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A NEW FORMULATION OF BUBBLE DYNAMICS
FOR
SONOLUMINESCENCE

(ソノルミネッセンス解析の為の
気泡の新しい動力学)

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A NEW FORMULATION OF BUBBLE DYNAMICS
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Preface

In this thesis, a new model of bubble dynamics is constructed for the study of the recently discovered single-bubble sonoluminescence (SBSL). In the model, effect of non-equilibrium evaporation and condensation at bubble wall and that of thermal conduction both inside and outside a bubble are taken into account. Numerical calculations are performed under a condition of SBSL and that of non-light-emission. The most important point in this thesis is the calculation including the effect of non-equilibrium evaporation and condensation at bubble wall for the first time in the studies of SBSL. The results reveal that the effect is considerable on bubble dynamics. It is clarified that the partial pressure of water vapor in a bubble differs considerably from the saturated vapor pressure at collapses of the bubble. It is also clarified that the liquid temperature at bubble wall increases considerably at collapses due to the latent heat of intense condensation. It means that chemical reactions take place not only inside a bubble but also outside a bubble. In the last chapter, rates of chemical reactions in a bubble are numerically calculated including the effect. The results of this thesis are also important in the study of sonochemistry.

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Chapter 1

Introduction

Abstract

The experimental studies of the single-bubble sonoluminescence (SBSL) are reviewed. The theoretical studies of SBSL, which are still in the course of their developments, are also reviewed. An overview of the present thesis is also given.

1.1 Sonoluminescence

1.1.1 Single-Bubble Sonoluminescence

When the liquid water containing gas is irradiated by strong ultrasonic wave, bubbles are numerously created. It is called "cavitation". The bubbles expand and contract according to the oscillations of the surrounding pressure (ultrasonic field). When the surrounding pressure is small, bubbles expand. When it is large, they contract. Under some conditions, bubbles stably repeat the expansion and the contraction. It is called "stable cavitation", which occurs when the ultrasonic field is relatively weak. When the ultrasonic field is relatively strong, the contractions of the bubbles are violent. The bubbles are deformed into daughter-droplets at or just after their collapses. It is called "transient cavitation"[1].

Sonoluminescence (SL) is the light emission phenomenon when bubbles strongly collapse. It was discovered accidentally by Marinesco and Trillat in 1933[2]. They found that photographic plate immersed in liquid water irradiated by ultrasonic wave was fogged[2]. In 1934, Frenzel and Schultes clarified that the fog was due to the light emission from the liquid water[2]. From the discovery, SL has long been studied both experimentally and theoretically[2]. However, in those experiments, many bubbles emit light at the same time. Additionally, the light (SL) was mainly from the bubbles of the "transient cavitation" because strong ultrasound was used to obtain strong light. It means that many bubbles are deformed into daughter droplets just

after the every light emission. The existence of many bubbles also results in the change of bubbles because some neighboring bubbles are combined to be a larger bubble. Deformation of a bubble from the spherical shape also takes place due to the existence of the neighboring bubbles because the pressure field of the ultrasound at the bubble changes by them. The above facts mean that it is very difficult to analyze the experimental data of sonoluminescence because the behavior of many bubbles are very complicated. This kind of SL is called "multi-bubble sonoluminescence" (MBSL) as compared to the recently discovered "single-bubble sonoluminescence" (SBSL)[3]. In the present section, SBSL is reviewed, which has many surprising and mysterious features. In the present stage, it is even unclear whether SBSL has the same origin with that of MBSL or not[3].

1.1.2 Experiments

In 1988, D.F.Gaitan succeeded for the first time in the experiments of SBSL[4]. In 1991, B.P.Barber et al. in University of California succeeded the experiments of SBSL[5]. In Fig.1-1, the experimental set-up by B.P.Barber et al. is shown[6]. The degassed water in a spherical pyrex flask is irradiated by the ultrasonic wave driven by a piezoelectric transducer(PZT) on the flask. The frequency of the ultrasonic wave is chosen as a standing wave is formed in the flask. Next, a current pulse is passed through toaster wire (NiCr) mounted inside the flask[7]. Then, the vaporous cavities are formed as a result of boiling near the wire.

Fig.1-1 Block diagram of the apparatus used to generate and observe SBSL. The degassed water in a spherical flask is irradiated by the ultrasonic wave driven by a piezoelectric transducer (PZT). The emitted light is detected with a PMT biased by the high-voltage(HV) supply.[6]

The cavities are quickly filled with non-condensable gas (air) because small amount of gas (air) is dissolved even in degassed water. The radiation pressure of the sound field then moves the gas bubbles to the nearest velocity node where they coalesce to be a single bubble[7]. When the amplitude of the ultrasonic wave is relatively small, the single bubble repeats expansion and contraction stably (stable cavitation). Above the threshold amplitude of the ultrasonic wave, the single bubble emits light when it collapses. The single bubble remains oscillating stably below the upper threshold of the ultrasonic amplitude. This situation is called "single-bubble sonoluminescence" (SBSL). Thus the word "SBSL" sometimes means not only the light emission from a single bubble but also that during the stable oscillations of the bubble. Under the condition of SBSL, the light emission takes place for each acoustic cycle in clock-like precision. In Fig.1-2, the synchronous relationship is shown between the acoustic field(top), the measured radius-time curve(middle), and the SBSL emissions measured with a photomultiplier tube(PMT) (bottom)[3,8]. The emissions occur at a fixed phase of the acoustic field. It is also seen from Fig.1-2 that the emissions occur at the strong collapses of the bubble. The radius of the bubble was measured by light scattering (see Ref.[8]).

B.P.Barber et al. discovered that the pulse width of SBSL is less than 50 ps[5,6]. "Less" means that the pulse of SBSL is too short to be resolved by the fastest available microchannel plate photomultiplier tube(PMT).

Fig.1-2 Synchronous relationship between the acoustic field(top), the measured radius-time curve(middle), and the SBSL emissions measured with a photomultiplier tube(PMT)(bottom). The emissions occur at a fixed phase of the acoustic field. The frequency and the amplitude of the acoustic field is 22.3 kHz and 1.2 atm, respectively.[3]

Additionally, they discovered that the jitter (the deviation from the average value) in the time between successive emissions is also less than 50 ps[6]. The time interval between successive emissions is about $33\mu s$, which is completely the same with the period of the ultrasonic wave (26.5 kHz). Thus, the jitter is only 10^{-6} of the period of SBSL flushes. SBSL is an excellent clock!

B.P.Barber et al. have studied SBSL experimentally since their discovery. Following is a list of the important experimental features of SBSL.

1. The pulse width is less than 50 ps.[5,6]
2. The jitter in the time between successive flushes is less than 50 ps.[6]
3. The spectrum of SBSL from an air bubble is broadband and can be fitted by blackbody spectrum (Fig.1-3)[9]. The blackbody temperature is in the order of $10^4 \sim 10^5 K$ depending on the physical conditions of the experiments such as the liquid temperature and the amplitude of the ultrasonic wave. SBSL can be seen by unaided eyes and its color is blue.[5,9]
4. The intensity of the light increases as the liquid temperature decreases (The intensity at $10^\circ C$ is 5 times larger than that at $20^\circ C$).[9]
5. Increasing the noble gas content of a nitrogen bubble to about 1 % dramatically increases the light emission (Fig.1-4)[7]. For example, the light intensity from a bubble which consists of 99 % nitrogen and 1 % argon is about 100 times larger than that from a pure nitrogen bubble. However, the light intensity decreases as the noble gas content increases over 1 %.

Fig.1-3 Calibrated spectral density of SBSL from an air bubble. The average spectral energy density of a single flash can be obtained by dividing by the acoustic frequency of 27 kHz. The dotted line was obtained via the D lamp calibration. The points with error bars were obtained by calibrating their apparatus with a QTH standard spectral irradiance. The solid line is a 25,000 K blackbody spectrum.[9]

Fig.1-4 Intensity of SBSL as a function of the percentage (mole fraction) of noble gas mixed with N_2 . The data are normalized to the SBSL of an air bubble at $24^\circ C$ (2×10^5 photons per flash). The acrylic walls of the flask passes light wavelengths larger than 380 nm.[7]

Fig.1-5 Spectrum of SBSL for various gas mixtures dissolved into water at a pressure head of 150 mmHg in a 33 kHz sound field at 24°C. Although the He bubble is over 10 times dimmer than the 2% Xe bubble, the He bubble has a much larger UV spectral density. The data have been corrected for the absorption of water and quartz and for the voltage dependence of the quantum efficiency of the photodetector.

Nevertheless, the light intensity from a pure argon bubble is still larger than that from a pure nitrogen bubble.[7]

6. The spectrum of SBSL strongly depends on the nature of the gas inside the bubble: Xenon yields a spectral peak at about 300 nanometers, whereas the helium spectrum is so strongly ultraviolet that its peak is obscured by the cutoff of water(Fig.1-5)[7].

7. The intensity of the light increases as the amplitude of ultrasonic wave increases. However, above a threshold amplitude, bubble oscillations are no more stable and SBSL can not be observed.[5,10]

Now, experiments of SBSL have been succeeded also in Lawrence Livermore National Laboratory[11] and Naval Postgraduate School in U.S.A.[12].

1.1.3 Theory

In the present stage, no theory explains all the experimental features of SBSL. However, the shock wave mechanism studied by C.C.Wu and R.H.Roberts[13] is considered to be most reliable. They showed that the spherical shock wave is formed inside a bubble when it collapses by numerical calculations of Euler's equation for the motion of air in the bubble[13]. The shock wave becomes stronger as it focuses at the center of the bubble. The temperature and the pressure increases drastically when the shock wave focuses. Then, air is ionized and the light is emitted from the plasma. Their estimation of the intensity and the duration of the light agrees well with the experimental results by B.P.Barber et al.[5,6]. In their estimation, it is assumed that

the light emission is due to thermal bremsstrahlung from the ionized air (plasma). The blackbody type spectrum of SBSL can also be explained by the mechanism. However, the mechanism does not explain the effect of noble gas doping on SBSL.

For a size of a stable bubble, it is suggested by S.J.Putterman that the size is determined not by the initial bubble radius at the beginning of the experiment but by the amplitude and the frequency of the ultrasonic wave[14]. It means that the bubble radius changes from the initial value to a stable value by gas diffusion[10]. When a bubble expands, some amount of gas diffuses into the bubble from the surrounding liquid because the pressure inside the bubble decreases. When a bubble contracts, some amount of gas diffuses out of the bubble into the surrounding liquid because the pressure inside the bubble increases. The bubble radius at stable condition is determined by the condition that the inward flow of gas at the expansion phase equals to the outward flow at the contraction phase[14]. However, no theory predicts bubble radius at stable condition quantitatively. In other words, conditions for "stable cavitation", which are required for SBSL, have not been understood theoretically yet. In the present thesis, the author has developed theory of bubble dynamics in order to understand the stable cavitation and SBSL.

