

Luminescence from laser-induced bubbles in water-glycerol mixtures: Effect of viscosity

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The luminescence pulses emitted from collapsing laser-induced bubbles in water-glycerol mixtures are studied as a function of the mixture concentration and applied hydrostatic pressure. The primary effect of increasing the glycerol concentration is to increase the viscosity of the fluid. The pulse duration of the luminescence is found to increase by more than a factor of two as the concentration increases up to 33% glycerol by volume, where the viscosity is nearly four times that of pure water. At higher glycerol concentrations the pulse duration remains nearly unchanged, until no luminescence can be observed at concentrations above 60%, corresponding to a viscosity greater than 15 times that of water. The pulse duration further increases with applied pressures up to 8 bar, similar to that observed earlier in pure water.

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I. INTRODUCTION

The phenomenon of luminescence from a collapsing bubble [1] has been the topic of a number of research studies, ranging from single- and multibubble sonoluminescence [2] to laser-induced bubbles [3–7] and others, yet it is still poorly understood. Many observations from these studies, such as the blackbody spectrum of the light and the linear increase of the luminescence pulse width with the maximum bubble size [4] for laser-induced bubbles, remain without a consistent theoretical explanation. However, while the exact details of much of the physics surrounding the light pulse is unknown, it is generally accepted that the adiabatic compression that occurs during the collapse of the bubble causes extreme heating of the gas inside the bubble, and this heating and the subsequent plasma formation is responsible for the luminescence.

Part of the challenge of creating a comprehensive theory is that the small size and fast time scales of the bubble near the collapse point, and the extreme conditions present at that time, make the details of this final phase of the collapse difficult to probe. Over a period of a few nanoseconds, the bubble interior experiences extremely high temperatures and pressures, accompanied by nonlinear motion of the bubble wall, and formation of a plasma in the heated gas. Because of these extreme conditions, there is currently no experimental way to directly confirm the dynamics at the collapse point. Rather than being able to probe the bubble directly, the final moments of the bubble dynamics and the luminescence pulse must be investigated indirectly by varying the experimental parameters and observing how they affect the bubble dynamics and collapse luminescence.

In order to better understand the luminescence, we have studied the properties of the light pulse in bubbles in water-glycerol mixtures. Because glycerol and water are miscible and glycerol has a much higher viscosity than water, using water-glycerol mixtures with different concentrations of glycerol allows the creation of samples with widely varying viscosities. This allows us to monitor how viscosity affects the dynamics of the bubbles and the luminescence pulses. To create the bubbles, a high-intensity pulsed laser is focused to a point in the fluid. The use of laser-induced bubbles for this study has the advantage that laser bubbles are significantly larger and have a correspondingly larger pulse width than

bubbles found in sonoluminescence. The laser bubbles can have a maximum radius of up to 2 mm and pulse widths up to 20–30 ns. Comparatively, bubbles in sonoluminescence typically only reach sizes of up to 50 μm in radius and have pulse widths on the order of 200 ps. Because of the longer duration of the pulses found with laser bubbles, the pulse widths can be directly recorded using a fast photomultiplier tube and oscilloscope rather than utilizing the very involved, indirect methods required to measure the sonoluminescence pulse widths [8,9]. Following our previous study examining the effect of external pressure on the bubbles in water [7], we utilize hydrostatic pressures from 1–8 bar. Mixtures at concentrations between pure water and 100% glycerol are employed, where for each glycerol concentration the pulse duration and intensity of the luminescence pulse is measured as a function of the maximum bubble radius at each pressure. In addition, we have examined the subsequent oscillations of the bubbles in order to gain insight on how viscosity influences the overall dynamics of the bubbles.

Of course, water-glycerol mixtures have long been used in hydrodynamic experiments to vary the fluid viscosity over a wide range. Even the early measurements on luminescence in bubbles were carried out in water-glycerol mixtures [2,10]. More recent work [11] has shown that high viscosities can destabilize the bubble trapping in single-bubble sonoluminescence, which acts to greatly reduce the light output. There has also been recent work on the effects of viscosity on the bubble dynamics in water-glycerol mixtures [12].

