\text{long}} = 89$ ns for the long cable, respectively. These theoretical time delays can be compared with the temporal evolution of the HV pulses as monitored with an oscilloscope showing good agreement (as shown in figure 2 for the long cable).

The oscillation of the HV power along the HV cable is equivalent to a ring down of the electrical power in the system with a characteristic time constant $\tau_{\text{ring-down}}$ that can be calculated from:

$$\tau_{\text{ring-down}} = \frac{L}{v_{\text{pulse}} (1 - \sqrt{R_{\text{pulser}} R_{\text{electrode}}})}$$

with $L$ the cable length in between the points of reflection and $R_{\text{pulser}}$ and $R_{\text{electrode}}$ the power reflection coefficient for the pulser and for the electrode, respectively. The reflection coefficient for the interface between HV cable and liquid may be dominated by the interface between the HV cable dielectric and the water liquid since the dielectric has a diameter of a few mm, whereas the plasma electrode has a diameter of only 50 $\mu$m (see figure 1(b)). As discussed above, this reflection coefficient $R_{\text{electrode}}$ is approximately 0.5. If we assume that $R_{\text{pulser}} = 1$, we can estimate a ring down time for the ‘short cable’ of $\tau_{\text{ring-down, short}} = 60$ ns and for the ‘long cable’ of $\tau_{\text{ring-down, long}} = 150$ ns.

3.2. Shadowgraphy

The ns plasma is ignited in distilled water and initiates the formation of a bubble in the liquid and a radial acoustic wave due to the initial pressure pulse. The temporal evolution of the bubble size and the radial acoustic wave is measured using shadowgraphy. This is shown for various HV voltages and moments in time in figure 4 (the HV tungsten tip, serving as the electrode, can be identified by its shadow at the right side of all images). In the beginning of the pulse, the image is dominated by plasma emission itself. The shape of the gas channels exhibits a bush-like structure $[8, 31]$. At around 10 $\mu$s, the cavitation bubble starts to become spherical, indicating that surface tension defines the bubble shape. For $U_{\text{avg}} = 14$ kV, the maximum bubble size is reached at 30 $\mu$s. At higher voltages, larger bubble sizes are reached at slightly later times. It is striking that the contrast in the images changes significantly in the phase between 330 ns and 1 $\mu$s, indicating that the density difference between gas channel and surrounding liquid significantly changes.

The shadowgraphy images are used to identify two characteristic properties of the phenomenon, the propagation of the emitted sound waves and the temporal variation of the cavitation bubble itself:

- Analysis of the emitted propagation of sound waves: the emitted sound waves in the liquids are clearly visible as propagating radial waves in figure 4. Images taken at 26 and 28 ns after the beginning of the HV pulse are shown in figure 5 using gate times of only 2 ns because the plasma itself is very bright. At later times, much longer gate times of 50 $\mu$s are used. Due to the brightness of the plasma itself, the imaging of the radial sound waves yields only reliable data after 44 ns after plasma ignition. A remnant of the plasma emission is still visible directly surrounding the HV tungsten tip due to the long gate time used for recording this image. Nevertheless, a dark region due to the density contrast is clearly observed. The outer perimeter of that region corresponds to the position of the radial sound wave front at $t = 44$ ns that can be converted into a velocity, if we assume that the sound wave is initiated at plasma ignition at $t = 0$. For times later than 50 ns, the average velocity of the wave is 1463 m s$^{-1}$, being constant for the different voltages which corresponds well to the speed of sound in water. For the ignition and earlier times until 24 ns, the plasma and the
remnant of the emission are too bright to see a clear edge of the shock wave front. Therefore the first measurable velocity of the shock wave deviating from the speed of sound can be calculated for \( t = 44 \text{ ns} \). The pressure was then calculated as described in Rice and Walsh [32]:

\[
p = c_1 \rho_0 u_s (10^{\frac{c_1 - c_2}{c_1}} - 1) + p_0
\]

with \( c_1 = 5190 \text{ m s}^{-1} \) and \( c_2 = 25306 \text{ m s}^{-1} \) derived from the Hugoniot curve, \( u_s \) the velocity of the shockwave, \( \rho_0 \) the ambient hydrostatic density and \( p_0 \) the ambient hydrostatic pressure.

This yields values \( (p_{\text{initial}}) \) of the order between 14 and 45 GPa in the liquid depending on the HV voltage, as it is plotted

**Figure 4.** Shadowgraphs of the different phases from plasma ignition to bubble expansion and collapse for different HV voltages \( U_{kV} \) (columns) at different times (rows). The different gate durations are given for each row in the first column varying from values of 2 ns gate (at 6 ns), 50 ns gate (at 330 ns–1.5 \( \mu \)s) and 100 ns gate (at 10.5–351 \( \mu \)s). The dark region to the right is the shadow of the tungsten wire.
The initial pressure $p_{\text{initial}}$ times an initial volume $V_{\text{initial}}$ corresponds to an initial energy $E_0$ that is deposited into the liquid by plasma ignition. If we compare $E_0$ with the electrical power $U_{\text{HV}}^2/R$ that is dissipated in the system, we may deduce a scaling of $\langle p_{\text{initial}} \rangle \cdot V_{\text{initial}}/\Delta t = U_{\text{HV}}^2/R$ with $\Delta t = 10$ ns pulse length. This scaling is shown as solid line in figure 6 (solid squares). The initial pressure $\langle p_{\text{initial}} \rangle$ times an initial volume $V_{\text{initial}}$ corresponds to an initial energy $E_0$ that is deposited into the liquid by plasma ignition. If we compare $E_0$ with the electrical power $U_{\text{HV}}^2/R$ that is dissipated in the system, we may deduce a scaling of $\langle p_{\text{initial}} \rangle \cdot V_{\text{initial}}/\Delta t = U_{\text{HV}}^2/R$ with $\Delta t = 10$ ns pulse length. This scaling is shown as solid line in figure 6 assuming a constant electrical resistance $R = 2.5 \, \text{k} \Omega$. Figure 6 also shows the gas pressure $p_{\text{gas}}$ (open symbols) inside an initial bubble with radius of 25 $\mu$m that is used as a boundary condition to model the expansion of the cavitation bubble. The pressure $p_{\text{gas}}$ denotes an estimate for the pressure at 10–20 ns after the begin of the HV pulse, whereas $\langle p_{\text{initial}} \rangle$ corresponds to an average pressure during the first 44 ns after the begin of the HV pulse. Since the pressure is expected to decrease continuously after plasma ignition at $t = 0$ s, it is conceivable that $p_{\text{gas}}$ is systematically lower than $\langle p_{\text{initial}} \rangle$. Details of the model involving the definition of $p_{\text{gas}}$ are described below.

