Single-Bubble and Multibubble Sonoluminescence

Kyuichi Yasui

National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku, Nagoya, 462-8510, Japan

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Computer simulations of radiation processes in an air bubble and an argon bubble are performed under a condition of single-bubble sonoluminescence (SBSL) based on a quasiadiabatic compression model of a bubble collapse. It is clarified that emissions from excited molecules are strongly quenched by high pressure and temperature inside a SBSL bubble and SBSL originates in the emissions from plasma. It is pointed out that sonoluminescence from cavitation fields (MBSL) originates in emissions from excited molecules, which is not quenched due to the much lower pressure and temperature inside the MBSL bubbles.

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In 1990, Gaitan [1] first reported single-bubble sonoluminescence (SBSL) that a stably oscillating bubble in liquid water irradiated by ultrasonic wave emits light at each collapse with clocklike precision. The pulse width of the light is experimentally measured to range from 40–350 ps [2,3].

More than 50 years before the discovery of SBSL, the light emission from cavitation bubbles driven by ultrasonic waves was discovered, which is now called multibubble sonoluminescence (MBSL) [4]. In the system, a few hundred or a few thousand bubbles exist in the liquid and many of the bubbles emit light at the compression phase of the ultrasound.

In 1995, Matula *et al.* [5] reported the difference between the spectra of SBSL and MBSL, that SBSL spectrum is continuous and has no characteristic lines such as the OH line (310 nm) and the sodium line (589 nm) in a 0.1 M sodium chloride solution, while MBSL spectrum has them. The reason for the difference has not yet been understood theoretically. The relationship between SBSL and MBSL is still unclear, though some theoretical interpretations have been proposed [6,7].

In 1998, Matula and Crum [8] reported the experiment of SBSL that an air bubble emits no detectable light at room temperature while an argon bubble emits light sufficient for observation with the unaided eyes. In the present study, computer simulations of radiation processes inside an air bubble and an argon bubble are performed under a condition of SBSL based on the quasiadiabatic compression model [9] of a bubble collapse in order to investigate the results of Matula and Crum [8].

The quasiadiabatic compression model used in the present study is fully described in Ref. [9]. It is assumed that the pressure is spatially uniform inside a bubble, and that the temperature is spatially uniform inside a bubble except at the thermal boundary layer near the bubble wall. According to the computer simulations of the fundamental equations of fluid dynamics inside a collapsing bubble by Yuan *et al.* [10,11], the variation of pressure and temperature inside a bubble is a few tens of a percent. Thus, the present assumptions of the spatial uniformity of pressure and temperature are crude. However, the present model is useful because the rates of chemical reactions cannot be calculated practically when the temperature and pressure vary spatially inside a bubble. In the present model, the effect of chemical reactions inside a bubble, that of ionization of gases, that of nonequilibrium evaporation and condensation of water vapor at the bubble wall, and that of the thermal conduction both inside and outside a bubble are taken into account. The chemical kinetics model of air (nitrogen, oxygen, and water vapor) is described in Ref. [12].

Following is the model of radiation processes in an air bubble and an argon bubble. Under the present condition, the light emission from an air bubble is expected to be mainly by excited nitrogen molecules: the radiative transition from the second excited state to the first excited state [first positive band, $N_2(1+)$] and that from the third excited state to the second excited state [second positive band, $N_2(2+)$]. The intensities are calculated by the following equations under the assumption of an optically thin gas layer [13]. For $N_2(1+)$, $I = \frac{8}{5}\pi^2 r_e h^2 c^3 f_{00}[N_2] \times \phi e^{-hc/(kT\lambda_{00})} \frac{4}{3}\pi R^3/(\lambda_{00}^4 kT)$, where r_e is the classical electron radius, h is the Planck constant, c is the light velocity, λ_{00} is the wavelength of the 0,0 vibrational transition [$\lambda_{00} = 1.046 \times 10^{-6}$ (m)], f_{00} is the electronic f number when the wavelength is λ_{00}($f_{00} = 0.025$), $[N_2]$ is the number density of nitrogen molecules, ϕ is the dimensionless factor of order unity ($\phi = 0.2$), k is the Boltzmann constant, T is the temperature, and R is the bubble radius [13]. It should be noted that the $N_2(1+)$ band extends from red light to the infrared radiation [13]. For $N_2(2+)$, $I = 2\pi^2 r_e h^2 c^3 f_{00}[N_2]\phi e^{-hc/(kT\lambda_{00})} \frac{4}{3}\pi R^3/(\lambda_{00}^4 kT)$, where $f_{00} = 0.09$, $\phi = 0.2$, and $\lambda_{00} = 3.4048 \times 10^{-7}$ (m) [13]. It should be noted that the $N_2(2+)$ band is mainly in the blue light region [13]. At high temperature above 10 000 K, the light emission from plasma contributes significantly—free-free and free-bound transitions. There are two mechanisms in free-free transitions; one is electron-ion bremsstrahlung that a free electron emits light