II. APPARATUS

The experimental cell and laser system for creating the bubble are similar to those used in a previous study [7]. A stainless steel cell holds the water-glycerol mixture, with quartz windows used to monitor the luminescence pulse with a fast photomultiplier tube (PMT), a Hamamatsu H6780-03 with a rise time under 2 ns, which is directly coupled to the 50 Ω input of an Agilent 54820 oscilloscope. The PMT module, with a built-in high voltage supply, is biased with 0.8V from a power supply, giving it an estimated gain of 50 000–100 000. An optical density filter is placed in front of the photomultiplier to keep the signal small enough that space charge does not affect

the pulse shape; we have found that pulses smaller than 1 V on the scope avoid this problem. At glycerol concentrations up to 16% an OD2 filter was used (reducing the signal by approximately 100) while at higher concentrations where the signals were smaller an OD1 filter was used (10 \times reduction).

An aspherical lens is mounted in the bottom wall of the chamber, which focuses a 6 ns pulse at 1064 nm from a Q-switched Nd:YAG laser (Spectra-Physics INDI) into the center of the cell, with a spot size estimated to be about 10 μm . A fitting on the top hole of the chamber allows the cell to be pressurized using a tank of high-purity dry nitrogen gas, monitored with a large Bourdon pressure gauge with an accuracy of about 1%. We assume that the nitrogen gas has no effect on the bubble luminescence, as observed earlier in our laboratory [4]. At the higher pressures of this work an increased fraction of nitrogen will be present in the bubbles, but is still estimated to be less than a part in 10⁴ of the total gas at 10 bar. The mixtures are formed by combining measured volumes of very high purity water (18 M Ω) with reagent-grade glycerol (Fisher).

To create the bubbles the laser energy is slowly increased until the point where ionization of the water just begins to occur, noted by the visible flash from the cell. Although the laser energy only varies by less than 5% from shot to shot, we find that the maximum bubble size varies greatly with each shot. This is probably because a nucleating impurity is necessary to cause the initial water ionization, since the energy absorption of water alone is not sufficient for this purpose. Variations in the impurity size would considerably change the total energy absorbed, and hence the maximum bubble size. This is actually an advantage in these measurements, since a large range of bubble sizes are easily produced. Photographs of the light emitted by the ionization plasma [4] show a nearly spherical shape, with radii between 50–100 μm , and only a slight elongation in the direction of the laser beam is visible. The spectrum of the light is blackbody in form, with fits giving a temperature of about 17 000 K [5]. The initial plasma lasts for 50–100 ns before recombining, and the absorbed energy is then manifested in the expanding bubble. We find with this creation process that stable bubbles up to 1 mm in radius can be produced, at pressures up to about 10 bar. At higher pressures or larger radii, however, the bubbles rapidly become unstable due to a fission instability, where they split into two prior to the collapse point [4,5], and such double pulses are ignored in the data collection.

The composition of the gas being compressed in the bubble collapse is not known, but is most likely primarily made up of the neutral atomic species of the liquid. For the glycerol solutions this would be atomic hydrogen, oxygen, and carbon resulting from the plasma recombination, and any water vapor that is unable to condense out on the bubble surface during the last stages of the collapse [13,14]. The 17 000 K temperature of the initial plasma will certainly dissociate all molecules in the plasma volume, and since the bubble then rapidly expands the gas will be at very low pressure over most of its $\approx 100 \mu\text{s}$ lifetime, making molecular recombination unlikely to be appreciable.