1.1.4 Applications

Theoretical and experimental investigations of SBSL are still in the course of their developments because only a few years have past since its discovery. Thus SBSL has not been applied in the industry yet. However, some applications of SBSL have already been suggested. Firstly, the flushes of SBSL can be applied directly. For example, an application as a source of the picosecond light pulses is possible. An application as a clock is also possible because the periodicity of SBSL is excellent. Secondly, applications of the extremely high temperature and pressure inside a bubble are suggested. For example, applications to chemical reactions are possible. Actually, MBSL has already been applied to chemical reactions, which is called "sonochemistry". In this case, the light emissions are not important, while high temperature and pressure are important. Especially, the short duration of the high temperature and pressure is extremely useful. The speed of cooling inside a bubble is much more larger than that in a usual chemical instrument. Thus bubble oscillations are useful for the production of amorphous iron[3]. Iron compounds are decomposed into iron atoms in bubbles, followed by the formation of amorphous iron due to the extremely high speed of cooling (iron atoms can not be crystalized). The most attractive applications now is that to nuclear fusion using the extremely high temperature and pressure inside a SBSL bubble, which has been tested in Lawrence Livermore National Laboratory[15]. They suggest that the extremely high temperature and pressure attained in

an instrument for laser nuclear fusion can be attained in a bubble under a condition of SBSL.

1.2 An Overview of the Present Thesis

In the present thesis, a model of bubble dynamics is constructed, including effect of non-equilibrium evaporation and condensation at bubble wall and that of thermal conduction both inside and outside a bubble. In chapter2, the adiabatic model of bubble dynamics is developed to a model including effect of non-equilibrium evaporation and condensation at bubble wall. Numerical calculations of bubble oscillations are performed both by the adiabatic model and the developed model. The results indicate that the effect of non-equilibrium evaporation and condensation at bubble wall affects bubble dynamics considerably. For example, it is clarified that the partial pressure of water vapor in a bubble differs considerably from the saturated vapor pressure at collapses of the bubble, which means that "non-equilibrium effect" of evaporation and condensation is important in bubble dynamics.

In chapter3, effect of thermal conduction inside a bubble is included in the model constructed in chapter2. Numerical calculations are performed both for the models with and without thermal conduction inside a bubble under a condition of SBSL and that of non-light-emission. Calculated results indicate that thermal conduction inside a bubble affects bubble dynamics considerably. The calculated radius-time curve by the model with thermal

conduction fits well with the experimental data by B.P.Barber et al.[16].

In chapter4, effect of thermal conduction outside a bubble is included in the model constructed in chapter3. Numerical calculations are performed under a condition of SBSL and that of non-light-emission. It is concluded that the liquid temperature at bubble wall increases considerably at collapse of a bubble. It is caused by the latent heat of intense condensation and by thermal conduction. (At collapse, the intense condensation takes place because the partial pressure of water vapor in the bubble increases dramatically.) It is concluded that chemical reactions take place not only inside a bubble but also outside a bubble.

In chapter5, rates of chemical reactions in an air bubble are calculated numerically under a condition of SBSL. It is concluded that appreciable amount of OH , H_2O_2 , HO_2 , O_3 , H_2 , H , and O molecules are created in a bubble. Connection with SBSL is also discussed.

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Chapter 2

Effect of Evaporation and Condensation

Abstract

A simple new model of bubble dynamics is constructed including effect of non-equilibrium evaporation and condensation of water vapor at bubble wall. A new equation of bubble radius is derived including the effect. Comparison is given between the model and the adiabatic model by numerical calculations. It is concluded that the effect of evaporation and condensation is considerable on bubble dynamics. It is also concluded that the partial pressure of water vapor in a bubble differs considerably from the saturated vapor pressure at collapses of a bubble.

2.1 Introduction

After the discovery of SBSL, many researchers study it theoretically[1-4]. However, effect of non-equilibrium evaporation and condensation of water vapor is neglected in those studies[1-4]. The effect is known to be considerable on bubble dynamics in the study of the pressure wave produced by the collapse of a bubble in a liquid[5]. In this chapter, a simple new model of bubble dynamics is constructed including the effect, which is the first step of more accurate study of SBSL.

In the next section, the adiabatic model is described, which is frequently employed in the study of SBSL. For example, the adiabatic model was used in the calibration of the experimental data of radius-time curves under a SBSL condition[1,2]. In section2.3, the new model is described in which effect of non-equilibrium evaporation and condensation of water vapor is taken into account. In section2.4, results of numerical calculations are shown both by the adiabatic model and the new model.

2.2 Adiabatic Model

In the model, pressure and temperature are assumed to be spatially uniform in a bubble. It is a good approximation only when $|\dot{R}| \ll c_g$, where

$\dot{R} = \frac{dR}{dt}$ is the velocity of the bubble wall, and c_g is the speed of sound in the bubble. The liquid temperature on the external side of the bubble wall is assumed to be constant(T_0) during bubble oscillations. Thus temperature

discontinuity(ΔT) exists at the bubble wall ($\Delta T = T - T_0$, where T is the temperature inside the bubble). In the adiabatic model, no heat exchange is taken into account between a bubble and the surrounding liquid. Thus the change of the internal energy of a bubble(ΔE) is brought only by pV work.

$$\Delta E(t) = -p(t) \cdot \Delta V(t) \quad (2.1)$$

where $p(t)$ is the pressure inside the bubble at time t and $V(t)$ is the volume of the bubble. $V(t)$ is related to the bubble radius $R(t)$ by

$$V = \frac{4}{3}\pi R^3 \quad (2.2)$$

As an equation of bubble radius, Keller equation is employed, in which compressibility of liquid is taken into account to the first order in the bubble wall Mach number relative to the speed of sound in the liquid[6-8].

$$\left(1 - \frac{\dot{R}}{c}\right) R \ddot{R} + \frac{3}{2} \dot{R}^2 \left(1 - \frac{\dot{R}}{3c}\right) = \left(1 + \frac{\dot{R}}{c}\right) \frac{1}{\rho_L} [p_B(t) - p_s(t + \frac{R}{c}) - p_\infty] + \frac{R}{\rho_L c} \frac{dp_B(t)}{dt} \quad (2.3)$$

where $\ddot{R} = \frac{d^2 R}{dt^2}$, c is the speed of sound in the liquid, ρ_L is the liquid density, $p_B(t)$ is the liquid pressure on the external side of the bubble wall, $p_s(t)$ is a nonconstant ambient pressure component such as a sound field, and p_∞ is the undisturbed pressure. When a bubble is irradiated by an acoustic wave of which wave length is much larger than the bubble radius, $p_s(t) = -A \sin \omega t$ where A is the pressure amplitude of the acoustic wave and ω is the angular frequency of it. $p_B(t)$ is related to the internal bubble pressure $p(t)$ by

$$p_B(t) = p(t) - \frac{2\sigma}{R} - \frac{4\mu\dot{R}}{R} \quad (2.4)$$

where σ is the surface tension and μ is the liquid viscosity. In order to calculate $p(t)$, van der Waals equation of state is employed.

$$(p(t) + \frac{a}{v^2})(v - b) = R_g T \quad (2.5)$$

where a and b are the van der Waals constants, v is the molar volume and R_g is the gas constant. The van der Waals constants are determined by

$$a = \frac{n_{air}}{n_t} a_{air} + \frac{n_{H_2O}}{n_t} a_{H_2O} \quad (2.6)$$

$$b = \frac{n_{air}}{n_t} b_{air} + \frac{n_{H_2O}}{n_t} b_{H_2O} \quad (2.7)$$

where a_{air} and b_{air} (a_{H_2O} and b_{H_2O}) are the van der Waals constants of air (water vapor), n_{air} (n_{H_2O}) is the number of air (water vapor) molecules in the bubble, and n_t is the total number of gas and vapor molecules in the bubble ($n_t = n_{air} + n_{H_2O}$). The values are as follows[9]: $a_{air} = 1.402 \times 10^{-1} (J \cdot m^3/mol^2)$, $a_{H_2O} = 5.536 \times 10^{-1} (J \cdot m^3/mol^2)$, $b_{air} = 3.753 \times 10^{-5} (m^3/mol)$, $b_{H_2O} = 3.049 \times 10^{-5} (m^3/mol)$.

The temperature inside the bubble is calculated by solving eq.(2.8).

$$E = \frac{n_{air}}{N_A} \int_0^T C_{V,air}(T') dT' + \frac{n_{H_2O}}{N_A} \int_0^T C_{V,H_2O}(T') dT' - \left(\frac{n_t}{N_A} \right)^2 \frac{a}{V} \quad (2.8)$$

where $C_{V,air}(T)$ ($C_{V,H_2O}(T)$) is the heat capacity of air (vapor) at constant volume at temperature T , N_A is the Avogadro number, and a is the van der Waals constant. Eq.(2.8) is derived as follows. The internal energy(E) of a bubble is a function of temperature(T) and volume(V) for the van der Waals gas. Thus

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV \quad (2.9)$$

From the definition of heat capacity at constant volume,

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{n_{air}}{N_A} C_{V,air}(T) + \frac{n_{H_2O}}{N_A} C_{V,H_2O}(T) \quad (2.10)$$

For the van der Waals gas, the second term in eq.(2.9) is non-zero[9].

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p = \left(\frac{n_t}{N_A}\right)^2 \frac{a}{V^2} \quad (2.11)$$

Inserting eqs.(2.10)(2.11) into eq.(2.9) and integrating the first term by the temperature from 0(K) to $T(K)$ and the second term by the volume from infinity to V , one obtains eq.(2.8). For the temperature dependence of the heat capacity at constant volume ($C_{V,air}(T)$ and $C_{V,H_2O}(T)$), empirical formulas are employed, which are derived by experiments[10](see Appendix 2-A).

The molar volume v is calculated by

$$v = \frac{N_A V}{n_t} \quad (2.12)$$

The density inside the bubble (ρ_g) is calculated by

$$\rho_g = \frac{\left(M_{H_2O} \frac{n_{H_2O}}{n_t} + M_{air} \frac{n_{air}}{n_t}\right) \times 10^{-3}}{v} \quad (kg/m^3) \quad (2.13)$$

where $M_{H_2O}(M_{air})$ is the molar weight of water(air) in (g/mol), v is in (m^3/mol).

2.3 A Model with Evaporation and Condensation

The difference between this model and the adiabatic model is the inclusion of the effect of non-equilibrium evaporation and condensation of water vapor

at bubble wall in this model. In this model, pressure and temperature are assumed to be spatially uniform in a bubble as in the adiabatic model. The liquid temperature on the external side of the bubble wall is assumed to be constant(T_0) during bubble oscillations. Thus at the bubble wall, temperature discontinuity($\Delta T = T - T_0$) exists as in the adiabatic model.