Figure 6. Analysis of the emitted propagation of the sound wave: Averaged initial pressure $\langle p_{\text{initial}} \rangle$ within the first 44 ns after ignition derived from the propagation velocities of the initial sound waves as a function of the ignition voltage $U_{\text{HV}}$. The solid line depicts a scaling of $\langle p_{\text{initial}} \rangle \propto U_{\text{HV}}^2$. The open symbols denote the fitting pressure $p_{\text{gas}}$ inside an initial bubble with radius of 25 $\mu$m to model the expansion of the cavitation bubble.

- Analysis of the size of the cavitation bubble: the cavitation bubble expands due to the high initial pressure created by plasma ignition. The bubble sizes are extracted from the shadowgraphy images based on the strong contrast between liquid and gas inside the bubble. The shadowgraphy images in figure 4 clearly indicate that the bubble expands much slower than the propagation of the sound waves. The cavitation bubble reaches sizes up to a radius of 1 mm at $U_{\text{HV}} = 26$ kV, whereas the maximum bubble radius is only 0.6 mm for a HV voltage of $U_{\text{HV}} = 14$ kV. This is modeled using cavitation theory shown as solid lines in figure 7. The only fitting parameters are the pressure $p_{\text{gas}}$, the initial radius $R_0$ of the volume of the gas that is trapped in the bubble after plasma ignition, and the pressure in the ambient liquid $p_{\infty}$. This fitting procedure will be discussed below. After maximum expansion, the bubble collapses and remains small until it leaves the tungsten tip due to buoyancy.

Figure 5. Shadowgraphs of the initial phase at 26 and 28 ns after ignition using a gate time of the camera of 2 ns, and at the beginning of bubble expansion phase at 44, 94, and 144 ns using a gate time of 70 ns. The dark region to the right is the shadow of the tungsten tip. The plasma was ignited at 14 kV with a repetition frequency of 1 Hz.
3.3. Emission spectra

3.3.1. Temporal evolution. Figure 8 shows the temporal evolution of the emission spectra for the experiments using the short cable (a) and the long cable (b), respectively. Two phases can be distinguished. Phase I consists of a broad continuum, covering the whole detectable wavelength range during the first 0–30 ns after ignition followed by Phase II where the spectral line emissions of H\(\alpha\) and of atomic oxygen at 777 nm become distinct.

The temporal separation of the two phases becomes more pronounced for the experiment using the long cable. This separation of the spectral characteristics was also investigated by Pongrác et al [6]. In addition, the H\(\alpha\) line is also visible during Phase I for the experiment using the long cable (figure 8(b)) although it remains faint compared to the overall continuum. This is an indication that the processes responsible for line emission are also present during Phase I, but the lines are presumably hidden underneath the continuum.

Figure 9 shows the H\(\alpha\) line intensity for the experiments using the long cable (solid symbols) and the short cable (open symbols). Oscillations of the line intensities can be observed for both cable lengths, that coincide with the traveling times of the HV pulses in the system (indicated as arrows in figure 9). Very good agreement can be found with the predictions of \(\Delta t_{\text{short}}\) of 35 ns for the short cable and of \(\Delta t_{\text{long}}\) of 89 ns for the long cable, as discussed above.

The exponential decay of the line intensity is fitted with a ring down time constant of \(\tau_{\text{ring-down}}\) of 50 ns for the short cable denoted as dashed line in figure 9. This fits well with the ring down times of the short cable of the order of 60 ns, as estimated above. It is important, however, to keep in mind that the estimate for \(R_{\text{electrode}}\) of 0.5 regards only the interface between the dielectric of the cable and the liquid. The complete electrode assembly as depicted in figure 1 is, however, more complex so that a lower value for \(R_{\text{electrode}}\) is conceivable.

The decay time constant of the line intensity using the long cable length, however, yields 80 ns which is close to the decay time of the short cable, but much shorter than the estimated ring down time above. This may arise from the fact that the BCS inside the long cable is at a central position (see sections a and b in figure 1) and may cause additional reflections since both sections a and b in the long cable (see figure 1) have a similar length as the total length of the short cable. Therefore, the observation of similar ring down times is conceivable. In addition, the setup with the long cable was slightly modified by a connector that is directly soldered into the transmission line to easily replace the plasma electrodes by a plugin connection. This contact may also induce further temporal delays and a broadening of the reflected pulse for the long cable measurements.

3.3.2. Phase I: continuum emission. In the literature, it is argued that a ns pulse with a rise time of ns or below ignites a plasma directly inside the water without the presence of an
initial bubble [4, 30]. This is explained by possible nanopore formation on the picosecond scale, which could not be verified nor falsified up to now. Nevertheless, we rely on this hypothesis and assume that the initial pulse is ignited directly inside water creating streamers which leave behind gas channels inside the liquid. When the oscillating HV pulses reach the electrode again, a secondary plasma is ignited inside these gas channels and the expanding bubble. Therefore, the secondary plasma is ignited in another environment than the initial pulse, which implies different chemical and physical processes during the different plasma phases [30].