The bubble dynamics are monitored by a 100 mW diode laser beam at 975 nm whose 3 mm diameter beam passes through the point where the bubble is created, and whose

amplitude past the bubble is monitored by a photodiode. The shadow area of the bubble decreases the photodiode signal, and we assume the bubble size is proportional to the square root of the signal. The time to the first collapse point is easily determined, and from this the maximum radius R_m can be determined from the Rayleigh collapse formula for an ideal fluid,

$$R_m = 0.55 \sqrt{\frac{p - p_v}{\rho}} T_c, \quad (1)$$

with p the applied pressure, ρ the liquid density, and p_v the liquid vapor pressure. Because of the increasing viscosity of the glycerol-water solutions there will be corrections to this formula, but in practice the corrections are fairly small until the solution becomes nearly pure glycerol. With pure glycerol (a viscosity about 1400 times that of water) the collapse time increases about 10% [12]. Since most of our data is for solutions less than 60% by volume (viscosity 15 times that of water) we neglect these corrections. The shadow technique can only be regarded as giving an approximation to the bubble oscillations, since there is still light coming through the very center of the bubble that is difficult to evaluate quantitatively, and the additional problem that the illuminating laser beam does not have a uniform profile.

III. RESULTS

For each concentration and pressure, approximately 30 data points are acquired in order to take an average over the data, since each laser shot results in a bubble of different size and dynamics. Figure 1 shows examples of luminescence pulses observed with different glycerol concentrations. The duration of the pulse is taken to be the full-width at half-maximum, and this is corrected for the PMT rise time as noted in Ref. [4]. Previous work has shown that in pure water the duration of the luminescence pulse increases linearly with the bubble radius, and that a further increase can be seen by increasing the ambient pressure. Figure 2 shows the results of the pulse width measurements in a 50% glycerol mixture as a function of maximum bubble radius, and the dependence on pressure. It is apparent that both trends observed in water continue in glycerol mixtures. Compared to pure water, however, for a given pressure and bubble size the bubbles in glycerol mixtures produce longer luminescence pulses. For example, in the 50% glycerol mixture at a pressure of 4 bar, the observed pulse width of a 0.8 mm bubble is on the order of 20 ns, while in water at the same pressure the pulse width is closer to 6–7 ns. The lines in Fig. 2 are linear fits to the data, where we assume the intercept is zero.

The slope of the best-fit lines are plotted in Fig. 3 as a function of glycerol concentration and pressure. It is readily seen that increasing the glycerol concentration increases the pulse widths, as noted above. The only exception is the 1% solution where at least at lower pressures the width decreases compared to pure water, before then increasing in the 5% solution. It is not clear why this initial decrease occurs, but could possibly be related to the formation of an initial surfactant layer of glycerol at the bubble surface, which would then remain relatively constant as the glycerol