when it is accelerated in the field of a positive ion [14], and the other is electron-atom bremsstrahlung that a free electron emits light when accelerated in the field of a neutral atom [14,15]. The intensity of electron-ion bremsstrahlung is calculated by $P_{\mathrm{Br,ion}} = 1.57 \times 10^{-40} q^2 N^2 T^{1/2} \frac{4}{3}\pi R^3$, where q is the degree of ionization, N is the number density of atoms, and all the quantities are expressed in SI units [16]. The intensity of electron-atom bremsstrahlung [17] is calculated by $P_{\mathrm{Br,atom}} = 4.6 \times 10^{-44} q N^2 T \frac{4}{3}\pi R^3$. The light emission by the free-bound transition is called a radiative recombination of electrons and positive ions. The intensity is estimated by $P_r = \frac{4}{3}\pi R^3 q^2 N^2 \sigma_{fb} \bar{v} h \bar{\nu}$, where σ_{fb} is the cross section of radiative recombination, $\bar{v}$ is the mean velocity of a free electron, and $\bar{\nu}$ is the mean frequency of the emitted photon.

It should be noted that the present model differs from the model of Moss *et al.* [18,19] in the point that it is assumed that a bubble collapse is quasiadiabatic, while in Moss's calculations a spherical shock wave appears in a collapsing bubble. In 1998, Yuan *et al.* [10,11] clarified theoretically that a shock wave is absent in a collapsing bubble due to the effect of thermal conduction [20]. It should also be noted that the recent model of Hilgenfeldt, Grossmann, and Lohse [21,22] is similar to the present one.

The calculations are performed under a condition of SBSL used by Matula and Crum [8]. The frequency and the amplitude of the ultrasonic wave are 30 kHz and 1.4 bar, respectively. The ambient bubble radius is 5 μm. In Fig. 1, the calculated radius-time curve of an air bubble is shown for one acoustic cycle. It is seen that a bubble expands at first according to the negative acoustic pressure and it reaches the maximum radius of 46 μm at $t = 15.8$ μs. Then it collapses rapidly to the minimum radius of 0.7 μm at $t = 19.8$ μs, due both to the positive acoustic pressure and the inertia of the surrounding liquid.

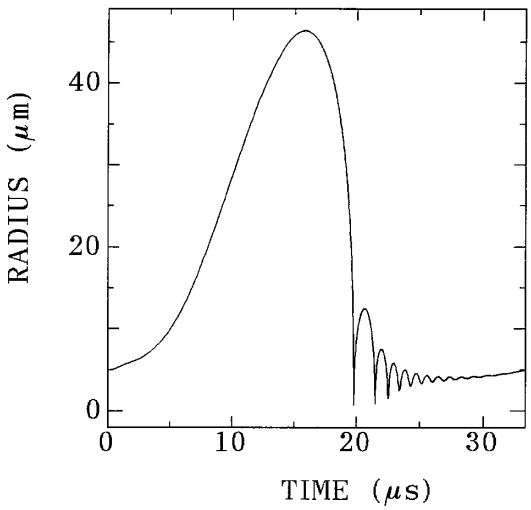

FIG. 1. Calculated radius-time curve of an air bubble for one acoustic cycle (33 μs).

In Figs. 2(a) and 2(b), the calculated results for an argon bubble (with 1% air) at around the minimum bubble radius are shown as functions of time for 0.002 μs (2000 ps). The minimum bubble radius is 0.5 μm at $t = 19.8023$ μs. In Fig. 2(a), the temperature inside a bubble is shown. It is seen that the maximum temperature in this case (14 500 K) is much higher than that of an air bubble [6400 K (see Table I)] due to the smaller molar heat of argon (monoatomic gas) and the lower thermal conductivity. In Fig. 2(b), the contributions of each of the radiation processes are shown. It is seen that electron-atom bremsstrahlung and radiative recombination are dominant.