As discussed before, the emission spectra of the initial pulse shown in figure 8 reveal a broadband continuum during Phase I that can be explained by bound–free radiation from recombination of charged species and from free–free radiation from Bremsstrahlung. The contribution of recombination and bremsstrahlung is explained as follows: as discussed above, we assume that the ignition occurs inside the liquid [7], because the inertia of the liquid prevents the fast formation of a gas gap on the short time scale [16]. In addition, plasma ignition creates locally very high pressures in the range of GPa, as can be deduced either from the sound speeds of the radial acoustic waves or from the observation of very broad emission lines. As a simple estimate, we assume that the initial species density during ignition is identical to the species density in liquid water of $3 \times 10^{28}$ m$^{-3}$. Based on the rate constant for two-body recombination of $k_{\text{recomb},2} = 1.2 \times 10^{-7}$ cm$^{-3}$ s$^{-1}$ at $T_e = 500$ K and a $1/T_e$ scaling [33], we can deduce a life time $\tau_{\text{recomb},2} = 1/(n_e k_{\text{recomb},2})$ of $5 \times 10^{-12}$ s at an electron density $n_e$ of $3 \times 10^{27}$ m$^{-3}$, as will be derived below. Since $\tau_{\text{recomb},2}$ is of the order of ps or even smaller, all charged states are quenched much faster than the HV pulse length of 10 ns and dissociation of water molecules most likely is dominated by the inherent dissociative recombination. This explains the very high pressure and high temperature, which expand the initial plasma region and a cavitation bubble evolves. Due to the fast time scales, one may assume an adiabatic expansion that implies a strong decrease of pressure, temperature and species density. Consequently, the reflected HV pulses during the ring down time interact with smaller species densities at later times after the initial plasma ignition.

Due to the decreasing pressure inside the bubble, line emission becomes dominant when the plasma is re-ignited by the reflected HV pulses. Stark broadening of the H$_\alpha$ line and of the atomic oxygen line at 777 nm is used to determine the time-resolved electron density of these re-ignited discharges. Figure 10 shows the determined electron densities for the plasma generated using the short cable. Van der Waals broadening is neglected in this calculation, as will be discussed in detail in section 4.4.

The electron density shows an exponential decay in time, superimposed with strong oscillations. Both, the decay and the oscillations correspond to those shown in the line intensity shown in figure 9. The decay of the electron density has a similar time constant of $\tau_{\text{decay}} = 70$ ns.

The analysis of the spectral lines also allows the determination of electron temperatures, as shown in figure 11.
for the plasma using the short cable. The electron temperature shows strong oscillations with the same frequency as the oscillations in electron density and line intensity. The oscillations, however, are shifted in time compared to the electron density oscillations. A maximum in temperature always occurs at a density minimum and is then followed by a temperature decrease and a density increase. This sequence is reminiscent of plasma ignition, where few electrons are initially strongly heated, multiply by ionization and thus lose their energy. This observation strongly supports the hypothesis of plasma re-ignition caused by the periodic energy input by the oscillating HV power in the system.

Additionally, the electron temperature increases with time yielding values up to 4 eV. The uncertainty in the determination of the electron temperatures can be quite large, because the uniqueness of the line profile fit is limited. This is expressed by individual error bars in figure 11. Nevertheless, an overall increase in electron temperature can be seen that can be well explained taken the decreasing species density with adiabatic expansion and increasing bubble diameter into account. At later times, the neutral density is smaller so that plasma re-ignition takes place in a bubble with smaller gas density. Due to the longer mean free path, the seed electrons can be accelerated more easily leading to a higher temperature at later stages. From cavitation theory discussed below, one may assess a time dependent neutral density $n_{\text{gas}}(t)$ during the adiabatic expansion of the bubble. With a typical cross section of $10^{-15} \text{ cm}^2$, one may deduce a time dependent mean free path of $\lambda(t) = 1/(n_{\text{gas}}(t)\sigma)$ that is plotted as dashed line in figure 11. In addition, the water vapor in the expanding bubble may undergo a phase transition to the liquid state, as discussed below, resulting in a partial pressure equivalent to the saturation pressure of 2.34 kPa at 100% humidity and thus a smaller neutral density. This can be converted into a mean free path shown as solid line in figure 11. One can see that the increase in $T_e$ with time is correlated with a corresponding increase in mean free path in the expanding bubble.

The interpretation of the observed decay times of the electron density resolves the opposing statements in the literature since some authors observe a very fast decrease of plasma emission after the HV pulse [3, 4, 7], whereas others observe much longer decay times [6, 30]. Since the time constants for recombination are identical, those opposing observations most likely originate from the different powering schemes of the individual setups leading to very different ring down times of the electrical HV power.

4. Discussion

The experimental observations can be summarized as follows:

- Plasma ignition causes the generation of sound waves. The velocities of these radial waves are used to determine initial pressures $\langle p_{\text{init}} \rangle$ in the range between 15 and 44 GPa as average values for the first 44 ns.
- Plasma ignition causes the generation of a cavitation bubble that expands until a radius of up to 1000 μm before it collapses again around 45–100 μs after plasma ignition. After the collapse, no re-bounce of the bubble is observed.
- The emission spectrum directly after plasma ignition is dominated by recombination and Bremsstrahlung radiation.
- The expanding gas inside the cavitation bubble is frequently re-ignited by reflected HV pulses that oscillate between power supply and plasma chamber.
- During re-ignition of the expanding gas, line emission becomes visible. From this, electron densities and temperatures can be deduced yielding values up to $10^{25} \text{ m}^{-3}$ and temperatures between 0.1 eV and 4 eV, respectively.

These experimental findings are correlated in the following with predictions from theory. At plasma ignition and during expansion of the bubble, the system covers extremely different time and lengths scales so that an overall theoretical description is very challenging. As a first step, we separate the description in two phases. Model I describes the slow processes during bubble expansion using cavitation theory based on continuum equations. Model II describes the fast processes during plasma ignition. Here, a more microscopic and atomistic model based on particle in cell or molecular dynamics codes that cover the transport of energy and species in the liquid directly after ignition would be required. Since such modeling approaches are not yet available, we estimate the dynamic of the ignition phase only by a few assumptions and balance equations for pressure and energy.