Followings are the different points compared with the adiabatic model. The number of water vapor(n_{H_2O}) changes with time by evaporation or condensation at bubble wall.

$$n_{H_2O}(t + \Delta t) = n_{H_2O}(t) + 4\pi R^2 \dot{m} \Delta t \quad (2.14)$$

where $\dot{m}$ is the *net* rate of evaporation per unit area and unit time(when $\dot{m} < 0$, condensation takes place).

$$\dot{m} = \dot{m}_{eva} - \dot{m}_{con} \quad (2.15)$$

$$\dot{m}_{eva} = \frac{10^3 N_A}{M_{H_2O}} \frac{\alpha_M}{(2\pi R_v)^{\frac{1}{2}}} \frac{p_v^*}{T_0^{\frac{1}{2}}} \quad (2.16)$$

$$\dot{m}_{con} = \frac{10^3 N_A}{M_{H_2O}} \frac{\alpha_M}{(2\pi R_v)^{\frac{1}{2}}} \frac{\Gamma p_v}{T^{\frac{1}{2}}} \quad (2.17)$$

where $\dot{m}_{eva}(\dot{m}_{con})$ is the actual rate of evaporation(condensation) per unit area and unit time[5,11]. Eq.(2.15) means that the *net* rate of evaporation is the difference between the actual rate of evaporation and that of condensation. In eqs.(2.16)(2.17), α_M is the accommodation coefficient for evaporation or condensation(assumed constant), R_v is the gas constant of water vapor in ($J/kg \cdot K$), p_v^* is the saturated vapor pressure at temperature T_0 , and p_v is

the actual vapor pressure.

$$p_v = \frac{n_{H_2O}}{n_t} p \quad (2.18)$$

The correction factor(Γ) in eq.(2.17) is expressed as

$$\Gamma = \exp(-\Omega^2) - \Omega\sqrt{\pi} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^\Omega \exp(-x^2) dx \right) \quad (2.19)$$

in which

$$\Omega = \frac{\dot{m}}{p_v} \left(\frac{R_v T}{2} \right)^{\frac{1}{2}} \quad (2.20)$$

In this model, the heat exchange accompanied by evaporation and condensation is taken into account at the bubble interface. Evaporating vapor molecules carry their own energy into the bubble from the surrounding liquid. Condensing vapor molecules carry their own energy into the surrounding liquid from the bubble. Thus the change of the internal energy of a bubble(ΔE) is expressed by

$$\Delta E(t) = -p(t) \cdot \Delta V(t) + 4\pi R^2 \Delta t (\dot{m}_{eva} e_{eva} - \dot{m}_{con} e_{con}) + 4\pi R^2 \Delta t \left. \frac{dm}{dt} \right|_{diff} e_{air} \quad (2.21)$$

where $e_{eva}(e_{con})$ is the energy carried by an evaporating (condensing) vapor molecule, $\left. \frac{dm}{dt} \right|_{diff}$ is the rate of diffusion of air per unit area and unit time, and e_{air} is the energy carried by a diffusing air molecule. In this model, the latent heat of evaporation and condensation is neglected. The first term in the right hand side of eq.(2.21) is the work by pressure $p(t)$. The second term is the energy carried by evaporating(condensing) vapor molecules. The third term is the energy carried by diffusing air molecules.

The energy carried by a condensing vapor molecule (e_{con}) is calculated by

$$e_{con} = \frac{1}{N_A} \int_0^{T''} C_{V,H_2O}(T') dT' \quad (2.22)$$

where the potential energy between molecules is neglected. In this calculation, $T'' = T$ (the temperature inside the bubble) is assumed. The energy carried by an evaporating vapor molecule (e_{eva}) is assumed to be given by eq.(2.22) with $T'' = T_0$ (the liquid temperature). The energy carried by a diffusing air molecule (e_{air}) is assumed to be given by

$$e_{air} = \frac{1}{N_A} \int_0^T C_{V,air}(T') dT' \quad (2.23)$$

In this model, a new equation of bubble radius is derived, which takes into account the effect of evaporation and condensation of water vapor.

$$\begin{aligned} & \left(1 - \frac{\dot{R}}{c} + \frac{\dot{m}}{c\rho_L}\right) R\ddot{R} + \frac{3}{2}\dot{R}^2 \left(1 - \frac{\dot{R}}{3c} + \frac{2\dot{m}}{3c\rho_L}\right) \\ &= \frac{1}{\rho_L} \left(1 + \frac{\dot{R}}{c}\right) \left(p_B - p_s\left(t + \frac{R}{c}\right) - p_\infty\right) \\ & \quad + \frac{\ddot{m}R}{\rho_L} \left(1 - \frac{\dot{R}}{c} + \frac{\dot{m}}{c\rho_L}\right) \\ & \quad + \frac{\dot{m}}{\rho_L} \left(\dot{R} + \frac{\dot{m}}{2\rho_L} + \frac{\dot{R}\dot{m}}{2c\rho_L}\right) \\ & \quad + \frac{R}{\rho_L c} \frac{dp_B}{dt} \end{aligned} \quad (2.24)$$

A similar equation of bubble radius including the effect of evaporation and condensation has already been derived by S.Fujikawa and T.Akamatsu[5]. However their equation is not reduced to Keller equation even when $\dot{m} = \ddot{m} = 0$ [5]. Eq.(2.24) is reduced to Keller equation when $\dot{m} = \ddot{m} = 0$. Derivation

of eq.(2.24) is given in Appendix 2-B. $p_B(t)$ is related to $p(t)$ by eq.(2.25)[5].

$$p_B(t) = p(t) - \frac{2\sigma}{R} - \frac{4\mu}{R}(\dot{R} - \frac{\dot{m}}{\rho_L}) - \dot{m}^2 \left(\frac{1}{\rho_L} - \frac{1}{\rho_g} \right) \quad (2.25)$$

As an equation of state, van der Waals equation (eq.(2.5)) is employed as in the adiabatic model. In this model, the van der Waals constants(a and b in eqs.(2.6)(2.7)) vary with time because the molar fraction of water vapor in the bubble ($\frac{n_{H_2O}}{n_t}$) varies with time. The temperature inside the bubble(T) is calculated by solving eq.(2.8) as in the adiabatic model.

In this calculation, the diffusion of air into the surrounding liquid is also taken into account. However, the effect is negligibly small for a few cycles of bubble oscillations as is shown in section 2.4. In other words, the calculated results are not affected by the effect. Below is the description of the calculation of the effect.

$$n_{air}(t + \Delta t) = n_{air}(t) + \left. \frac{dm}{dt} \right|_{diff} \cdot 4\pi R^2 \Delta t \quad (2.26)$$

$\left. \frac{dm}{dt} \right|_{diff}$ is calculated by

$$\left. \frac{dm}{dt} \right|_{diff} = D \cdot \left. \frac{\partial c_{air}}{\partial r} \right|_{r=R} \quad (2.27)$$

where D is the diffusion coefficient of air in liquid water, r is the radius from the center of the bubble, and c_{air} is the concentration of air in the liquid. It is assumed[12]

$$\left. \frac{\partial c_{air}}{\partial r} \right|_{r=R} = \frac{c_0 - c_s}{R} \quad (2.28)$$

where c_s is the saturated air concentration in the liquid at $r = R$, and c_0 is the air concentration in the liquid at $r = \infty$. In this calculation, $c_0 = 0$ is

assumed. c_s is calculated by Henry's law[9].

$$c_s = \frac{10^3 \rho_L N_A p_{air}}{M_{H_2O} K_B} \quad (m^{-3}) \quad (2.29)$$

where p_{air} is the partial pressure of air in the bubble in (Pa) ($p_{air} = \frac{n_{air}}{n_t} p$), and K_B is the Henry's constant of air in water in (Pa). At $T_0 = 20^\circ C$, $K_B = 6.737 \times 10^9$ (Pa), $D = 1.76 \times 10^{-9}$ (m^2/s)[13,14].

As in the adiabatic model, the density inside the bubble(ρ_g) is calculated by eq.(2.13).

2.4 Results and Discussions

Calculations are performed under a condition of $T_0 = 20^\circ C$ and $R_0 = 4.5(\mu m)$, where R_0 is the initial bubble radius. Physical quantities employed in the calculations are listed in Table 2-1. The frequency and the amplitude of the acoustic field is chosen to be 26.5 kHz and 1.325 atm, respectively. The undisturbed pressure is taken to be $p_\infty = 1$ atm. Calculations start from the time $t = 0$ (μs) with the initial conditions that $R = R_0$, $\dot{R} = 0$, $\frac{dp}{dt} = 0$, $\dot{m} = \ddot{m} = 0$, and $p_s(0) = 0$.

(A) Adiabatic model

Under the physical conditions employed in the calculations described above, a periodic solution is obtained by numerical calculations as is shown in Figs.2-1-(b)(c) by the adiabatic model. The pressure of the acoustic field($p_s(t)$) employed in the calculation is shown in Fig.2-1-(a) as a function of time. The bubble radius(R) is shown in Fig.2-1-(b). The temperature inside

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the bubble(T) is shown in Fig.2-1-(c). Both the radius and the temperature change with time periodically with the frequency of the acoustic field. Other physical quantities of the bubble such as pressure(p), density(ρ_g), and internal energy(E) all change with time periodically with the same frequency, though they are not shown in the figures here.

20°C	
bubble	
R_0 (m)	4.5
ρ_l (kg/m ³)	1.2×10^3
ρ_g (kg/m ³)	1.2×10^{-3}
initial values	
p (Pa)	1.01×10^5
T (K)	300
E (J)	1.0×10^{-10}
ρ_g (kg/m ³)	1.2×10^{-3}
ρ_l (kg/m ³)	1.2×10^3

Table 2-1

Physical quantities employed in the calculations. T_0 is the liquid temperature, R_0 is the initial bubble radius. $n_{air,0}(n_{H_2O,0})$ is the initial number of air(water vapor) molecules in the bubble. p_v^* is the saturated vapor pressure, c is the speed of sound, σ is the surface tension, μ is the viscosity, and ρ_L is the density of liquid water.

T_0	$20^\circ C$
bubble	
$R_0(\mu m)$	4.5
$n_{air,0}$	1.23822×10^{10}
$n_{H_2O,0}$	2.20415×10^8
liquid(water)	
$p_v^*(Pa)$	2.3381×10^3
$c(m/s)$	1483.0
$\sigma(N/m)$	7.275×10^{-2}
$\mu(Pa \cdot s)$	1.002×10^{-3}
$\rho_L(kg/m^3)$	9.982×10^2

Fig.2-1 Calculated results by the adiabatic model for three acoustic cycles.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time.

Fig.2-1-(b) The bubble radius(R) as a function of time.

Fig.2-1-(c) The temperature inside the bubble(T) as a function of time with logarithmic vertical axis.

(B) Model with evaporation and condensation

In this calculation, the accommodation coefficient for evaporation or condensation(α_M) is assumed to be $\alpha_M = 0.04$ [5]. As in the adiabatic model, a periodic solution is obtained by numerical calculations as is shown in Figs.2-2-(b,c,d). In Fig.2-2-(a), the pressure of the acoustic field($p_s(t)$) employed in the calculation is shown as a function of time. In Fig.2-2-(b), the bubble radius(R) is shown as a function of time. The temperature inside the bubble(T) is shown in Fig.2-2-(c). In Fig.2-2-(d), the total number of molecules in the bubble(n_t) and the number of vapor and air molecules (n_{H_2O} and n_{air}) are shown with logarithmic vertical axis. As is seen in Fig.2-2, the radius(R), the temperature(T), and the number of molecules(n) all change with time periodically with the frequency of the acoustic field (strictly, n_{air} is almost constant (see the discussion below)). Other physical quantities of the bubble such as pressure(p), density (ρ_g), and internal energy(E) all change with time periodically with the same frequency, though they are not shown in the figures here.

