Measurement of Pressure and Density Inside a Single Sonoluminescing Bubble

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The average pressure inside a sonoluminescing bubble in sulfuric acid has been determined by two independent techniques: (1) plasma diagnostics applied to Ar atom emission lines, and (2) light scattering measurements of bubble radius vs time. For dimly luminescing bubbles, both methods yield intracavity pressures ∼1500 bar. Upon stronger acoustic driving of the bubble, the sonoluminescence intensity increases 10 000-fold, spectral lines are no longer resolved, and radius vs time measurements yield internal pressures >3700 bar. Implications for a hot inner core are discussed.

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Single-bubble sonoluminescence (SBSL, i.e., light emission from intense heating of gas and vapor inside a rapidly collapsing bubble in a liquid irradiated with ultrasound) [1–4] has received much recent attention largely due to the extreme conditions that have been predicted [5–8]. As has been previously done in multibubble sonoluminescence [9,10], quantification of the intracavity conditions is an important goal in determining the peak energies that can be achieved with acoustic cavitation [11,12]. SBSL from concentrated sulfuric acid (H_2SO_4) is well suited for this purpose; at relatively low applied acoustic pressure (P_a), well-resolved neutral and monocationic noble gas atom emission lines are observed [8,13–15].

Here, we show that standard tools of plasma diagnostics can be applied to the observed Ar emission lines to measure densities inside the cavitating bubble. Combining this density with recently measured temperatures from Ar lines [13] allows for an accurate determination of pressures of nearly 1500 bar in the spatiotemporal region occupied by the emitting Ar atoms.

When driven at relatively low P_a, these bubbles are dim; nevertheless, they exhibit Ar^+ line emission, the populated states of which lie over 37 eV above the Ar $3p^6$ ground state [8]. For this same system, use of light scattering to measure the bubble dynamics yields density and pressure values *consistent with* the plasma diagnostics: 1600 bar and 1400 bar, respectively. At higher P_a where the Ar lines become broadened and unresolvable [13], light scattering measurements give pressures of over 3700 bar for H_2SO_4 and over 8000 bar for other systems such as noble gas bubbles in water [16]. These observations suggest that the inner core of strongly driven sonoluminescing bubbles can be substantially hotter than for the weakly driven case where the Ar^+ lines were first discovered.

Of the 23 Ar $4p$-$4s$ lines between 690 and 950 nm, we focus our attention here on the profiles of the 696.54 and 763.51 nm lines. These lines were chosen for several reasons: (1) the same metastable $4s$ state ($^3P_2$) is involved in both electronic transitions, (2) the lines are intense and well isolated, (3) the profile of the 696.54 nm line has been previously studied in a high-pressure (200 bar) Ar plasma at 8000 to 15 000 K, and (4) the diffraction grating used here has a high efficiency (∼80%) in this bandwidth. These qualities allow for accurate determinations of Ar atom temperatures and emission line profiles.

Comparison of the Ar lines in the 735 to 780 nm region generated from a Hg(Ar) spectral calibration lamp to those generated during SBSL from a dimly luminescing bubble in 85% H_2SO_4 containing 40 torr Ar shows the SBSL lines to be significantly redshifted and broadened [Fig. 1]. As the P_a is increased, the SBSL Ar lines further broaden and become highly asymmetric to the red of the line center. The increased broadening and development of asymmetries

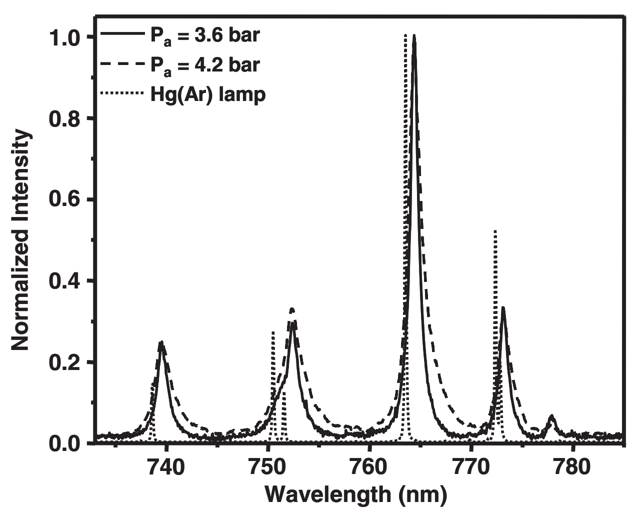

FIG. 1. Comparison of SBSL Ar atom emission spectra obtained from 85% H_2SO_4 containing 40 torr dissolved Ar at an applied P_a of 3.6 and 4.2 bar (as measured with a needle hydrophone at the approximate bubble location) and that from a Hg(Ar) spectral calibration lamp. All spectra were corrected for absorption by the solution and cell wall as well as the optical response of the spectral acquisition system against National Institute of Standards and Technology traceable standard lamps. All spectra have had the underlying continuum subtracted for clarity.