4.1. Model I: cavitation theory

When a local pressure difference induces the rupture of a liquid, bubbles are formed and cavitation occurs. Such pressure differences may be caused by fast objects moving in liquids (cavitation at ship propeller blades), by external
acoustic waves in the liquid (sonoluminescence), or by electrical breakdown at HV tips in electrolytes (plasma generation in liquids). After their initial formation, these cavitation bubbles usually oscillate under the influence of two forces, the pressure difference between trapped gas inside the bubble and the surrounding liquid and the surface tension of the interface between bubble and liquid.

An expanding or collapsing bubble may experience a pressure \( p_B \) at the interface of the bubble with radius \( R \) and the surrounding liquid. The pressure in the liquid far away from the bubble is \( p_\infty \). The bubble radius changes with a velocity \( U = R \) and causes a movement of the surrounding liquid with velocity \( u \) at radius \( r \). The sound velocity of an acoustic wave in the surrounding liquid at pressure \( p_\infty \) is \( c_\infty \). Due to the pressure increase in the liquid during expansion, the local sound velocity may vary, denoted as \( c(r) \).

The simplest description of the expansion of a bubble has been derived by Rayleigh 1917 by regarding a spherical bubble with vacuum that expands or collapses in an incompressible liquid at pressure \( p \) [34]. Later, this has been extended to compressible liquids taken into account that a pressure pulse may propagate in the liquid only with the sound velocity at maximum. This yields the Rayleigh–Plesset equation [35–39]:

\[
RR\left(1 - \frac{R}{C}\right) + \frac{3}{2}R^2\left(1 - \frac{R}{3C}\right) = h\left(1 + \frac{R}{C}\right)
\]

\[
+ \left(1 - \frac{R}{C}\right)R \frac{\partial h}{C} \frac{\partial t}. \tag{5}
\]

With \( R \) the radius of the interface between bubble and liquid, \( C \) the speed of sound at the location of that interface, and \( h \) the enthalpy defined as:

\[
h = \int_{p_\infty}^{p_r} \frac{dp}{\rho}. \tag{6}
\]

The enthalpy \( h \) is calculated from the pressure dependent density of water \( \rho(p) \) using the equation of state of water:

\[
h = \frac{n}{n - 1} \frac{1}{\rho_0} (B + p_\infty) \left(\frac{p_{\text{liquid}}(R) + B}{B + p_\infty}\right)^{\frac{n-1}{n}} - 1
\]

with the coefficient \( B = 3000 \times 10^5 \text{ Pa} \) and \( n = 7 \). The experiments in our setup indicate that the velocity of the emitted radial acoustic waves are significantly larger than the expansion of the bubble radius itself. Therefore, we can neglect the second order term proportional to \( \frac{\partial h}{\partial r} \) in equation (9). Nevertheless, we keep all first order terms and take into account that the sound velocity \( C \) at the location of the interface at \( R \) depends on the pressure \( p_{\text{liquid}}(R) \) and the sound velocity \( c_\infty = 1435 \text{ ms}^{-1} \) at ambient pressure according to:

\[
C = c_\infty \left(\frac{p + B}{p_\infty + B}\right)^{\frac{n-1}{n}}. \tag{8}
\]

This yields finally:

\[
RR\left(1 - \frac{R}{C}\right) + \frac{3}{2}R^2\left(1 - \frac{R}{3C}\right) = h\left(1 + \frac{R}{C}\right)
\]

\[
+ \left(1 - \frac{R}{C}\right)R \frac{\partial h}{C} \frac{\partial t}. \tag{9}
\]

The initial pressure at the HV electrode corresponds to the electric field pressure initiated by the tungsten wire (diameter 50 μm) and a tip radius of \( R_0 = 25 \mu \text{m} \) during the pulse length of 10 ns. The electric field pressure is given as:

\[
p_{E-\text{field}} = \frac{1}{2} \epsilon_0 E_{HV}^2 \left(1 - \frac{1}{\epsilon_1} + \frac{k}{\epsilon_1}\right)
\]

\[
- \frac{2\sigma}{R} - 4\ell_0 R \frac{\partial R}{R}. \tag{10}
\]

\( p_{E-\text{field}} \) is a free parameter, \( \gamma = 1.33 \) the adiabatic coefficient for water, \( \sigma \) the surface tension and \( \eta \) the viscosity of water. The numerical solution of equation (9) yields \( T(t) \) that can be converted into a temperature \( T(t) \) of the adiabatically expanding gas according to:

\[
T(t) = T_0 \left(\frac{R_0}{R(t)}\right)^{3(\gamma-1)}. \tag{12}
\]

\( T_0 \) corresponds to the reference temperature at an initial bubble radius \( R_0 \). Equation (9) is solved numerically with the boundary conditions \( R(t = 0) = R_0 \) and \( R(t = 0) = 0 \) and the pressure given in equation (11). The constants for water as a liquid are \( \sigma = 0.072 \text{ N m}^{-1} \), \( \eta = 0.001 \text{ Pa s} \), \( \rho_0 = 1000 \text{ kg m}^{-3} \), and \( \gamma = 1.33 \) for water vapor. The expansion is initiated by \( p_{E-\text{field}} \) for a duration of 10 ns, assuming a radius of the HV tip of 25 μm at a voltage \( U_{HV} = 20 \text{ kV} \). Since the dielectric constant \( \epsilon_{water} \) is of the order of 80, the second and third term in equation (11) for \( p_{E-\text{field}} \) can be neglected. The remaining unknown is the initial pressure \( p_{gas,R0} \) being a fit parameter. From the comparison of the modeled \( T(t) \) and the observation of a typical maximum bubble radius of the order of 600 μm, one can fit \( p_{gas,R0} \) to \( 5 \times 10^4 \text{ Pa} \) for an initial radius of \( R_0 = 25 \mu \text{m} \). The high pressure of 0.5 GPa is consistent with the high pressures in the GPe range deduced from the shadowgraphy measurements discussed above.