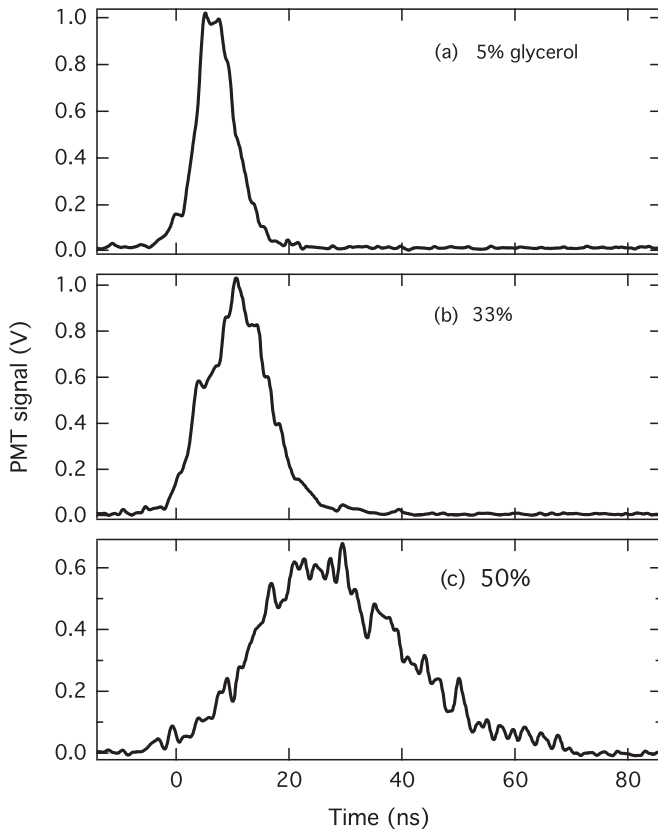


FIG. 1. Luminescence pulses observed near the collapse point of laser-induced bubbles in glycerol solutions (volume percentage), at a pressure of 8 bar. The maximum radii of these bubbles were: a) 0.50 mm, b) 0.39 mm, c) 0.67 mm.

concentration is further increased. The increase in the pulse width with hydrostatic pressure is relatively consistent with the increase seen in pure water. Further increases in glycerol concentration lead to a steadily increasing duration of the pulse until the pulse width reaches approximately 2–3 times the duration observed in water. After this point, the pulse widths no longer increase and instead maintain a relatively constant value. At high glycerol concentrations the frequency of a captured luminescence pulse produced by a bubble begins to drop. In pure water the frequency is about one in every three bubbles, but above 50% the luminescence events become noticeably reduced, and in the 60% solution the luminescence becomes a very rare event, where it is necessary to produce 50–100 bubbles before a luminescence pulse is observed. In the 75% solution no luminescence at all can be observed, even though bubbles are still being generated by the laser.

As a comparison, Fig. 4 shows the same slope graphed versus the viscosity of the solution. This serves to show, for a fixed maximum bubble radius, how the pulse width changes with viscosity. It is not known for certain whether the viscosity is the relevant parameter causing these changes (there are also changes in density and in surface tension); however it is the best first guess. The general form of Fig. 4 is the same as Fig. 3, the only change being a faster rate of increase at the beginning, since the viscosity increases nearly exponentially with the concentration. After the initial pulse width decrease

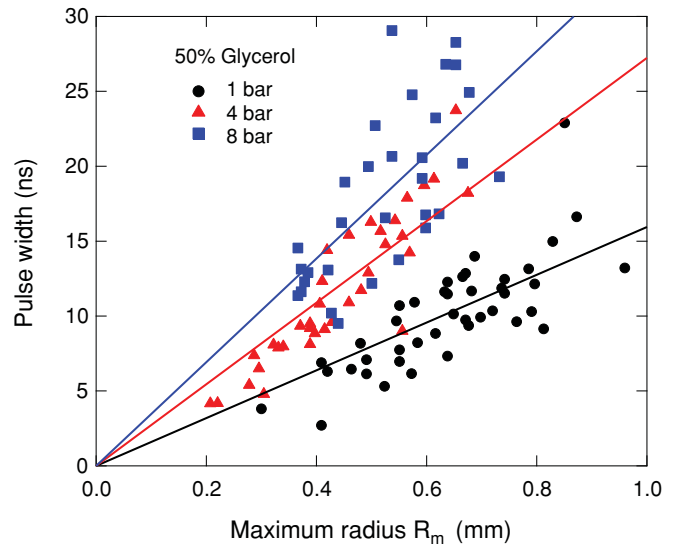


FIG. 2. (Color online) Pulse width as a function of the maximum bubble radius for pressures of 1, 4, and 8 bar. The solid lines are linear fits to the data.

observed for a viscosity just above the viscosity of water at one centipoise, the pulse widths rapidly increase until more than twice the pulse width seen in water is reached. This occurs at a viscosity that is just under four times the viscosity of water. Above this viscosity, the pulse widths remain relatively constant. As the viscosity continues to increase, luminescence becomes progressively more infrequent. For viscosities above approximately 15 times that of water, luminescence can no longer be observed at all, though, again, bubbles continue to be generated.