indicates an increase in the frequency of collisions between the radiating atoms with neutral and ionic species, the asymmetries near the line center being especially indicative of ion broadening [17,18]. The weak line at 777 nm in the SBSL spectra is due to oxygen atom emission arising from transitions between the $3p$ (10.7 eV) and the $3s$ (9.15 eV) manifold.

The intensities, profiles, and peak positions of atomic emission lines depend upon several factors including the physical and chemical environment surrounding the radiating atom, the intrinsic properties of the excited states involved in the transitions, and the configuration of the optical system [17–20]. The mechanisms typically identified as contributing to atomic line profiles (excluding laser-irradiated systems) include natural (i.e., spontaneous lifetime) broadening, Doppler broadening, Stark broadening, pressure broadening, and instrumental broadening [20]. Depending upon the conditions generated within the bubble during SBSL, some broadening mechanisms can be expected to contribute more significantly to the emission line profiles than others.

The observation of a plasma and high temperatures during SBSL in H_2SO_4 [8,13,15] means that Stark and pressure effects can be expected to be the dominant mechanisms contributing to the Ar emission linewidths and shifts. Both natural and Doppler broadening will be negligible. Since the lifetimes of the Ar excited states for spontaneous emission are tens of nanoseconds, natural linewidths are only $\sim 10^{-5}$ nm compared to the ~ 1 nm total linewidths observed here. Doppler broadening of a radiating Ar atom at 15 000 K would be at most ~ 0.01 nm if the mean free path of the radiating atom was large compared to the photon wavelength. This is unlikely since the radius of the entire emitting volume is already approaching the same order as the wavelength of emitted light [15,21].

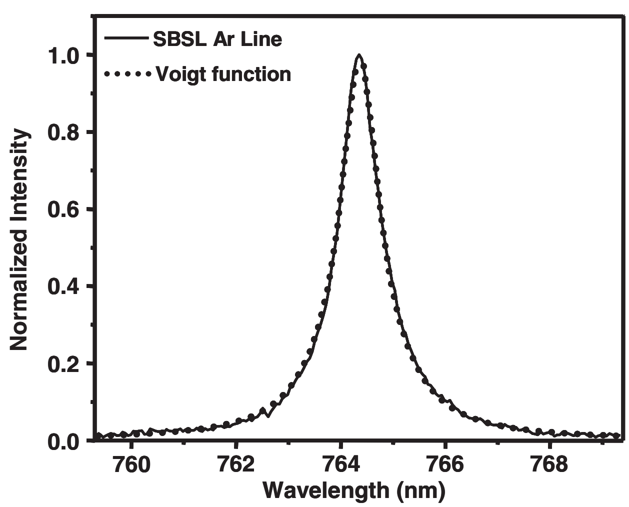

FIG. 2. Best fit of a pseudo-Voigt function to the SBSL Ar 763.51 nm line observed at an applied $P_a = 3.6$ bar. The wavelength of the spectral acquisition system was calibrated using the 763.51 nm Ar lamp line. The light was dispersed with a 1200 grooves $\cdot$ mm^{-1} diffraction grating blazed at 750 nm. The slit width was kept at 100 μm.

The relative contributions of the remaining instrumental, Stark, and pressure broadening can be assigned. To determine a pressure from the SBSL Ar 763.51 nm line, the instrumental broadening must be deconvolved from the total linewidth because instrumental and collisional broadening are statistically dependent events which have different line profiles (Gaussian vs Lorentzian, respectively). After fitting the SBSL Ar line to a pseudo-Voigt function [22] [Fig. 2] and deconvolution of the Gaussian portion, the Lorentzian component of the linewidth (i.e., from collisional broadening mechanisms) was found to be 0.94 nm (compared to a FWHM of 1.03 nm and an instrumental linewidth of 0.17 ± 0.02 nm from a low pressure calibration lamp).