The temporal evolution of the radius \( R(t) \), the velocity \( \dot{R}(t) \), the temperature \( T(t) \) setting \( T_0 = 1200 \text{ K} \), and the pressure is shown in figure 12. One can clearly see, that the bubble size within the first 10 ns does almost not change and
that the maximum velocity of 400 ms\(^{-1}\) is reached at 50 ns, which is well below the sound speed of an acoustic wave in 1 bar water of 1435 ms\(^{-1}\). The maximum bubble radius of 600 \(\mu\)m is reached at 50 \(\mu\)s. At the same time, the pressure dropped to 10\(^5\) Pa and the temperature to \(T = 0.05 \cdot T_0\) due to the adiabatic expansion. After that expansion, the bubble collapses reaching its minimum size again at 100 \(\mu\)s.

The fitting parameter of an initial pressure and volume can be used to determine the potential energy \(E_0\) that drives this expansion according to:

\[
E_0 = p_{\text{gas},0} V_0 = p_{\text{gas},0} \frac{4\pi}{3} R^3_0 .
\] (13)

Equation (9) is solved for varying initial pressure \(p_{\text{gas},0}\) expressed as \(E_0\) according to equation (13). The maximum bubble radius and time of collapse versus \(E_0\) is shown in figure 13. One can see, that the bubble radius and the time of collapse scale with \(\sqrt{E_0}\).

The modeling based on equation (9) is used to model the measured temporal evolution of the size of the cavitation bubble, as shown as solid lines in figure 7. The fitting parameter were the initial pressure \(p_{0,\text{gas}}\) in a bubble with a radius of 25 \(\mu\)m and the pressure \(p_\infty\) in the ambient. This pressure in the ambient should correspond to 10\(^5\) Pa or 1 bar. However, an excellent fit to the data as illustrated in figure 7 could only be found, if an ambient pressure in the range between 3 \(\times\) 10\(^5\) and 4.2 \(\times\) 10\(^5\) Pa has been used. The fitting procedure shows that the maximum bubble size and the time of collapse are usually strongly coupled properties—the bubble size depends on the potential energy driving the cavitation bubble given by the initial pressure \(p_0\) times the initial volume \(V_0\); the time of collapse is also given by the potential energy driving the cavitation, but also by the ambient pressure \(p_\infty\) that accelerates the collapse of the bubble after its maximum expansion. An ambient pressure slightly above 1 bar seems reasonable, because the sound waves that are emitted from the plasma emission travel through the liquid container of our setup, but are also reflected at the bounding walls. These reflected sound waves may interact with the expanding and collapsing bubble multiple times during one cycle, and may drive the bubble collapse a bit faster compared to the normal ambient pressure of 10\(^5\) Pa. The simulations also show that the influence of these reflected pressure waves on the initial phase of bubble expansion is small, because the pressures inside the bubble during the initial phase are much higher than \(p_\infty\).

The fitting of the bubble expansion and collapse showed excellent agreement for the parameters of \(p_0 = 10^5\) Pa and \(p_\infty = 3 \times 10^5\) Pa for the data using \(U_{\text{KV}} = 14\) kV (solid line fitting the open squares in figure 7), of \(p_0 = 5 \times 10^5\) Pa and \(p_\infty = 4 \times 10^5\) Pa for the data using \(U_{\text{KV}} = 18\) kV (solid line fitting the solid circles in figure 7), of \(p_0 = 13 \times 10^5\) Pa and \(p_\infty = 4.2 \times 10^5\) Pa for the data using \(U_{\text{KV}} = 22\) kV (solid line fitting the open triangles in figure 7), and of \(p_0 = 20 \times 10^5\) Pa and \(p_\infty = 4.2 \times 10^5\) Pa for the data using \(U_{\text{KV}} = 26\) kV (solid line fitting the solid squares in figure 7). All these parameter correspond to an initial bubble size with radius 25 \(\mu\)m. The modeled values for \(p_{0,\text{gas}}\) are also plotted in figure 6 as a comparison to the measured \(\langle p_{\text{initial}}\rangle\).
comparison is reasonable taken into account that \( \langle p_{\text{initial}} \rangle \) is an average over 44 ns during the initial pressure drop from the high initial pressure of 100 GPa at ignition (see below) down to lower pressures as the bubble starts to expand. The increase in \( p_{\text{gas}} \) and \( \langle p_{\text{initial}} \rangle \) is very similar.

Our results depend sensitively on the initial pressure for a given bubble size. The relevant parameter, however, is the initial dissipated energy \( p_{\text{gas}} V_0 \) and a higher pressure but lower volume would lead to the same modeling result. In principle, the use of a higher pressure and a smaller volume with radius \( R_0 \) can also be used as boundary condition for the cavitation modeling. However, such solutions run into numerical difficulties, because the initial velocities are much closer to the sound speed. Therefore, we used the \( R_0 = 25 \, \mu \text{m} \) value as a fitting parameter, and extrapolated to smaller radii by simple assumptions, as discussed in the following.