Figure 5 shows how the bubble dynamics change with the increasing viscosity of the solutions. At low concentrations

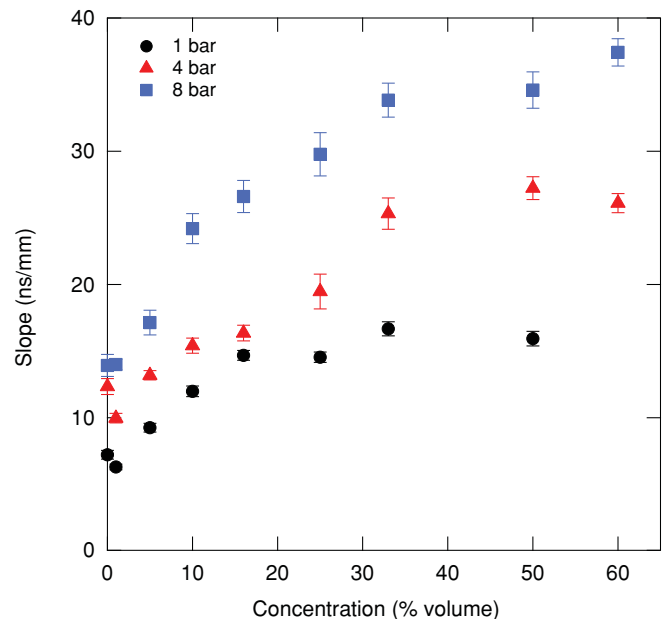


FIG. 3. (Color online) Slope of the linear fits to the pulse width versus maximum radius, as a function of the volume concentration of glycerol.

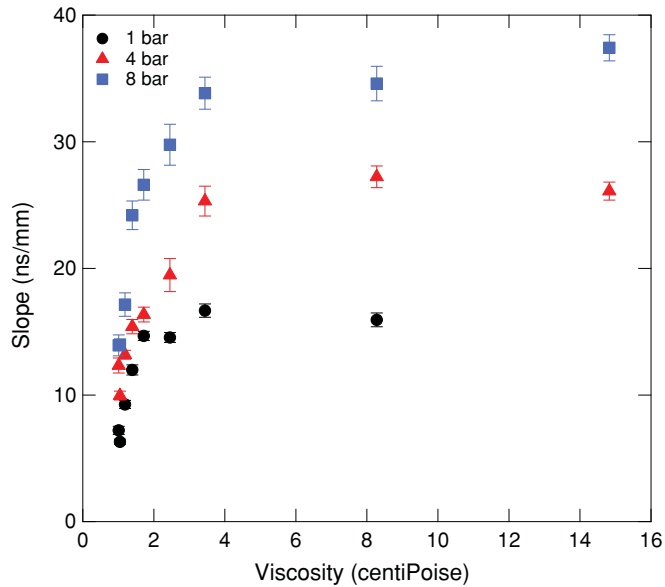


FIG. 4. (Color online) Slope of the linear fits to the pulse width versus maximum radius, as a function of the viscosity of the solutions.

with relatively small viscosity the oscillations past the first collapse point are very small in amplitude. This is likely a result of the strong initial collapse of the bubble. The high acceleration of the bubble wall near the collapse point means that much of the bubble energy is lost to acoustic radiation, and it is well known that the very high acceleration at the collapse point results in the emission of a shock wave. With the loss of energy the oscillations past the collapse point the oscillation amplitude will be considerably reduced. With increasing viscosity the collapse is not as strong, and the oscillation amplitudes increase considerably for the higher concentrations. Finally at the very highest viscosities the oscillations show fairly rapid damping where the energy is lost to viscous forces on the bubble wall. In pure glycerol only the first collapse is non-linear, with subsequent oscillations quickly becoming more sine-like.