In Table I, the calculated results of an air bubble and an argon bubble are summarized. It is seen that the calculated light intensity of $N_2(2+)$ and $N_2(1+)$ from an

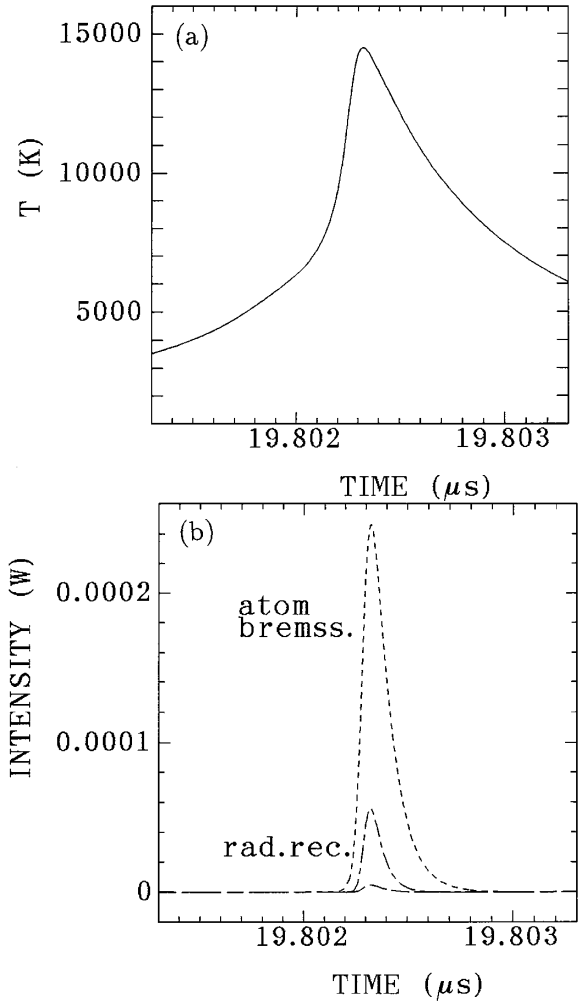

FIG. 2. Calculated results of an argon bubble (with 1% air) at around the minimum bubble radius as functions of time for 2,000 ps (0.002 μs). The time axes are the same. (a) The temperature inside the bubble (T). (b) The intensity of the light emitted by electron-atom bremsstrahlung (dotted line), that by radiative recombinations (dash-dotted line), and that by electron-ion bremsstrahlung (dashed line).

TABLE I. The calculated results of an air bubble and an argon bubble (with 1% air). The frequency and amplitude of the acoustic wave are 30 kHz and 1.4 bar, respectively. The ambient bubble radius is 5 μm. R_{max} is the maximum bubble radius, R_{min} is the minimum bubble radius, T_{max} is the maximum bubble temperature, p_{max} is the maximum pressure, I_{max} is the maximum light intensity, "pulse width" is that of the emitted light, and "mechanism" is that of the light emission. The brackets for an air bubble mean that in the experiment [8] no detectable light is emitted.

	Air	Argon (with 1% air)
R_{max}	46 μm	46 μm
R_{min}	0.7 μm	0.5 μm
T_{max}	6400 K	14 500 K
p_{max}	5×10^9 Pa	6×10^9 Pa
I_{max}	(0.2 mW)	0.4 mW
Pulse width	(350 ps)	140 ps
Mechanism	$N_2(2+)$	Atom bremss.
	$N_2(1+)$	Rad. rec.

air bubble is so large that it should be experimentally observed. The intensity of $N_2(2+)$ band is much larger than that of $N_2(1+)$ band and the light emission is mostly in the visible region. The intensity from an air bubble is estimated to be in the same order with or even larger than that from an argon bubble. It conflicts with the experimental result that no detectable light is emitted from an air bubble in water at room temperature [8]. It should be noted that for even a larger bubble the light intensity is estimated to be large enough to be observed (for $R_0 = 7$ μm, the maximum intensity is 0.3 mW with the pulse width of 340 ps). It means that the present estimation of the intensity of $N_2(2+)$ and $N_2(1+)$ is wrong. In other words, the emissions from the excited molecules are strongly quenched by high pressure and temperature inside a bubble. It is known that radiative deexcitation of molecules is strongly quenched by the collisions with molecules, by which the excess energy is transferred to heat by the excitation of the vibrational state of the colliding molecule [23]. It is also known that this effect is dominant under high pressure and temperature because quite frequent molecular collisions take place.

According to the present simulation, 8% of nitrogen molecules inside an air bubble are dissociated per collapse by the following chemical reaction: $N_2 + O \rightarrow NO + N$. As a result, NO, HNO_2, and N are created, which supports the Lohse's hypothesis [24] that nitrogen and oxygen in an air bubble are dissociated and dissolve into the surrounding liquid in a few hundred acoustic cycles.