4.2. Model II: plasma ignition

The values for \( p_0 \), \( V_0 \) and thus \( E_0 \) are fitting parameters used in the cavitation model I to describe the starting condition for the expanding gas yielding a good agreement between the observed maximum bubble radius and an energy \( E_0 \) of the order of \( 10^{-5} \) J at a pressure of \( 5 \times 10^9 \) Pa in a volume with radius \( R_0 \). To convert this energy \( E_0 \) into an initial species density \( N_0 \), times an average energy \( k_B T \) according to an ideal gas law, one needs an estimate about the absolute values of either \( N_0 \) or \( T_0 \). For this, the possible pathways for plasma ignition are discussed in model II: at first one may postulate that the electric field pressure at the tip of the tungsten wire exerts a negative pressure difference causing the rupture in the liquid at a negative pressure difference above \( 2.4 \times 10^7 \) Pa [12]. For a given voltage of 20 kV, such a high pressure can only be reached when the curvature radius of the tungsten tip is less than 5 \( \mu \text{m} \). This is much smaller than the tip radius in the experiment of 25 \( \mu \text{m} \). Nevertheless, one may assume that this field strength is reached at the edges of the 50 \( \mu \text{m} \) diameter tungsten tip or at irregularities at the tip surface itself. Therefore, one may postulate that an initial region with a local radius of 5 \( \mu \text{m} \) is exposed to a local electric field pressure of \( 2.4 \times 10^7 \) Pa and rupture occurs, leading to the formation of nanobubbles [23]. Any macroscopic movement of the liquid cannot occur on the time scale of 10ns due to the inertia of the liquid since the model I describing \( R(t) \) shows a change of less than 1 \( \mu \text{m} \) within the first 10 ns consistent with the analysis of Tereshonok et al [16, 17]. Consequently, it is very likely that the plasma ignites inside the liquid initiated by small electron avalanches inside these nanobubbles [7].

After ignition, the water is converted into the plasma state. If we assume that the energy \( E_0 \) remains constant during the 10 ns plasma pulse and only spreads by heat conduction from the region of ignition the value of \( E_0 = 3.2 \times 10^{-5} \) J or 3.3 kW within the 10 ns can be converted into a temperature, if we regard a species density of \( 3.3 \times 10^{28} \) m\(^{-3} \) water molecules around the HV tip in a given volume that cannot be displaced within the first ns. Two extreme cases can be distinguished, ignition in a small region with radius 5 \( \mu \text{m} \) compared to the starting point for the bubble expansion at \( R_0 = 25 \, \mu \text{m} \): (i) \textit{ignition: } \( 3.2 \times 10^{-5} \) J dissipated energy divided by the total number of species inside a volume with a radius of 5 \( \mu \text{m} \), equivalent to the region of ignition, corresponds to an energy per particle of around 15 eV, which is well above the ionization energy of 12.26 eV. Consequently, one would expect 100% ionization degree. The pressure yields 100 GPa in a volume with radius 5 \( \mu \text{m} \); (ii) \textit{begin of bubble expansion: } \( 3.2 \times 10^{-5} \) J dissipated energy divided by the total number of species inside a volume with a radius of 25 \( \mu \text{m} \) equivalent to the region that drives bubble expansion, corresponds to a temperature of 1200 K at a pressure of 0.5 GPa.

These postulated consecutive phases of \textit{ignition} followed by the \textit{beginning of bubble expansion} may be dominated by heat conduction that causes the initial small region with radius of 5 \( \mu \text{m} \) and 100% ionization to expand and to create a larger gas filled bubble at 1200 K with a radius of 25 \( \mu \text{m} \) while keeping the energy \( E_0 \) constant. This picture implies pressures up to 100 GPa in the very beginning of the HV pulse and only GPa at a few 10s of ns, which fits perfectly to the observation of average pressures within the first 44 ns of \( \langle p_{\text{initial}} \rangle \) between 15 and 44 GPa. These average pressures \( \langle p_{\text{initial}} \rangle \) fit well to the modeled pressure \( p_{\text{gas}} \) between 1 and 20 GPa at a bubble radius of 25 \( \mu \text{m} \). It is also reasonable that \( \langle p_{\text{initial}} \rangle \) is larger than \( p_0 \), because \( \langle p_{\text{initial}} \rangle \) is an average of the initial 44 ns of plasma ignition followed by cavitation, whereas \( p_{\text{gas}} \) describes the pressure at later times. The velocity of heat conduction after plasma ignition equals the speed of sound: if we assume that \( E_0 \) is initially dissipated in a volume with radius 5 \( \mu \text{m} \), heat conduction will spread this excitation with the sound speed of 1435 m s\(^{-1} \) to a radius of 25 \( \mu \text{m} \) within 14 ns. This time span is very consistent with the characteristic times of our experiments and supports very well the hypothesis of a phase that is dominated by heat transport. The upper limit for a volume \( V_{\text{lim}} \) to which \( E_0 \) spreads causing the evaporation of water vapor should be given by an average temperature that falls below the boiling temperature \( T_{\text{lim}} \) of 373 K. This volume \( V_{\text{lim}} = E_0 / (n k_B T_{\text{lim}}) \) implies a maximum radius \( R_{\text{lim}} \) of 32 \( \mu \text{m} \). This shows that the starting condition of \( R_0 = 25 \, \mu \text{m} \) is very consistent with these very rough estimates about plasma ignition.

It is important to note that this assessment is only a hypothesis and any direct modeling of the ignition process including the formation of nanobubbles and the transport of energy and radiation after ignition requires a model on the molecular levels and is beyond the scope of the fluid models above being only a good approximation for the later stages of cavitation.

Summarizing, one may state that \textit{model II}—plasma ignition—is characterized by a faster energy transport compared to the mass transport leading to a direct conversion of water at liquid density into the excited state either as plasma or as hot gas during the first 10 ns after ignition. This is in contrast to \textit{model I}—bubble expansion—where mass transport is now faster than energy transport since the dynamic is governed to first order by the adiabatic expansion of the trapped hot gas inside the bubble where the transfer of energy at the interface of the bubble wall to the liquid occurs on a
longer time scale. Both models are connected by an initial radius $R_0$ and pressure $p_{0,\text{gas}}$ at the end of the ignition phase and at the beginning of the cavitation phase.

### 4.3. Bubble expansion and the transition from super critical water to water vapor and to condensation

The adiabatic expansion of water vapor during the adiabatic bubble expansion implies a strong variation of pressure and temperature. The modeled values of pressure as a function of temperature $p(T)$ is depicted in figure 14 together with the phase boundaries of water between the phases gas, liquid, and ice. The fitting parameters are again the initial pressure $p_0$ in the initial volume $V_0$ with radius $R_0$. Figure 14 indicates that the pressure and temperature decreases to $10^{-3}$ Pa and to $50$ K, respectively when the bubble radius reaches a maximum radius of $600 \mu$m. It is also interesting to note that the water vapor undergoes the transition from its super critical state (indicated by the gray area in figure 14) to the liquid and the solid state. This transition to liquid and to solid occurs at $110$ ns and at $510$ ns, respectively.