Since both Stark and pressure broadening result in Lorentzian line shapes, the relative contribution of each to the total linewidth must be determined from the SBSL temperature and plasma electron density (n_e). By comparing the relative intensities of the Ar emission lines, the observed collapse temperature (T_c) for this system driven at an applied P_a of 3.6 bar [Fig. 1] was found to be 10 000 K [13]. To estimate n_e, the asymmetry of the SBSL Ar 763.51 nm line was used to determine the static ion broadening parameter (A), following a technique described by Jones *et al.* [18]. Since A scales as $n_e^{1/4}$ [17], we can compare the A determined here to values of A obtained at known n_e for the Ar 763.51 nm line [23]. From this, $n_e = 3.8 \times 10^{17}$ cm^{-3}, as determined for SBSL with an applied P_a of 3.6 bar; this value agrees well with that estimated from Ref. [24] (4×10^{17} cm^{-3} at 2000 bar). Stark widths scale linearly with n_e at a specific temperature [17] and have been determined for the Ar 763.51 nm line [25]. From this, we use the n_e (3.8×10^{17} cm^{-3}) and T_c (10 000 K) determined from the SBSL Ar line and find the Stark contribution to be 0.3 nm. Because Stark broadening and pressure broadening can be treated independently [17], the Stark width is subtracted from the total Lorentzian linewidth, leaving 0.6 nm due to pressure broadening.

The density of the region surrounding the emitting Ar atoms can be calculated from T_c (10 000 K) and the linewidth (0.6 nm) by substituting the appropriate values into Eq. (1) obtained from collision theory,

$$\Delta\nu = \sqrt{(8kT_c)/(\pi^3\mu_{\mathrm{Ar}})}\sigma_{\mathrm{Ar}} n_{\mathrm{Ar}}. \qquad (1)$$

In Eq. (1), $\Delta\nu$ is the FWHM due to pressure broadening, k is the Boltzmann constant, T_c is the measured Ar temperature, μ_{Ar} is the reduced mass of the collision partners, n_{Ar} is the density within the observed emitting region, and σ_{Ar} is the collision cross section defined as $\pi(2r_{\mathrm{Ar}})^2$ where r_{Ar} is the Ar van der Waals radius (188 pm). Here, for purely pressure broadening, it is assumed that all radiating Ar atoms undergo collisions with other Ar atoms [a reasonable assumption, considering the negligible vapor pressure (0.04 torr at 298 K) of 85% H_2SO_4].

The effective local density felt by the emitting Ar atoms during SBSL in 85% H_2SO_4 in the observed emitting region is found to be 1.0×10^{21} cm^{-3}. To convert this to an effective collapse pressure (P_c), some specific equation of state (EOS) must be used; at these relatively modest densities, however, the choice of EOS makes little difference in the calculated pressure. From the van der Waals EOS, we estimate that the average effective P_c felt by the emitting Ar atoms is 1400 bar.

At this pressure and temperature, the average time between collisions is less than 1 ps. For both lower and higher acoustic drives, the SBSL flash width is between 5 and 10 ns as measured with a Hamamatsu H5783-03 photomultiplier tube; this means an Ar atom undergoes thousands of collisions during the SBSL flash. This is sufficient to ensure local thermodynamic equilibrium among the emitting heavy particles, but not necessarily among the electrons in the emitting plasma [26,27].