Now we will discuss the following question: Why is the light emission from air bubbles experimentally observed in a cavitation field [5,25], while it is not observed from an air bubble in a single-bubble system [8]? In a cavitation field (multibubble field), the maximum bubble temperature and pressure are much less than those in a single-bubble system [26,27]. Thus, quenching rate of the light emission in a multibubble system is much less than that in a single-bubble system. The quenching rate is estimated by the following equation [28]: $r_n = [A][B]\sigma_Q^2 \times e^{-E/kT}\sqrt{8\pi kT/\mu}$, where $[A]$ and $[B]$ are the number densities of the excited molecule (A) and the quenching molecule (B), respectively, σ_Q^2 is the quenching cross section divided by π, E is the energy required for the quenching reaction, k is the Boltzmann constant, T is the temperature, and μ is the reduced mass of the molecules A and B. Using the typical bubble pressure and temperature in a multibubble system of 10^7 Pa and 3000 K [26,27] and the calculated values for a single–bubble system of 5×10^9 Pa and 6400 K (Table I), the ratio of the quenching rates of the two systems is $r_n(\mathrm{MBSL})/r_n(\mathrm{SBSL}) = 10^{-3}$ or less. Thus it is concluded that the light emission in a multibubble system is much less quenched than that in a single-bubble system. The ratio of the intensity of multibubble sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) is estimated as follows: $I(\mathrm{MBSL})/I(\mathrm{SBSL}) = np(\mathrm{MBSL})r_n(\mathrm{SBSL})/p(\mathrm{SBSL})r_n(\mathrm{MBSL}) \sim 100-1000$, where n is the number of air bubbles emitting light in a multibubble system ($\sim$100–1000), and p(MBSL) and p(SBSL) are the intensities of light from an air bubble when quenching is absent in a multibubble system and a single-bubble system, respectively [using the above values of the bubble temperature and pressure, $p(\mathrm{MBSL})/p(\mathrm{SBSL}) \sim 10^{-3}$]. Thus the answer to the above question is as follows: In a multibubble system, the quenching rate is much less than that in a single-bubble system due to the much lower bubble pressure and temperature. Additionally, in a multibubble system the number of bubbles emitting light is $\sim$100–1000, while that in a single-bubble system is, of course, 1. These two factors make the light intensity of MBSL much larger than that of SBSL of an air bubble.

Now we will discuss the difference between SBSL and MBSL in general. For a few decades, the spectra of MBSL have been studied experimentally [5,26,29]. It is reported that MBSL spectra often have characteristic lines such as the OH line and the sodium line in a sodium chloride solution [5,26,29]. However, SBSL spectra are continuous and have no characteristic lines [5,30]. The difference is explained by the present result that emissions from excited molecules are strongly quenched by high pressure and temperature inside a SBSL bubble. According to the reported MBSL spectra [5,26,29], light emissions from excited molecules are not quenched in a MBSL case. It is because the achieved pressure and temperature inside a bubble in a MBSL case are much lower than those in a SBSL case as summarized in Table II. The temperature and pressure of a MBSL bubble listed in Table II are determined by spectra [26] and chemical kinetic thermometry [27]. Those of a SBSL bubble are determined by spectra [30] and computer simulations

TABLE II. The comparison between SBSL and MBSL. It should be noted that both SBSL and MBSL originate in the quasiadiabatic compression of a bubble and MBSL can be SBSL-like when the acoustic amplitude is large enough.

	SBSL	MBSL (typical)
Temperature	10 000–50 000 K	3000–5000 K
Pressure	10^9–10^{10} (Pa)	10^7–10^8 (Pa)
Light Emission	Plasma	Molecules

[9,31,32]. It should be noted again that both SBSL and MBSL originate in the same quasiadiabatic compression of a bubble as theoretically clarified by Yuan *et al.* [10,11] that no shock wave is formed inside a collapsing bubble. Thus it is concluded that the difference between SBSL and MBSL is the achieved pressure and temperature inside a bubble. It suggests that even in a cavitation bubble field some of the bubble collapses are SBSL-like and molecular emissions are strongly quenched. Indeed, Giri and Arakeri [33] reported that the spectrum of MBSL is similar to that of SBSL when the acoustic amplitude is large enough.

In conclusion, both SBSL and MBSL originate in the quasiadiabatic compression of a bubble. The difference of SBSL and MBSL is the achieved pressure and temperature inside a bubble; for SBSL the pressure and temperature are so high that light emissions from excited molecules are strongly quenched, while in the case of MBSL they are not quenched due to the much lower pressure and temperature. Even in cavitation bubble fields (MBSL), some of the bubble collapses can be SBSL-like if the acoustic amplitude is large enough.

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