Such phase transitions, however, require a specific time constant for condensation, which can occur either in the volume of the bubble or by adsorption of gas species at the inner walls of the bubble. The time constant $\tau$ for this surface adsorption can be derived by balancing the surface collision fluence with the total number of gas phase species inside a bubble with radius $R$ [17]:

$$\frac{1}{4}n_{\text{gas}}v_{\text{thermal}}\beta\tau 4\pi R^2 = n_{\text{gas}} \frac{4\pi}{3} R^3$$

(14)

with $n_{\text{gas}}$ the density of gas phase species, $v_{\text{thermal}} = \sqrt{3k_B T / m}$ the thermal velocity of water molecules with mass $m$ and temperature $T$ in a volume with radius $R$. $\beta$ denotes the sticking coefficient of water molecules. During bubble expansion the radius $R$ varies, but also the temperature and maybe also the sticking coefficient. As a rough estimate, we set $\beta = 1$ and $T$ to $300$ K, which is reasonable during the later stages of bubble expansion. This estimate might also not be too bad for the initial phase of bubble expansion, because the temperature is expected to be higher, but at the same time, the sticking coefficients should be lower, since at higher temperatures the water molecules easily desorb again from the inside of the bubble walls, rendering an effective sticking coefficient well below unity. This leads to a time constant for condensation of:

$$\tau = \frac{4R}{3v_{\text{therm}}}.$$  

(15)

This time constant can be included in the Rayleigh–Plesset equations, by replacing the initial pressure $p_{0,\text{gas}}$ being a measure for the initial species density, with $p_{0,\text{gas}} \times \exp(-t/\tau)$. The numerical solution of bubble expansion including condensation is shown in figure 15 in comparison to the model without condensation, as discussed in figure 12. One can clearly see that condensation is not affecting the initial phase of bubble expansion too much. Only at around $1 \mu$s, the pressure drops significantly. The limit is expected to be the water saturation pressure of $2.34$ kPa, as the balance between adsorption and desorption.

Our experimental observations may be consistent with such a condensation model: (i) a clear spherical bubble becomes visible at about $10 \mu$s after plasma ignition since the pressure inside the bubble is significantly lowered due to condensation yielding a strong contrast in the shadowgraphy images; (ii) the variation of the electron temperature in figure 11 seems to be much stronger compared to the
variation of the mean free path assuming no condensation in the time period between 100 and 400 ns after plasma ignition. If we take condensation into account, however, the mean free path strongly changes from the average value of over saturated water vapor (dotted line in figure 11) to the value corresponding to the water saturation pressure (solid line in figure 11). Such a change in mean free path should also lead to an abrupt change in electron temperature that is observed in the experiment.

This condensation model is also supported by the significant change in contrast in the shadowgraphy images after plasma ignition. Apparently, condensation sets in, causing an abrupt change in density and thus a much stronger contrast between gas channel and surrounding liquid. This is exemplified in figure 16 showing an image at 88 ns after ignition (a) corresponding to super critical water, and at 330 ns after ignition during condensation (b), and at 1 μs after ignition (c) corresponding to the completion of condensation. One can see that the radial sound waves propagate a bit further after 1 μs compared to 330 ns, but also that the contrast of the central region is much stronger and the interface between gas bubble and surrounding liquid becomes more pronounced.

Any strong variation of the neutral gas density should become visible in line emission via the appearance or absence of van der Waals broadening, as discussed in the following.

4.4. Impact of neutral gas density on the line emission

The predicted gas densities from cavitation theory can be compared to the line broadening mechanisms observed in the optical spectra. Line emission can only be evaluated after \( t = 30 \text{ ns} \) where the cavitation theory predicts a gas density of \( 2 \times 10^{28} \text{ m}^{-3} \). Such a high density would imply a van der Waals width of about 100 nm and 38 nm for \( \text{H}_2 \) and \( \text{O}_2 \), respectively (using \( T = 860 \text{ K} \) from the cavitation model).

This, however, is more than three times the observed line widths. If one assumes a density of \( 6 \times 10^{27} \text{ m}^{-3} \) instead, the line widths can be explained by van der Waals broadening only. Therefore, we conclude that the predicted gas densities from the cavitation model are only a rough estimate and presumably only an upper limit for the proper gas density variation during expansion. Since the accuracy of the cavitation model depends only on the initial pressure \( P_{\text{gas,0}} \) describing perfectly the observed bubble expansion, we assume that \( P_{\text{gas,0}} \) is rather accurate and the ambiguity in the gas density \( n \) originates from the ambiguity in the temperature \( T \) according to \( p = n k_B T \) since different combinations of density and temperature would result in the same pressure. For example, the initial temperature \( T_0 \) might be three times higher so that the gas density is three times lower. Since the cavitation model predicts only the temperature with respect to a reference temperature \( T_0 \), this \( T_0 \) is free parameter. Besides this ambiguity, condensation may play a significant role during bubble expansion. The additional loss of water vapor by condensation at the bubble walls will cause the gas density inside the expanding bubble to drop even faster than predicted by the cavitation model. Such a condensation takes place over a time span of 100 ns [17] leading eventually to the water saturation pressure of \( 2.34 \times 10^7 \text{ Pa} \) equivalent to a density of \( 1 \times 10^{24} \text{ m}^{-3} \), as a lower density limit where van der Waals broadening induces line widths less than 0.1 nm and can, therefore, be neglected for times \( t > 100 \text{ ns} \).