IV. DISCUSSION

The origin of the increase of the luminescence pulse width with increasing glycerol concentration is not entirely clear, but a likely explanation is that it is associated with a viscous slowing of the bubble wall in the very last stages of the initial collapse. If the compressive heating is still strong enough to result in plasma formation, the lowered wall velocity might allow the plasma to remain intact and hot for a longer period of time than in pure water. The increasing viscosity is also probably the reason for the decrease in the frequency of bubbles that are observed to emit luminescence. At some point the slowed compression will not be enough to generate high temperatures and produce the ionization needed for the luminescence.

It is also possible, however, that other factors could come into play to explain the increased pulse width other than viscosity. The increasing liquid density could play a role in the collapse phase, acting to increase the inertia of the

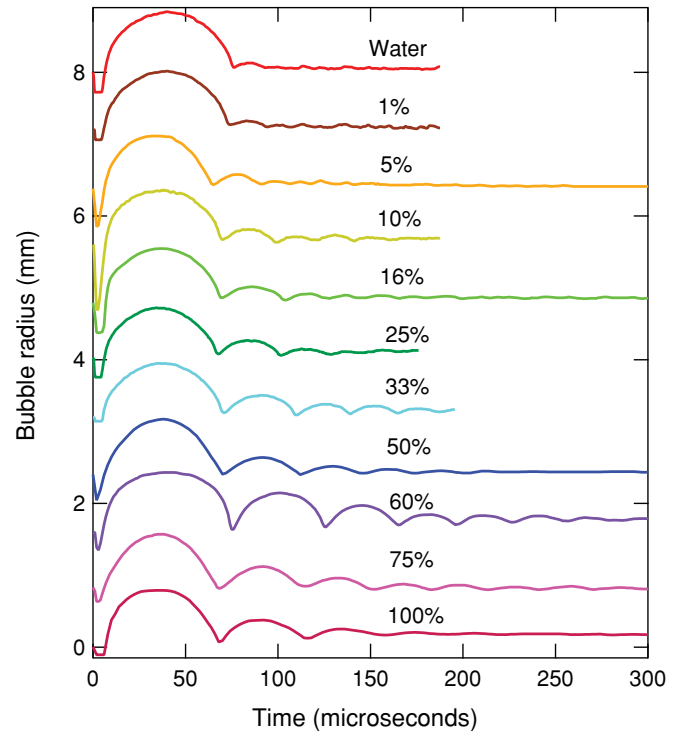


FIG. 5. (Color online) Changes in the bubble dynamics with increasing glycerol concentration, for bubbles at 6 bar of pressure and having nearly the same radii and collapse times. The curves have been arbitrarily shifted in the vertical direction for the purpose of display.

bubble wall and subsequently the compression of the gas in the bubble. The increasing density may also increase somewhat the total resulting gas in the bubble, if the liquid volume ionized by the laser is constant. More gas would tend to oppose the compression of the bubble. The role of the increasing carbon atom concentration in the gas is also not clear. The ionization potential of carbon is 11.2 eV, compared to 13.6 eV for hydrogen and oxygen, and hence will act to increase the total ionization at a given temperature. Some of these factors could certainly tend to increase the plasma duration, but in our opinion it is likely that the increased viscosity is the major factor in the luminescence duration.

There is certainly a need for more theoretical work in order to understand these results. The effect of viscosity on the bubble dynamics needs to be better characterized on the nanosecond time scale near the collapse point. The rapid increase in the duration of the luminescence emission with viscosity seen in Fig. 4 shows that this is probably a key parameter governing the nature of the luminescence. Existing theories either leave out viscosity entirely [13], or do not investigate the effects of changing the viscosity [14]. These theories also assume that the primary gas in the bubble is water vapor, while our estimation is that the atomic oxygen and hydrogen and carbon still play a major role. Certainly it will also be necessary to gain a more detailed understanding of the heating process and the plasma formation leading to the luminescence emission. As noted in the Introduction, there are still many observed effects, such as the increase

of the luminescence pulse width with bubble size and with hydrostatic pressure, which are not readily predicted by current theories. Hopefully the present data highlighting the role of the liquid viscosity can help in guiding such theoretical efforts.

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