From Fig.2-2-(d), it is seen that evaporation of water vapor takes place in the expansion phase of bubble oscillations. It is because the partial pressure of water vapor in the bubble(p_v) decreases in the expansion phase. On the other hand, at collapses, condensation of water vapor takes place. It is because p_v increases at the collapses.

Fig.2-2 Calculated results by the model with evaporation and condensation for three acoustic cycles.

-(a) The pressure of the acoustic field($p_s(t)$) employed in the calculation as a function of time.

Fig.2-2-(b) The bubble radius(R) as a function of time.

Fig.2-2-(c) The temperature inside the bubble(T) as a function of time with logarithmic vertical axis.

Fig.2-2-(d) The number of molecules in the bubble as a function of time with logarithmic vertical axis. The line shows the total number of molecules (n_t), the dash dotted line shows the number of vapor molecules (n_{H_2O}), and the dotted line shows the number of air molecules (n_{air}).

It is also concluded from the numerical calculations that p_v differs considerably from the saturated vapor pressure(p_v^*) at collapses of a bubble. For example, $p_v = 8 \times 10^8(Pa)$ when the bubble radius is the minimum, while $p_v^* = 2 \times 10^3(Pa)$ (p_v is 10^5 times larger than p_v^* !). On the other hand, in the expansion phase, $p_v \sim p_v^*$ holds well. For example, $p_v = 2 \times 10^3(Pa)$ when the bubble radius is the maximum. The number of air molecules in the bubble(n_{air}) remains almost constant during a few cycles of bubble oscillations as is seen in Fig.2-2-(d). The number of air molecules dissolving into the liquid in one cycle is less than 0.02% of that of air molecules remaining in the bubble. Thus the effect of diffusion of air into the liquid is negligibly small in a few cycles concerned here (for a long time scale such as 1(s), the diffusion of air is expected to play an important role).

In this model, it is implicitly assumed that the temperature inside the bubble exists at all time. It corresponds to the assumption of quasi-equilibrium state in the bubble. To see the validity of the assumption, the mean collision time(t_c) of molecules in the bubble is estimated below[9].

$$t_c = \frac{1}{z} = \frac{V}{\sqrt{2}\sigma_a\bar{v}n_t} \quad (2.30)$$

where z is the collision frequency, σ_a is the cross section of a molecule, and $\bar{v}$ is the mean velocity of a molecule.

$$\bar{v} = \sqrt{\frac{8kT}{\pi m_a}} \quad (2.31)$$

where m_a is the mass of a molecule, and k is the Boltzmann constant.

The cross section of a molecule(σ_a) is $\sigma_a \sim 5 \times 10^{-19}(m^2)$ [9]. In the slow expansion phase in the bubble oscillation, the calculated physical quantities are as follows: $R \sim 10^{-5}(m)$, $T \sim 10^2(K)$, and $n_t \sim 10^{10}$. From eqs.(2.30)(2.31), $t_c \sim 10^{-9}(s)$. On the other hand, the characteristic time scale of the slow expansion phase(t_1) is in the order of $10^{-6}(s)$ (The velocity of the bubble wall is $\dot{R} \sim 1(m/s)$ in the slow expansion phase. If the characteristic time(t_1) is determined by $\frac{\dot{R} \cdot t_1}{R} \sim 10^{-1}$, then $t_1 \sim 10^{-6}(s)$.) Thus $t_1 \gg t_c$ holds in the slow expansion phase. It means that the assumption of quasi-equilibrium state is a good one in the slow expansion phase. Next the collapse phase is examined. At collapse, calculated values are as follows: $R \sim 10^{-6}(m)$, $T \sim 10^3(K)$, $n_t \sim 10^{10}$, and $|\dot{R}| \sim 10^2(m/s)$. From eqs.(2.30)(2.31), $t_c \sim 10^{-12}(s)$. On the other hand, the characteristic time scale(t_1) is $t_1 \sim 10^{-9}(s)$. Thus, also in the collapse phase, $t_1 \gg t_c$ holds. It means that the assumption of quasi-equilibrium is a good one even in the collapse phase of the bubble oscillation.

(C) Comparison between the adiabatic model and the model with evaporation and condensation

In Figs.2-3, the comparisons are shown between the calculated results by the adiabatic model and those by the model with evaporation and condensation (hereafter it is called "the model with EC") for one acoustic cycle. The dash-dotted line shows the calculated results by the adiabatic model, while the line shows those by the model with EC. In Fig.2-3-(a), the bub-

ble radius(R) is shown as a function of time. The temperature(T) and the pressure(p) inside the bubble are shown in Fig.2-3-(b) and -(c), respectively. It is concluded from the figures that the effect of evaporation and condensation of water vapor is considerable on bubble dynamics.

However, the model with EC constructed in this chapter is incomplete. Because effect of thermal conduction due to the temperature gradient inside a bubble is neglected. An advanced model which takes into account the effect is described in chapter3. For more quantitative discussions, the model should be used rather than the model constructed in this chapter.

Fig.2-3 Comparison between the calculated results by the adiabatic model(dash dotted line) and those by the model with evaporation and condensation(line) for one acoustic cycle.

-(a) The bubble radius(R) as a function of time.

Fig.2-3-(b) The temperature inside the bubble(T) as a function of time with logarithmic vertical axis.

Fig.2-3-(c) The pressure inside the bubble(p) as a function of time with logarithmic vertical axis.

2.5 Conclusion

A simple new model of bubble dynamics is constructed including effect of non-equilibrium evaporation and condensation of water vapor at bubble wall. A new equation of bubble radius(eq.(2.24)) is derived including the effect. Numerical calculations are performed both by the adiabatic model and the present model. It is concluded that the effect of evaporation and condensation is considerable on bubble dynamics. It is also concluded that the partial pressure of water vapor(p_v) differs considerably from the saturated vapor pressure(p_v^*) at collapses of a bubble.

Appendix 2-A. Molar Energy

From ref.[10], the empirical formulas of the heat capacity at constant volume(C_V) are eqs.(2.A1)(2.A2) for water vapor as a function of temperature(T in (K)).

$$270(K) \leq T \leq 800(K)$$

$$C_{V,H_2O}$$

$$= 0.341911906 - 1.29224 \times 10^{-4}T + 4.17008 \times 10^{-7}T^2 - 2.00401 \times 10^{-10}T^3 \quad (cal/g \cdot K) \quad (2.A1)$$

$$800(K) \leq T \leq 1500(K)$$

$$C_{V,H_2O}$$

$$= 0.267970906 + 1.53443 \times 10^{-4}T + 3.31531 \times 10^{-8}T^2 - 1.78435 \times 10^{-11}T^3 \quad (cal/g \cdot K) \quad (2.A2)$$

In this study, eqs.(2.A3)-(2.A6) are employed as the molar energy, which are approximately derived from eqs.(2.A1)(2.A2).

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$$T \leq 270(K)$$

$$\int_0^T C_{V,H_2O}(T')dT' = 0.333476814T \quad (cal/g) \quad (2.A3)$$

$$270(K) \leq T \leq 800(K)$$

$$\begin{aligned} \int_0^T C_{V,H_2O}(T')dT' \\ = 90.03873978 + 0.327769676(T - 270) \\ + 0.000067755(T - 270)^2 \quad (cal/g) \end{aligned} \quad (2.A4)$$

$$800(K) \leq T \leq 1500(K)$$

$$\begin{aligned} \int_0^T C_{V,H_2O}(T')dT' \\ = 282.7891515 + 0.403820815(T - 800) \\ + 0.000080224(T - 800)^2 \quad (cal/g) \end{aligned} \quad (2.A5)$$

$$1500(K) \leq T$$

$$\begin{aligned} & \int_0^T C_{V,H_2O}(T')dT' \\ &= 604.7735038 + 0.512508069(T - 1500) \end{aligned}$$

(cal/g)

(2.A6)

If each equation is multiplied by JM_{H_2O} where J is the mechanical equivalent of heat ($J = 4.184(J/cal)$) and M_{H_2O} is the molar weight of water ($M_{H_2O} = 18.015(g/mol)$), then each value is expressed in (J/mol).

For air, the heat capacity at constant volume is given by eqs.(2.A7)(2.A8) from ref.[10].

$$250(K) \leq T \leq 600(K)$$

$$C_{V,air}$$

$$\begin{aligned} &= 0.175782892 - 4.20419 \times 10^{-5}T \\ &+ 9.61128 \times 10^{-8}T^2 - 1.16383 \times 10^{-11}T^3 \end{aligned}$$

(cal/g · K)

(2.A7)

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$$600(K) \leq T \leq 1500(K)$$

$$C_{V,air}$$

$$= 0.140225892 + 7.71027 \times 10^{-5}T \\ - 8.56726 \times 10^{-9}T^2 - 4.75772 \times 10^{-12}T^3$$

$$(cal/g \cdot K)$$

(2.A8)

In this calculation, eqs.(2.A9)-(2.A12) are employed as the molar energy, which are approximately derived by eqs.(2.A7)(2.A8).

$$T \leq 270(K)$$

$$\int_0^T C_{V,air}(T')dT' = 0.171101319T \quad (cal/g)$$

(2.A9)

$$270(K) \leq T \leq 800(K)$$

$$\int_0^T C_{V,air}(T')dT'$$

$$= 46.19735614 + 0.168358411(T - 270)$$

$$+ 0.000022543(T - 270)^2 \quad (cal/g)$$

(2.A10)

$$800(K) \leq T \leq 1500(K)$$

$$\begin{aligned} & \int_0^T C_{V,air}(T') dT' \\ &= 141.759716 + 0.195071591(T - 800) \\ & \quad + 0.000020337(T - 800)^2 \quad (cal/g) \end{aligned} \quad (2.11)$$

$$1500(K) \leq T$$

$$\begin{aligned} & \int_0^T C_{V,air}(T') dT' \\ &= 288.2751933 + 0.220546302(T - 1500) \\ & \quad (cal/g) \end{aligned} \quad (2.12)$$

If each equation is multiplied by JM_{air} where M_{air} is the molar weight of air ($M_{air} = 28.97$), then each value is expressed in (J/mol).

It should be noted that the approximations (2.A3)(2.A9) are invalid when $T \ll 270(K)$, because a knowledge of quantum theory is required at low temperatures. However, the approximations do not affect the calculated results at least in the case of the model with evaporation and condensation, because T is sufficiently high in the case.