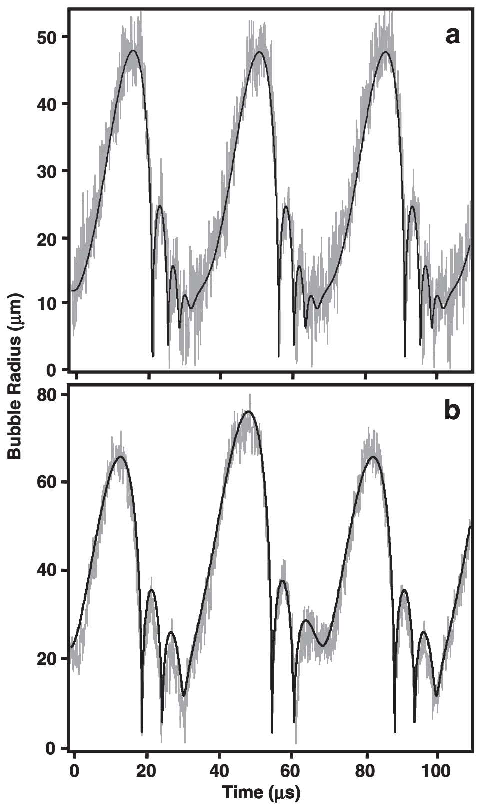

FIG. 3. (a) Bubble radius as a function of time for a bubble driven near the level at which the plasma diagnostics were performed, and (b) a bubble driven near the maximum sustainable sonoluminescence brightness. The low P_a bubble (a) is fit with an R_o value of 13 μm and effective P_a of 1.4 bar to reach an R_c of 3.1 μm. The high P_a bubble (b) is fit with an R_o value of 17 μm and an effective P_a of 1.7 bar to reach an R_c of 3.5 μm. The light from a 1 mW HeNe laser was scattered off the bubble at angles of 40° to 80° and was collected with a Hamamatsu 2027 photomultiplier tube and delivered to an Hewlett-Packard Infinium oscilloscope. Each data set is taken from a single shot to ensure that no averaging artifacts were introduced.

SBSL pressure was also estimated by directly comparing the observed Ar 696.54 nm linewidth to the 696.54 nm linewidths observed from high-pressure (200 bar) Ar plasmas [24]. For the SBSL spectrum obtained from a dimly luminescing bubble driven at an applied $P_a = 3.8$ bar (with a measured T_c of 10 000 K [13]), the 696.54 nm FWHM was found to be 1.17 nm after deconvolving the instrumental broadening. Since the study of the 696.54 nm line reports linear broadening vs pressure, but stopped at 200 bar, a linear extrapolation to higher pressures was assumed. The SBSL P_c determined in this manner from the width of the Ar 696.54 nm line was found to be 1100 bar at 10 000 K, in good agreement with the P_c calculated from the SBSL Ar 763.51 nm line.

An independent measurement of the SBSL density and pressure was also determined from radius vs time, $R(t)$, data. The $R(t)$ curves were determined via light scattering [2,16] and were fit using the Rayleigh-Plesset (RP) equation coupled to a thermal conduction term [15,28,29]. Since the maximum observed interfacial velocity (400 m s^{-1}) is less than the speed of sound in the liquid (1500 m s^{-1}), use of the RP equation is valid. This equation simulates the data using the ambient radius (R_o) and *effective* P_a input parameters to yield values for the maximum radius (R_{max}), collapse radius (R_c), and maximum temperature at collapse (T_c).

The ideal gas EOS is used to determine the n_{Ar} when the bubble is at R_o [30]. We assume that the number of Ar atoms does not significantly change as the bubble reaches R_c [31]; deviations from ideal behavior are expected to be small since the R_c is significantly larger than the van der Waals hard core. Incorporation of n_{Ar}, R_c, and T_c into the van der Waals EOS yields the P_c.

Analysis using this method for a dim bubble [Fig. 3(a)] (driven by a low P_a and characterized by Ar line emission that matches that used in the plasma diagnostics) gives $n_{Ar} = 1.2 \times 10^{21}$ cm^{-3}, $T_c = 10\,000$ K, and $P_c =$ 1600 bar, which agrees well with the plasma diagnostics. When the P_a is increased, the larger and more chaotic bubble [Fig. 3(b)] emits a continuum that is 10^4 times brighter than that observed for the dim bubble. To calculate the P_c for the higher P_a bubble, the T_c is taken to be a conservative 15 000 K; this value was determined for a dimmer bubble that is still emitting resolved Ar lines [13] from which a temperature can be calculated. For the higher P_a, n_{Ar} increase to 1.8×10^{21} cm^{-3} and P_c to 3700 bar.

Previously measured $R(t)$ curves for Xe bubbles in H_2SO_4 [15] can also be analyzed by this method; a 4 torr Xe bubble has $R_o = 5.5$ μm and collapses to 1.1 μm with a blackbody emission temperature of 10 000 K. These parameters give $n_{Ar} = 1.8 \times 10^{21}$ cm^{-3} and

$P_c = 2500$ bar. It is interesting to note that for a water bubble [16] of 150 torr 1% Xe in O_2 with a blackbody emission temperature of 10 000 K and a measured R_c of 0.7 μm, this method yields a density of 6.2×10^{21} cm^{-3} and a pressure in excess of 8000 bar.