5. Conclusion

Plasma generation by nanosecond pulses in water with voltages between 14 and 26 kV at a pulse length of 10 ns has been studied by cavitation theory in combination with OES and shadowgraphy. The comparison between modeling and experiments indicate a dynamic of plasma ignition and expansion as illustrated in figure 17 and explained in the following:

- Figure 17(a): Ignition takes place in nanopores in the liquid with a density of \( 3.3 \times 10^{26} \text{ m}^{-3} \) water molecules. These nanopores are caused by a local negative pressure of 24 MPa that is required for liquid rupture. This local pressure is exerted by the electric field around edges of
the HV tip with a local radius of 5 μm or less at a voltage of 20 kV.

- Figures 17(a), (b): The dissipation of electrical energy during plasma ignition in a small region with radius 5 μm converts the liquid directly into the plasma state. Heat conduction causes then the energy to be distributed over a larger region around the HV tip. This initial transport of energy is much faster than the mass transport due to the inertia of the liquid which prevents any significant displacement during the HV pulse length of 10 ns. After the plasma pulse, the initial high pressure also causes cavitation and the plasma and hot gas drives the expansion of the bubble. Then, mass transport is faster compared to the energy transport. The analysis of the expansion phase with cavitation theory yields the best fit for an initial \( R_0 = 25 \) μm radius bubble with pressures ranging from \( p_0 = 10^6 \) Pa to \( 20 \times 10^6 \) Pa. This boundary condition corresponds to a typical energy \( E_0 \) for \( p_0 = 0.5 \times 10^9 \) Pa of \( E_0 = p_0 V_0 = 3.2 \times 10^{-5} \) J. Since this energy is dissipated during the 10 ns plasma pulse, we can deduce an absorbed electrical power of 3.3 kW. Based on the dissipated energy of \( 3.2 \times 10^{-5} \) J, one can assume 100% ionization in a small volume with a radius of 5 μm. The time constant for recombination at these high densities is of the order of ps. Therefore, a bright recombination continuum becomes visible.

- Figure 17(b): The strong thermalization after the initial plasma ignition in a small region with 5 μm radius leads to a temperature of 1200 K of the heated water in the bubble with radius of 25 μm for a pressure of \( 0.5 \times 10^9 \) Pa. The bubble has not yet expanded, rather a finite volume around the tip goes through a phase transition from liquid at 300 K to vapor at 1200 K at liquid water molecule density. This corresponds to super critical water vapor.

- Figures 17(b), (c): After the plasma pulse, the 1200 K water gas at \( 0.5 \times 10^9 \) Pa expands adiabatically and the pressure and temperature decreases while the bubble radius increases.

- Figures 17(c)–(e): Plasma ignition causes an initial pressure in the range between 10 and 100 GPa. This pressure spike initiates a sound wave that propagates with \( 7...8 \) km s\(^{-1}\) through the liquid. This sound wave travels radially around the tip of the tungsten wire, but also around the tungsten wire itself due to the pressure of the electric field. The sound waves travel faster than the expansion of the bubble.

- Figure 17(c): At 100 ns after plasma ignition, an electron density of \( 10^{25} \) m\(^{-3}\) is observed that decays with a time constant of \( \approx 70 \) ns. This decay time corresponds to the ring-down time of the oscillating HV power that is traveling between ns pulser and plasma chamber. Each HV pulse re-ignites a plasma that becomes visible as a modulation of the electron density with the period of the oscillating HV pulses. The electron temperatures vary...
between 0.1 and 5 eV depending on the corresponding electron density.

- Figures 17(c), (d): During expansion, condensation causes the pressure to drop significantly between 100 ns and 1 µs after plasma ignition, the mean free paths become large and causes a strong increase of the electron temperature during re-ignition.
- Figures 17(e), (f): The quickly expanding bubble causes a fast drop of the pressure and a drop of the temperature due to the adiabatic expansion. The temperature decays by two orders of magnitude, the pressure down to 100 Pa. The maximum bubble size of 1.2 mm is reached at 100 µs. Pressure and temperature drop according to the adiabatic expansion of the water vapor with an adiabatic coefficient of 1.33. At the end, the pressure reaches 10 mbar and the temperature 50 K.
- Figure 17(g): After the pressure drop and temperature drop, the surface tension reverses the movement and the bubble collapses again. The collapse occurs very fast. The pressure in the ambient, driving the collapse, is slightly above 1 bar, because the sound waves are reflected at the walls of the liquid container and act on the expanding and collapsing bubble.
- Figure 17(g): Due to the condensation of water vapor during the expansion, the pressure inside the collapsing bubble does not rise again in a similar manner. (The numerical solution of the cavitation problem without gas condensation reveals a rather periodic oscillation of the bubble radius with similar maximum sizes, because the damping due to the viscosity of the liquid is very small.) As a consequence, the bubble remains very small after the collapse and buoyancy will eventually cause the bubble to leave the HV tip region.

This sequence of ignition inside the liquid, followed by cavitation due to the expansion of super critical water illustrates the efficiency of a nanosecond plasma-in-liquid process, because a liquid volume is instantly converted into the plasma state. Due to the nature of super critical fluids an intimate coupling of plasma generated reactive species and liquid species occurs. During expansion, this reactive mixture condenses and is converted back to the liquid state, which initiates very efficient liquid reactions with longer time constants. This is much different to plasmas-above-the-liquid systems, where the transfer of reactive species from the gas phase into the liquid phase may be limited by small Henry constants. Plasmas generation in liquids using much larger rise times should be also less efficient, because here bubble creation precedes plasma ignition and the creation of super critical water may be suppressed.

Any further understanding of these plasmas requires experimental efforts to monitor the initial phase of plasma ignition, where all lines are hidden in a continuum and only a radiation transport modeling should be able to quantitatively describe the measured spectra. This effort should also be complemented by an atomistic modeling of plasma generation, where methods from the field of laser induced plasmas in solids should be best suited, because, also there, a significant power density is dissipated in a very high density plasmas.

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ORCID iDs

K Grosse https://orcid.org/0000-0002-5770-9569
J Held https://orcid.org/0000-0003-1206-7504
A von Keudell https://orcid.org/0000-0003-3887-9359

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