Appendix 2-B. Derivation of Eq.(2.24)

Equation of bubble radius (eq.(2.24)) is derived here including effect of evaporation and condensation of vapor at bubble wall. The derivation starts from

the following two equations[7].

$$\frac{\partial \varphi}{\partial t} + \frac{1}{2}u^2 + \frac{p_L - p_\infty}{\rho_L} = 0 \quad (2. B1)$$

$$\nabla^2 \varphi - \frac{1}{c^2} \frac{\partial^2 \varphi}{\partial t^2} = 0 \quad (2. B2)$$

with the boundary condition[5].

$$\rho_L \left(\left(\frac{\partial \varphi}{\partial r} \right)_R - \dot{R} \right) = -\dot{m} \quad (2. B3)$$

where p_L is the pressure in the liquid, φ is the velocity potential of the liquid, u is the velocity of the liquid, r is the radius from the center of the bubble, and the other symbols have already appeared in the text. In eq.(2.B2), the compressibility of liquid is taken into account. The general solution of eq.(2.B2) is given by eq.(2.B4) under the spherical symmetry.

$$\varphi = -\frac{f(t - \frac{r}{c})}{r} - \frac{g(t + \frac{r}{c})}{r} \quad (2. B4)$$

where f and g are arbitrary functions. From eqs.(2.B3)(2.B4),

$$\frac{f'}{R} = c \left(\dot{R} - \frac{\dot{m}}{\rho_L} + \frac{\varphi(R)}{R} \right) + \frac{g'}{R} \quad (2. B5)$$

From eqs.(2.B4)(2.B5),

$$\left(\frac{\partial \varphi}{\partial t} \right)_R = -c \left(\dot{R} - \frac{\dot{m}}{\rho_L} + \frac{\varphi(R)}{R} \right) - \frac{2g'}{R} \quad (2. B6)$$

Inserting eqs.(2.B3)(2.B6) into eq.(2.B1) yields

$$-c \left(\dot{R} - \frac{\dot{m}}{\rho_L} + \frac{\varphi(R)}{R} \right) - \frac{2g'}{R} + \frac{1}{2} \left(\dot{R} - \frac{\dot{m}}{\rho_L} \right)^2 + \frac{p_B - p_\infty}{\rho_L} = 0 \quad (2. B7)$$

where p_B is the liquid pressure on the external side of the bubble wall. Multiplying eq.(2.B7) by R and differentiating by t yields eq.(2.B8).

$$\begin{aligned}
 0 &= -c \left(\dot{R}^2 + R\ddot{R} + \left(\frac{d\varphi}{dt} \right)_R \right) \\
 &\quad + \frac{c}{\rho_L} (\ddot{m}R + \dot{m}\dot{R}) \\
 &\quad - 2\frac{dg'}{dt} + \frac{1}{2}\dot{R} \left(\dot{R} - \frac{\dot{m}}{\rho_L} \right)^2 + R \left(\dot{R} - \frac{\dot{m}}{\rho_L} \right) \left(\ddot{R} - \frac{\ddot{m}}{\rho_L} \right) \\
 &\quad + \frac{R}{\rho_L} \frac{dp_B}{dt} + \frac{\dot{R}}{\rho_L} (p_B - p_\infty)
 \end{aligned} \tag{2.B8}$$

From eqs.(2.B1)(2.B3),

$$\begin{aligned}
 &\left(\frac{d\varphi}{dt} \right)_R \\
 &= \frac{\partial\varphi}{\partial t} + \frac{\partial\varphi}{\partial r} \frac{dr}{dt} \\
 &= -\frac{1}{2} \left(\dot{R} - \frac{\dot{m}}{\rho_L} \right)^2 - \frac{p_B - p_\infty}{\rho_L} + \left(\dot{R} - \frac{\dot{m}}{\rho_L} \right) \dot{R}
 \end{aligned} \tag{2.B9}$$

When the incident field is a plane wave with angular frequency ω and pressure amplitude A [6],

$$2g'' = -\frac{c}{\rho_L} A \sin \omega t \tag{2.B10}$$

Inserting eqs.(2.B9)(2.B10) into eq.(2.B8) yields the equation of bubble radius eq.(2.24) in the text, in which $-A \sin \omega t$ is replaced by p_s (In eq.(2.24), $p_s(t + \frac{R}{c})$ is employed, considering the size of the bubble(R) under the assumption that p_s is spherically symmetric).

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Chapter 3

Effect of Thermal Conduction

Abstract

An advanced model of bubble dynamics is constructed, including effect of thermal conduction inside a bubble. Numerical calculations are performed under a condition of SBSL and that of non-light-emission. The results reveal that the effect of thermal conduction is considerable. The calculated results fit with the experimental data of radius-time curve much more satisfactorily than those by a model without thermal conduction. It is clarified that the effect of thermal conduction stabilizes bubble oscillations. It is also clarified that a bubble transduces the energy of the acoustic wave into heat. Connection with sonoluminescence is also discussed.

3.1 Introduction

The model constructed in chapter2 is incomplete because effect of thermal conduction due to the temperature gradient inside a bubble is neglected. In the present chapter, an advanced model is constructed including the effect.

In section3.2, the model constructed in chapter2 is modified in a few points, in which effect of the thermal conduction is still neglected. In section3.3, effect of the thermal conduction inside a bubble is added to the model described in section3.2. In section3.4, numerical results are given under an experimental condition of SBSL and that of non-light-emission[1]. This is the first calculation of bubble dynamics under a SBSL condition taking into account both effect of thermal conduction and that of evaporation and condensation of water vapor.

3.2 A Model without Thermal Conduction

In this section, the model constructed in chapter2 is modified in three points. One is on the liquid viscosity(μ). In the present chapter, pressure (p_B) dependence of μ is taken into account by eq.(3.1)[2].

$$\mu = A \exp(B \cdot p_B) \quad (3.1)$$

where A and B are constants. In this calculation, $A = 1.0019 \times 10^{-3} (Pa \cdot s)$ and $B = 7 \times 10^{-10} (Pa^{-1})$ are employed for water at $20^\circ C$.

Another is on the van der Waals constants(a and b). In the present chapter, the van der Waals constants are calculated by eqs.(3.2)(3.3)[3] instead

of eqs.(2.6)(2.7).

$$a = a_{air} \left(\frac{n_{air}}{n_t} \right)^2 + 2a_{air-H_2O} \left(\frac{n_{air}}{n_t} \right) \left(\frac{n_{H_2O}}{n_t} \right) + a_{H_2O} \left(\frac{n_{H_2O}}{n_t} \right)^2 \quad (3.2)$$

$$b = b_{air} \left(\frac{n_{air}}{n_t} \right)^2 + 2b_{air-H_2O} \left(\frac{n_{air}}{n_t} \right) \left(\frac{n_{H_2O}}{n_t} \right) + b_{H_2O} \left(\frac{n_{H_2O}}{n_t} \right)^2 \quad (3.3)$$

where a_{air} and b_{air} (a_{H_2O} and b_{H_2O}) are the van der Waals constants of air(water vapor), $a_{air-H_2O} = \sqrt{a_{air}a_{H_2O}}$, $\sqrt[3]{b_{air-H_2O}} = \frac{1}{2} (\sqrt[3]{b_{air}} + \sqrt[3]{b_{H_2O}})$.

The values of a_{air} , a_{H_2O} , b_{air} , and b_{H_2O} are described in chapter2.

The other is on the energy carried by a diffusing air molecules(e_{air}). In the present chapter, diffusion of air from the surrounding liquid into a bubble is also taken into account. e_{air} is given by eq.(3.4).

$$e_{air} = \frac{1}{N_A} \int_0^{T''} C_{V,air}(T') dT' \quad (3.4)$$

where $T'' = T_0$ when $\left. \frac{dm}{dt} \right|_{diff} \geq 0$ ($T'' = T$ when $\left. \frac{dm}{dt} \right|_{diff} \leq 0$).

However, the above three modifications do not affect at all the calculated results as compared with those by the previous model in chapter2.

Mach number(M) of the bubble wall relative to the instantaneous speed of sound in the bubble(c_g) is calculated by

$$M = \frac{|\dot{R}|}{c_g} \quad (3.5)$$

$$c_g = \sqrt{\frac{dp}{d\rho_g}} = \sqrt{\left(-\frac{R_g T}{(v-b)^2} + \frac{2a}{v^3} \right) \frac{dv}{d\rho_g}} \quad (3.6)$$

$$\frac{dv}{d\rho_g} = -\frac{v^2}{\left(M_{H_2O} \frac{n_{H_2O}}{n_t} + M_{air} \frac{n_{air}}{n_t} \right) \times 10^{-3}} \quad (3.7)$$

3.3 A Model with Thermal Conduction

The difference between this model and the modified model described in the previous section is the inclusion of the thermal conduction due to the temperature gradient inside a bubble in this model. In this model, the temperature jump(ΔT) at the bubble wall is calculated by eq.(3.8), which is derived from Boltzmann equation[4]. It is a well known fact in fluid dynamics that Euler's equations are no longer valid at around a phase boundary such as the bubble wall[4,5]. In order to employ Euler's equations in such a boundary layer, the temperature jump(ΔT) given by eq.(3.8) must be employed as a boundary condition[4].

$$\Delta T = -\frac{1}{2kn'}\sqrt{\frac{\pi m}{2kT}}\frac{2 - a'\alpha_e}{\alpha_e}\kappa\left.\frac{\partial T}{\partial r}\right|_{r=R} \quad (3.8)$$

where k is the Boltzmann constant in (J/K), n' is the number density of gas and vapor molecules in the bubble in (m^{-3}), m is the mean mass of a molecule in (kg), α_e is the thermal accommodation coefficient, a' is a constant($a' = 0.827$ [4]), and κ is the thermal conductivity of the gas in ($W/m \cdot K$). As a boundary condition, temperature at the bubble wall(T_B) is given by

$$T_B = T_0 + \Delta T \quad (3.9)$$

where T_0 is the liquid temperature (As in the previous model, the liquid temperature on the external side of the bubble wall is assumed to be constant(T_0) during bubble oscillations).

In this model, a boundary layer is assumed in the gas at the bubble

wall[6]. The thickness of the boundary layer is assumed to be $n\lambda$, where n is a constant and λ is the mean free path of a molecule in the bubble. The mean free path(λ) is calculated by eq.(3.10)[7].

$$\lambda = \frac{V}{\sqrt{2}\sigma' n_t} \quad (3.10)$$

where σ' is the cross section of a molecule in the bubble (In this calculation, $\sigma' = 0.4 \times 10^{-18}(m^2)$ is employed).

It is assumed that temperature in the boundary layer changes linearly with radius(r): from T at $r = R - n\lambda$ to T_B at $r = R$. Thus

$$\left. \frac{\partial T}{\partial r} \right|_{r=R} = \frac{T_B - T}{n\lambda} \quad (3.11)$$

Inserting eqs.(3.9)(3.11) into eq.(3.8), ΔT is calculated by eq.(3.8).