Using well-understood mechanisms of spectral line broadening, we have quantitatively determined the intracavity conditions generated during SBSL in H_2SO_4. Determination of a pressure of 1400 bar from the Ar emission line analysis is well correlated to the pressure determined from the $R(t)$ curve analysis. When the drive is increased to the point that broadening no longer allows line emission analysis, the $R(t)$ curve can still be used for the quantitative determination of the pressure. At the maximum P_a that can sustain sonoluminescence emission in H_2SO_4, the pressures reach 3700 bar.

These pressures represent a lower bound to the final pressures potentially reached in the collapsing bubble, since we have assumed uniform intracavity density; potential shock wave formation [5,32] is not treated. The pressure calculated from the emission lines reflects only the conditions in the spatiotemporal region occupied by the emitting Ar atoms. The hot inner core model of sonoluminescence [7,13,15] gives a higher maximum temperature than that measured from either Ar lines or blackbody fits to the continuum. These higher temperatures would correspondingly raise the maximum intracavity pressure achieved during bubble implosion.

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[1] M. P. Brenner *et al.*, Rev. Mod. Phys. **74**, 425 (2002).
[2] B. P. Barber *et al.*, Phys. Rep. **281**, 65 (1997).
[3] D. F. Gaitan *et al.*, J. Acoust. Soc. Am. **91**, 3166 (1992).
[4] B. P. Barber and S. J. Putterman, Nature (London) **352**, 318 (1991).
[5] W. C. Moss, D. B. Clarke, and D. A. Young, Science **276**, 1398 (1997).
[6] W. C. Moss *et al.*, Phys. Rev. E **59**, 2986 (1999).
[7] C. Camara, S. Putterman, and E. Kirilov, Phys. Rev. Lett. **92**, 124301 (2004).
[8] D. J. Flannigan and K. S. Suslick, Phys. Rev. Lett. **95**, 044301 (2005).
[9] W. B. McNamara III, Y. T. Didenko, and K. S. Suslick, Nature (London) **401**, 772 (1999).
[10] W. B. McNamara III, Y. T. Didenko, and K. S. Suslick, J. Phys. Chem. B **107**, 7303 (2003).
[11] R. Hiller, S. J. Putterman, and B. P. Barber, Phys. Rev. Lett. **69**, 1182 (1992).
[12] S. J. Putterman and K. R. Weninger, Annu. Rev. Fluid Mech. **32**, 445 (2000).
[13] D. J. Flannigan and K. S. Suslick, Nature (London) **434**, 52 (2005).
[14] D. J. Flannigan and K. S. Suslick, Acoust. Res. Lett. Online **6**, 157 (2005).
[15] S. D. Hopkins *et al.*, Phys. Rev. Lett. **95**, 254301 (2005).
[16] K. R. Weninger, P. G. Evans, and S. J. Putterman, Phys. Rev. E **61**, R1020 (2000).
[17] H. R. Griem, *Spectral Line Broadening by Plasmas* (Academic Press, New York, 1974).
[18] D. W. Jones, W. L. Wiese, and L. A. Woltz, Phys. Rev. A **34**, 450 (1986).
[19] N. Allard and J. Kielkopf, Rev. Mod. Phys. **54**, 1103 (1982).
[20] J. D. Ingle, Jr. and S. R. Crouch, *Spectrochemical Analysis* (Prentice Hall, Englewood Cliffs, 1988).
[21] G. Vazquez *et al.*, Phys. Rev. Lett. **88**, 197402 (2002).
[22] E. E. Whiting, J. Quant. Spectrosc. Radiat. Transfer **8**, 1379 (1968).
[23] V. Milosavljević and S. Djeniže, Astron. Astrophys. **398**, 1179 (2003).
[24] H. Poisel *et al.*, IEEE Trans. Plasma Sci. **14**, 306 (1986).
[25] M. S. Dimitrijević, Lj. Skuljan, and S. Djeniže, Phys. Scr. **66**, 77 (2002).
[26] L. S. Bernstein *et al.*, J. Phys. Chem. **100**, 6612 (1996).
[27] H. R. Griem, Phys. Rev. **131**, 1170 (1963).
[28] R. Hickling, J. Acoust. Soc. Am. **35**, 967 (1963).
[29] A. Prosperetti, J. Fluid Mech. **222**, 587 (1991).
[30] R. Löfstedt *et al.*, Phys. Rev. E **51**, 4400 (1995).
[31] A. Eller and H. G. Flynn, J. Acoust. Soc. Am. **37**, 493 (1965).
[32] C. C. Wu and P. H. Roberts, Phys. Rev. Lett. **70**, 3424 (1993).