The thermal conductivity (κ) depends on temperature and density of the gas and vapor. The temperature dependence is assumed to be linear as eq.(3.12).

$$\kappa_0 = \alpha T + \beta \quad (W/m \cdot K) \quad (3.12)$$

where $_0$ denotes the value at low density, and $\alpha = 5.39 \times 10^{-5}(W/m \cdot K^2)$, $\beta = 0.0108(W/m \cdot K)$ for air ($\alpha = 9.98 \times 10^{-5}(W/m \cdot K^2)$, $\beta = -0.0119(W/m \cdot K)$ for water vapor)[8]. Thermal conductivity(κ_0) of the mixture(air and water vapor) is calculated by eq.(3.13).[8]

$$\kappa_{0,mix} = 0.5 \left(\left(\frac{n_{H_2O}}{n_t} \kappa_{0,H_2O} + \frac{n_{air}}{n_t} \kappa_{0,air} \right) + \left(\frac{n_{H_2O}}{n_t} \frac{1}{\kappa_{0,H_2O}} + \frac{n_{air}}{n_t} \frac{1}{\kappa_{0,air}} \right)^{-1} \right) \quad (3.13)$$

where $H_2O_{(air)}$ denotes the value of $H_2O_{(air)}$. The density dependence of thermal conductivity(κ) is calculated by eq.(3.14)[3].

$$\kappa = \frac{b}{v} \left(\frac{1}{y} + 1.2 + 0.755y \right) \kappa_{0,mix} \quad (3.14)$$

where

$$y = \left(\frac{b}{v} \right) + 0.6250 \left(\frac{b}{v} \right)^2 + 0.2869 \left(\frac{b}{v} \right)^3 + 0.115 \left(\frac{b}{v} \right)^4 \quad (3.15)$$

where b is the van der Waals constant, and v is the molar volume of the gas and vapor in the bubble.

The change of the internal energy of a bubble(ΔE) is expressed by

$$\begin{aligned} \Delta E(t) &= -p(t) \cdot \Delta V(t) + 4\pi R^2 \Delta t (\dot{m}_{eva} e_{eva} - \dot{m}_{con} e_{con}) \\ &\quad + 4\pi R^2 \Delta t \left. \frac{dm}{dt} \right|_{diff} e_{air} + 4\pi R^2 \Delta t \cdot \kappa \frac{\partial T}{\partial r} \end{aligned} \quad (3.16)$$

where the last term in the right hand side of eq.(3.16) is the energy change due to the thermal conduction. The energy carried by a condensing vapor molecule(e_{con}) is calculated by

$$e_{con} = \frac{1}{N_A} \int_0^{T_B} C_{V,H_2O}(T') dT' \quad (3.17)$$

The energy carried by an evaporating vapor molecule(e_{eva}) is calculated by the same equation with the previous model. The energy carried by a diffusing air molecule(e_{air}) is expressed by eq.(3.4) with $T'' = T_B$ for $\left. \frac{dm}{dt} \right|_{diff} \leq 0$ ($T'' = T_0$ for $\left. \frac{dm}{dt} \right|_{diff} \geq 0$).

The other points are completely the same with the model described in section3.2.

Table 3-1

Physical quantities employed in the calculations.

-(a)

Physical quantities of liquid water. T_0 is the liquid temperature, p_v^* is the saturated vapor pressure, c is the speed of sound, σ is the surface tension, μ is the viscosity, and ρ_L is the density of liquid water. p_B is the liquid pressure.

T_0	$20^\circ C$
$p_v^*(Pa)$	2.3381×10^3
$c(m/s)$	1483.0
$\sigma(N/m)$	7.275×10^{-2}
$\mu(Pa \cdot s)$	$A \exp(B \cdot p_B)$ $A = 1.0019 \times 10^{-3}(Pa \cdot s)$ $B = 7 \times 10^{-10}(Pa^{-1})$
$\rho_L(kg/m^3)$	9.982×10^2

Table 3-1-(b)

Physical quantities employed in the calculation. f_a and p_a is the frequency and the amplitude of the acoustic field, respectively ($p_s(t) = -p_a \sin(2\pi f_a t)$). R_0 is the initial bubble radius, and $n_{air,0}(n_{H_2O,0})$ is the initial number of air(water vapor) molecules in the bubble.

	case(1)	case(2)
acoustic field		
$f_a(kHz)$	26.5	(same)
$p_a(atm)$	1.275	1.000
bubble		
$R_0(\mu m)$	4.5	10.5
$n_{air,0}$	1.23822×10^{10}	1.351945×10^{11}
$n_{H_2O,0}$	2.20415×10^8	2.8012×10^9

3.4 Results and Discussions

Calculations are performed in two cases for each model: (1) a condition of the single-bubble sonoluminescence (SBSL), (2) a condition of non-light-emission. Physical quantities employed in the calculations are listed in Table3-1. The liquid temperature (T_0) is chosen to be 20°C in the calculations. The accommodation coefficient for evaporation or condensation (α_M) is assumed to be $\alpha_M = 0.04$ [9,10]. The thermal accommodation coefficient(α_e) in eq.(3.8) is assumed to be $\alpha_e = 1.0$ [9]. The air concentration in the liquid water at $r = \infty$ (c_0) is assumed to be 10% of the saturated air concentration at the ambient pressure(p_∞)[11,12].

$$c_0 = \frac{10^3 \rho_L N_A p_\infty}{M_{H_2O} K_B} \times 0.1 \quad (\text{m}^{-3}) \quad (3.18)$$

It should be noted that the effect of air diffusion is negligibly small at least in a few acoustic cycles concerned in this study(see chapter2). Thus in this study, the choice of the value c_0 never affect the calculation results. However, for a long time scale such as 1(s) , the value c_0 is expected to play an important role in bubble dynamics.

Calculations start from the time $t = 0(\mu\text{s})$ with the initial conditions that $R = R_0$, $\dot{R} = 0$, $T = T_0$, $p_B = p_\infty$, $\frac{dp_B}{dt} = 0$, $\dot{m} = \ddot{m} = 0$, $\frac{d\rho_g}{dt} = 0$, $p_s(0) = 0$, (and $T_B = T_0$ (in the model with thermal conduction)). The initial number of vapor molecules in the bubble (n_{H_2O}) listed in Table3-1-(b) is determined by the partial pressure of vapor in the bubble(p_v) at $t = 0(\mu\text{s})$

which equals the saturated vapor pressure (p_v^*) at the liquid temperature (T_0). The initial number of air molecules (n_{air}) is determined by the pressure in the bubble (p) which satisfies $p = p_\infty + \frac{2\sigma}{R_0}$, assuming equation of state of the ideal gas.

Fig.3-1 Calculated results by the model with TC ($n = 3$) for case(1) for three acoustic cycles.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time.

Fig.3-1-(b) The bubble radius(R) as a function of time.

Fig.3-1-(c) The temperature inside the bubble(T) as a function of time with logarithmic vertical axis.

Fig.3-1-(d) The number of molecules in the bubble as a function of time with logarithmic vertical axis. The line shows the total number of molecules (n_t), the dash-dotted line shows the number of vapor molecules (n_{H_2O}), and the dotted line shows the number of air molecules (n_{air}).

Fig.3-1-(e) The internal energy of the bubble(E) as a function of time with logarithmic vertical axis.

(A) A condition of SBSL (case(1))

Results of the calculation under a condition of SBSL(case(1)) are shown in Figs.3-1-(b,c,d,e) by the model with thermal conduction described in section 3.3 (hereafter it is called "the model with TC"). In the calculation shown in Figs.3-1, the constant n , which determines the thickness of the boundary layer at the bubble wall, is assumed to be $n = 3[6]$.

As is shown in Figs.3-1-(b,c,d,e), all the physical quantities of a bubble except n_{air} change with time periodically with the frequency of the acoustic field ($p_s(t)$) applied on the bubble(Fig.3-1-(a)) (n_{air} slightly decreases(almost constant)). In Fig.3-1-(b), the bubble radius(R) is shown as a function of time. In Fig.3-1-(c), the temperature inside the bubble(T) is shown as a function of time. At the slow expansion phase in a bubble oscillation, the temperature inside the bubble(T) is almost identical to the liquid temperature(T_0). In other words, the slow expansion of a bubble is an isothermal process. On the other hand, at collapse of a bubble, the temperature(T) increases suddenly, followed by small oscillations due to the small bounces of bubble radius(see Fig.3-1-(b)). It should be noted that the vertical axis in Fig.3-1-(c) is in logarithmic scale. In Fig.3-1-(d), number of molecules in the bubble is shown as a function of time with logarithmic vertical axis. The line shows the total number of molecules ($n_t = n_{H_2O} + n_{air}$), the dash-dotted line shows the number of vapor molecules(n_{H_2O}), and the dotted line shows the number of air molecules in the bubble(n_{air}). It is seen from Fig.3-1-(d) that n_{H_2O}

changes drastically with time due to evaporation and condensation. At the slow expansion phase in a bubble oscillation, n_{H_2O} increases drastically by evaporation because the partial pressure of water vapor in the bubble (p_v) decreases considerably. On the other hand, at collapse of a bubble, n_{H_2O} decreases drastically by condensation because p_v increases significantly. The number of air molecules (n_{air}) remains almost constant for a few acoustic cycles concerned here. In Fig.3-1-(e), the internal energy of the bubble (E) is shown as a function of time with the logarithmic vertical axis. At the expansion phase in a bubble oscillation, the internal energy increases because evaporating vapor molecules carry their own energy into the bubble and heat flows from the surrounding liquid (temperature T_0) into the bubble (temperature $T \leq T_0$) by thermal conduction. (At the expansion phase, pV work reduces the internal energy. However, the contribution of $-p\Delta V$ on ΔE is smaller than the other terms in eq.(3.16) because the pressure inside the bubble (p) at the slow expansion phase is extremely low.) At the beginning of the first collapse in a bubble oscillation, the internal energy (E) decreases because condensing vapor molecules carry their own energy from the bubble into the surrounding liquid and heat flows from the bubble (temperature $T \geq T_0$) to the surrounding liquid (temperature T_0). However, at the strongest collapse, the internal energy increases drastically due to large pV work by the surrounding liquid. It is followed by a sudden decrease of the internal energy by thermal conduction. This is seen in Fig.3-1-(e) as a strong and short

pulse. After the strong pulse, the internal energy is reduced to the initial value by thermal conduction, though small oscillations of E are seen due to the oscillations of the bubble radius.

Fig. 4-3 Computed curve of total internal energy E as a function of time for a bubble of radius $R_0 = 1.0 \mu\text{m}$ and initial internal energy $E_0 = 0.5 \text{ J}$. The curve shows the effect of thermal conduction. The initial energy is $E_0 = 0.5 \text{ J}$ and the initial radius is $R_0 = 1.0 \mu\text{m}$. The curve shows the effect of thermal conduction. The initial energy is $E_0 = 0.5 \text{ J}$ and the initial radius is $R_0 = 1.0 \mu\text{m}$.

Fig.3-2 Contribution of each term in eq.(3.16) in integrated form for case(1) as a function of time for the first acoustic cycle($0 \leq t \leq 38(\mu s)$). The dotted line shows the contribution of pV work(W_1). The dash-dotted line shows the contribution of the energy flow accompanied by evaporating and condensing vapor molecules(W_2). The dashed line shows the contribution of thermal conduction(W_3).

In Fig.3-2, contribution of each term in eq.(3.16) is shown in integrated form as a function of time for the first acoustic cycle($0 \leq t \leq 38(\mu s)$). The dotted line shows the contribution of pV work(W_1) on the change of the internal energy of a bubble(ΔE).

$$W_1(t) = - \int_0^t p(t') \cdot \Delta V(t') dt' \quad (3.19)$$

The dash-dotted line shows the contribution of the energy flow accompanied by evaporating and condensing vapor molecules (W_2).

$$W_2(t) = 4\pi \int_0^t R^2(t') (\dot{m}_{eva} e_{eva} - \dot{m}_{con} e_{con}) dt' \quad (3.20)$$

The dashed line shows the contribution of thermal conduction (W_3).

$$W_3(t) = 4\pi \int_0^t R^2(t') \kappa(t') \left. \frac{\partial T}{\partial r} \right|_{r=R} dt' \quad (3.21)$$

In eq.(3.16), the energy change(ΔE) is also brought by the energy flow accompanied by diffusing air molecules. However, its contribution is negligibly small[10]. The time profile of each contribution(W_i) is interpreted as follows. At the slow expansion phase($0 \leq t \leq 17(\mu s)$ in Fig.3-2) in a bubble oscillation, the internal energy(E) of a bubble increases due to the energy flow accompanied by evaporating vapor molecules(W_2) and that by thermal conduction(W_3). Thus W_2 and W_3 both increases at the phase($0 \leq t \leq 17(\mu s)$) in Fig.3-2. However, some energy is carried out of a bubble due to pV work at the slow expansion phase($0 \leq t \leq 17(\mu s)$). Thus W_1 decreases at the phase in Fig.3-2. Just after $t = 20(\mu s)$, a strong collapse

of a bubble takes place. The internal energy(E) suddenly increases by pV work as is seen in Fig.3-1-(e) as a strong pulse. Thus W_1 significantly increases at the strong collapse ($t \sim 20\mu s$) as is seen in Fig.3-2. On the other hand, some energy is carried out of a bubble by thermal conduction at the point. Thus W_3 decreases at the point($t \sim 20\mu s$) in Fig.3-2. At the collapse ($t \sim 20\mu s$), condensation of vapor molecules takes place because the internal pressure of a bubble increases significantly. Thus some energy is carried out of a bubble by the condensing vapor molecules. It is the reason of the decrease of W_2 at the point. At the end of the acoustic cycle($t = 38(\mu s)$), the internal energy(E) of a bubble returns to the initial value(at $t = 0(\mu s)$) as is seen in Fig.3-1-(e) for different acoustic cycles. Thus the sum of W_1, W_2 , and W_3 is zero at the point($t = 38(\mu s)$). (Strictly speaking, the contribution of the energy flow by diffusing air molecules should be added. However, its contribution is negligibly small). It means that a bubble obtains energy by pV work(W_1) and returns the same amount of energy to the surrounding liquid as heat(W_2 and W_3). In other words, a bubble transduces the acoustic energy (W_1) into heat(W_2 and W_3).

For comparison, calculated results by the model without thermal conduction described in section 3.2 are shown in Figs.3-3-(b,c) when a bubble is irradiated by the acoustic field shown in Fig.3-3-(a) (hereafter the model is called "the model without TC"). As is seen in Figs.3-3-(b,c), all the physical quantities of a bubble except n_{air} change with time periodically with the

frequency of the acoustic field($p_s(t)$) applied on the bubble(Fig.3-3-(a)). In Fig.3-3-(b), the bubble radius(R) is shown as a function of time. In Fig.3-3-(c), the temperature inside the bubble(T) is shown as a function of time with logarithmic vertical axis. It is seen from the figure that T differs from the liquid temperature(T_0) considerably even at the slow expansion phase in a bubble oscillation. Thus it is concluded that thermal conduction affects the time profile of the temperature in a bubble significantly(Fig.3-1-(c) and Fig.3-3-(c) are completely different!). In Fig.3-4-(a), comparison is given between the radius-time curve calculated by the model with TC ($n = 3$ (line) and $n = 7$ (dotted line)) and that calculated by the model without TC(dash-dotted line) for one acoustic cycle ($\sim 38\mu s$). The open circles are the experimental data by B.P.Barber and S.J.Putterman[1]. It can be seen from the figure that the line($n = 3$) and the dotted line($n = 7$) are almost identical. It means that at least the radius-time curve scarcely depends on the parameter n . The radius-time curve calculated by the model with TC(line) fits the experimental data(circles) more satisfactorily than that calculated by the model without TC(dash-dotted line).

In Table3-2-(a,b), the calculated quantities are listed both by the model with TC(both $n = 3$ and $n = 7$ cases) and by the model without TC. In Table3-2-(a), calculated quantities at the maximum bubble radius(R_{max}) are listed. As is seen in Table3-2-(a), temperature inside a bubble (T) is almost equal to the liquid temperature($T_0 = 293.15K$) in case of the model

with TC, while T is much lower than T_0 in case of the model without TC. For the parameter n , physical quantities slightly depend on it. It should be noted that in case $n \leq 2$, the small bounces of bubble radius after the strong collapse are completely disappeared (the radius remains constant with respect to time). The reason is that the pressure inside the bubble(p) is lowered even to negative values due to the van der Waals attractive force between molecules, which is caused by significant temperature decrease due to thermal conduction. It conflicts with the experimental data[1] shown in Fig.3-3-(b) by open circles. Thus, at least in this case, n must be larger than 2. For $n \geq 8$, the thickness of the boundary layer($n\lambda$) becomes larger than the bubble radius(R) at some part of a bubble oscillation. Thus, at least in this case, $3 \leq n \leq 7$ should hold. It means that the real quantities should lie between the calculated values by $n = 3$ and those by $n = 7$.

Fig.3-3 Calculated results by the model without TC for case(1) for three acoustic cycles.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time. The vertical axis is the same one with that in Fig.3-1-(a).

Fig.3-3-(b) The bubble radius(R) as a function of time.

Fig.3-3-(c) The temperature inside the bubble(T) as a function of time with logarithmic vertical axis.

Fig.3-4 Comparison between the bubble radius calculated by the model with TC($n = 3$ (line) and $n = 7$ (dotted line)) and that by the model without TC(dash-dotted line) for case(1) as a function of time for one acoustic cycle($\sim 38\mu\text{s}$). The open circles are the experimental data by B.P.Barber and S.J.Putterman[1].

Table 3-2

Calculated results for case(1). T is the temperature, p is the pressure, ρ_g is the density, and E is the internal energy of a bubble. n_t is the total number of molecules, and n_{H_2O} is the number of vapor molecules in the bubble. T_B is the temperature at the bubble wall. Listed values are those at 4th cycle of the bubble oscillation started at $t = 0(\mu s)$. The values at 4th cycle are completely the same with those at 3rd cycle(5th cycle) in case of the model with TC (without TC).

-(a)

Calculated results at the maximum bubble radius (R_{max}).

	Without thermal conduction	With thermal conduction	
		n=3	n=7
$R_{max}(\mu m)$	34.6	37.3	37.3
$T(K)$	271.29	292.65	291.56
$p(Pa)$	2093	2108	2113
$\rho_g(kg/m^3)$	1.801×10^{-2}	1.663×10^{-2}	1.674×10^{-2}
$E(J)$	1.07×10^{-9}	1.36×10^{-9}	1.36×10^{-9}
n_t	9.7×10^{10}	1.138×10^{11}	1.139×10^{11}
n_{H_2O}	8.5×10^{10}	1.014×10^{11}	1.015×10^{11}
$T_B(K)$	-	292.98	292.86

Table 3-2-(b)

Calculated results at collapse of a bubble. M_{max} is the maximum Mach number of the bubble wall relative to the instantaneous speed of sound in the bubble. $\dot{R}_{(|\dot{R}|_{max})}$ is the velocity of the bubble wall when $|\dot{R}|$ has the maximum value.

	Without thermal conduction	With thermal conduction	
		n=3	n=7
M_{max}	0.376	1.3190	1.0643
$\dot{R}_{(\dot{R} _{max})}(m/s)$	-481	-943	-910

However, as is listed in Table3-2-(b), the assumption of the spatial uniformity of pressure(p) inside a bubble is out of order at the strong collapse of a bubble in case of the model with TC because the Mach number(M) of the bubble wall relative to the speed of sound inside the bubble increases up to ~ 1 . That is why the calculated quantities at the minimum bubble radius are not listed in case(1). For more accurate study, Euler's equations should be numerically calculated inside a bubble at such the strong collapse. It is expected that shock waves are produced inside a bubble at the collapse as is calculated by a different model by C.C.Wu and P.H.Roberts[13]. Thus in reality, physical quantities such as temperature, pressure and density depend on the spatial point in a bubble at such the strong collapse in case of the model with TC. Calculations under a condition of softer bubble oscillations, in which the model works correctly even at collapses, are performed in the following subsection(B).

From Table3-2-(b), it is qualitatively concluded that a collapse in case of the model with TC is stronger than that in case of the model without TC. It is because pressure inside the bubble at the collapse in case of the model with TC is lower than that in case of the model without TC, which is because temperature inside the bubble is lowered by thermal conduction in case of the model with TC.

(B) A condition of non-light-emission (case(2))

Results of the calculation under a condition of non-light-emission(case(2))

are shown in Figs.3-5-(b,c,d,e) by the model with TC. In this calculation, the constant n is assumed to be $n = 3$ [6]. As is seen in Figs.3-5-(b,c,d,e), all the physical quantities of a bubble except n_{air} change with time periodically with the frequency of the acoustic field($p_s(t)$) applied on the bubble(Fig.3-5-(a)) (n_{air} slightly decreases(almost constant)). In Fig.3-5-(b), the bubble radius(R) is shown as a function of time. In Fig.3-5-(c), the temperature inside the bubble(T) is shown as a function of time. At the slow expansion phase in a bubble oscillation, the temperature(T) is almost equal to the liquid temperature(T_0) (isothermal process). In Fig.3-5-(d), number of molecules in the bubble is shown as a function of time with logarithmic vertical axis. The line shows the total number of molecules($n_t = n_{H_2O} + n_{air}$), the dash-dotted line shows the number of vapor molecules(n_{H_2O}), and the dotted line shows the number of air molecules (n_{air}) in the bubble. At the slow expansion phase in a bubble oscillation, n_{H_2O} increases considerably due to evaporation. At the collapse phase, n_{H_2O} decreases due to condensation. n_{air} remains almost constant in a few acoustic cycles shown in Fig.3-5-(d). In Fig.3-5-(e), the internal energy of the bubble(E) is shown as a function of time. The time profile of the internal energy(E) is interpreted in the same way as in case(1)(Fig.3-3-(e)).

Fig.3-5 Calculated results by the model with TC ($n = 3$) for case(2) for three acoustic cycles.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time. The vertical axis is the same one with that in Fig.3-1-(a).

Fig.3-5-(b) The bubble radius(R) as a function of time.

Fig.3-5-(c) The temperature inside the bubble(T) as a function of time.

Fig.3-5-(d) The number of molecules in the bubble as a function of time with logarithmic vertical axis. The line shows the total number of molecules (n_t), the dash-dotted line shows the number of vapor molecules (n_{H_2O}), and the dotted line shows the number of air molecules (n_{air}).

Fig.3-5-(e) The internal energy of the bubble(E) as a function of time.

In Fig.3-6, contribution of each term in eq.(3.16) is shown in integrated form as a function of time. The dotted line shows the contribution of pV work(W_1)(eq.(3.19)), the dash-dotted line shows that of the energy flow accompanied by evaporating and condensing vapor molecules (W_2)(eq.(3.20)), and the dashed line shows that of thermal conduction(W_3)(eq.(3.21)). The time profile of each contribution (W_i) in Fig.3-6 is interpreted in the same way with that in Fig.3-2(case(1)). It is concluded that a bubble transduces the acoustic energy into heat.

In Fig.3-7-(b,c), calculated results by the model without TC are shown when a bubble is irradiated by the acoustic field shown in Fig.3-7-(a). As is seen in Figs.3-7-(b,c), all the physical quantities of a bubble change with time semi-periodically, while those calculated by the model with TC change with accurate periodicity. Both the time profile of the bubble radius(Fig.3-7-(b)) and that of the bubble temperature(Fig.3-7-(c)) are completely different from those calculated by the model with TC (Figs.3-5-(b,c)). It is concluded that thermal conduction affects a bubble dynamics considerably. It is seen that the thermal conduction stabilizes bubble oscillations by comparing the results by the model with TC and those by the model without TC.

Fig.3-6 Contribution of each term in eq.(3.16) in integrated form for case(2) as a function of time for the first acoustic cycle ($0 \leq t \leq 38(\mu s)$). The dotted line shows the contribution of pV work(W_1). The dash-dotted line shows the contribution of the energy flow accompanied by evaporating and condensing vapor molecules (W_2). The dashed line shows the contribution of thermal conduction(W_3).

Fig.3-7 Calculated results by the model without TC for case(2) for four acoustic cycles.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time. The vertical axis is the same one with that in fig.3-1-(a).

Fig.3-7-(b) The bubble radius(R) as a function of time.

Fig.3-7-(c) The temperature inside the bubble(T) as a function of time.

In Fig.3-8-(a), direct comparison is given between the radius-time curve calculated by the model with TC(line($n = 3$)) and that by the model without TC(dash-dotted line). The open circles are the experimental data by B.P.Barber and S.J.Putterman[1]. It is seen from Fig.3-8-(a) that the results by the model with TC fit with the experimental data more satisfactorily than those by the model without TC, especially at small bounces of bubble radius. In Fig.3-8-(b), the boundary layer assumed in the calculation is shown as a function of time. The thickness of the layer is calculated by $n\lambda$ where λ is the mean free path. In Tables3-3-(a,b,c), the calculated results for case(2) are listed both by the model with TC($n = 3$) and by the model without TC. In Table3-3-(a), calculated quantities at the maximum bubble radius(R_{max}) are listed. As is seen in Table3-3-(a), at R_{max} , temperature inside the bubble (T) is almost equal to the liquid temperature($T_0 = 293.15K$) in case of the model with TC, while T is much lower than T_0 in case of the model without TC. In Table3-3-(b), calculated quantities at the minimum bubble radius(R_{min}) are listed. From Table3-3-(b), at R_{min} , T in case of the model with TC is much lower than T in case of the model without TC. It is because the internal energy of the bubble(E) is strongly reduced by thermal conduction in case of the model with TC. It is seen from Table3-3-(b) that the physical quantities at R_{min} are significantly altered by the effect of thermal conduction. In Table3-3-(c), calculated quantities at the strong collapse are listed. In contrast to the case(1), the Mach number(M) of the bubble wall relative to

the speed of sound inside the bubble is much less than 1. It means that the assumption of the spatial uniformity of pressure inside a bubble is a realistic one. In this case(2), the model works correctly even at the strong collapse, while it doesn't in case(1).

It is seen from Table 3-3-(c) that a collapse in case of the model with TC is stronger than that in case of the model without TC. It is interpreted as in case(1). In Fig. 3-8-(c), comparison is shown between pressure in the bubble in case of the model with TC and that in case of the model without TC. From Fig. 3-8-(c), it is seen that the pressure inside the bubble in case of the model with TC is lower than that in case of the model without TC at the beginning of the strong collapse ($t \sim 130\mu s$), which is the reason of stronger collapse in case of the model with TC.

Fig.3-8-(a) Comparison between the bubble radius calculated by the model with TC($n = 3$)(line) and that by the model without TC(dash-dotted line) for case(2) as a function of time for one acoustic cycle($\sim 38\mu\text{s}$). The open circles are the experimental data by B.P.Barber and S.J.Putterman[1].

Fig.3-8-(b) The boundary layer assumed in the calculation by the model with TC for case(2) for one acoustic cycle. The line shows the radius-time curve. The boundary layer is above the dotted line and below the line.

Fig.3-8-(c) Comparison between the pressure inside the bubble(p) by the model with TC($n = 3$)(line) and that by the model without TC (dash-dotted line) for case(2) as a function of time for one acoustic cycle($\sim 38\mu s$) with logarithmic vertical axis.

Table 3-3

Calculated results for case(2). Listed values are those at 4th cycle of the bubble oscillation started at $t = 0(\mu s)$. The values at 4th cycle by the model with TC are completely the same with those at 3rd cycle, while it does not hold for the results by the model without TC(see the text and Figs.3-7).

-(a)

Calculated results at the maximum bubble radius (R_{max}).

	Without thermal conduction	With thermal conduction ($n = 3$)
$R_{max}(\mu m)$	29.0	28.92
$T(K)$	229.28	292.94
$p(Pa)$	6.04×10^3	7.44×10^3
$\rho_g(kg/m^3)$	8.13×10^{-2}	7.94×10^{-2}
$E(J)$	1.63×10^{-9}	1.987×10^{-9}
n_t	1.941×10^{11}	1.864×10^{11}
n_{H_2O}	5.89×10^{10}	5.12×10^{10}
$T_B(K)$	-	293.06

Table 3-3-(b)

Calculated results at the minimum bubble radius (R_{min}).

	Without thermal conduction	With thermal conduction ($n = 3$)
$R_{min}(\mu m)$	5.85	1.79
$T(K)$	1322	440
$p(Pa)$	3.10×10^6	4.3×10^7
$\rho_g(kg/m^3)$	7.99	3×10^2
$E(J)$	7.204×10^{-9}	1.87×10^{-9}
n_t	1.419×10^{11}	1.470×10^{11}
n_{H_2O}	6.76×10^9	1.175×10^{10}
$T_B(K)$	-	376

Table 3-3-(c)

Calculated results at collapse of a bubble. T_{max} is the maximum temperature (In the model without thermal conduction, T_{max} coincides with the temperature at $R = R_{min}$.)

	Without thermal conduction	With thermal conduction ($n = 3$)
M_{max}	0.048	0.290
$\dot{R}(\dot{R} _{max})(m/s)$	-26	-1.1×10^2
T_{max}	-	493

In some studies of bubble dynamics[14], the partial pressure of water vapor (p_v) in a bubble is assumed to be always equal to the saturated vapor pressure (p_v^*). However, from Table 3-3-(b), it is seen that p_v is larger than p_v^* by a few orders of magnitude at R_{min} ($p_v = 3.4 \times 10^6$ (Pa), while $p_v^* = 2.3 \times 10^3$ (Pa)). Thus it is concluded by this calculation that p_v differs considerably from p_v^* especially at around R_{min} . At the slow expansion phase, p_v is nearly equal to p_v^* (for example, at R_{max} , $p_v = 2.04 \times 10^3$ (Pa), while $p_v^* = 2.34 \times 10^3$ (Pa)). The assumption($p_v = p_v^*$) made in some studies[13] is relatively a realistic one at the slow expansion phase.

3.5 Conclusion

A simple model of bubble dynamics is constructed in which effect of thermal conduction and effect of evaporation and condensation of water vapor are included. Numerical calculations are performed in two cases:(1) a condition of the single-bubble sonoluminescence(SBSL), (2) a condition of non-light-emission(in both cases, a single bubble is irradiated by ultrasonic wave.) In case(1), the assumption of the spatial uniformity of pressure in a bubble is no more realistic one at the strong collapse of the bubble, while it is relatively a good one in case(2). In order to study SBSL(case(1)), advanced model including spatial dependence of pressure is required. From the calculations in case(2), it is concluded that the effect of thermal conduction is considerable on bubble dynamics. The calculated results fit with the experimental data

of radius-time curve much more satisfactorily than those by a model without thermal conduction. It is concluded that the effect of thermal conduction stabilizes bubble oscillations. It is also concluded that a bubble transduces the energy of acoustic wave into heat. Calculated results show that pressure of water vapor (p_v) differs considerably from the saturated vapor pressure (p_v^*) especially at around R_{min} .

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Chapter 4

Variation of Liquid Temperature

Abstract

The liquid temperature at bubble wall ($T_{L,i}$) is numerically calculated, including effect of the latent heat of non-equilibrium evaporation and condensation at the bubble wall under a condition of the single-bubble sonoluminescence (SBSL) and that of non-light emission. It is concluded that $T_{L,i}$ increases to the same order of magnitude with that of the maximum temperature attained in the bubble at strong collapses. It is caused by the latent heat of intense vapor condensation and by the thermal conduction from the heated interior of the bubble to the surrounding liquid. The intense vapor condensation takes place at strong collapses because the pressure inside the bubble increases dramatically. It is concluded that the latent heat of the intense condensation should be taken into account in the calculations of $T_{L,i}$ at strong collapses, while it has been not in the previous studies of SBSL.

4.1 Introduction

In 1994, B.P.Barber et al.[1] reported on sensitivity of SBSL to experimental parameters. Bubble's size at stable condition in acoustic field depends on several experimental parameters such as the acoustic pressure amplitude and the liquid temperature. Bubble's size is determined by mass exchange of air between the interior of the bubble and its surroundings[1]. Rate of mass exchange depends on the liquid temperature at bubble wall. Thus we begin with calculations of liquid temperature at bubble wall as the first step of the prediction of bubble's size at stable condition. In this chapter, effect of variation of liquid temperature at bubble wall is newly included in the model of bubble dynamics constructed in section3.3.

Calculations of liquid temperature at bubble wall are also important in the following two points. One is the possibility of high-pressure solidification of the liquid near the bubble wall suggested by R.Hickling[2]. During the final stage of a collapse of a cavitation bubble, pressure of liquid near the bubble wall is in the order of 1 GPa. R.Hickling suggests that solidification of liquid takes place near the bubble wall at such a strong collapse by the very high pressure[2]. He also suggests that the liquid temperature dependence of SBSL[3] is explained by the solidification. However, in his analysis, effects of the latent heat of intense vapor condensation and the thermal conduction are neglected in the estimation of the liquid temperature near bubble wall at a strong collapse. (At a strong collapse, intense vapor condensation takes

place at the bubble wall because the pressure inside the bubble increases dramatically (see chapter 2 and 3.) In the present study, the above effects are taken into account, which affect the liquid temperature near bubble wall considerably at a strong collapse as is seen in section 4.3.

The other point is the possibility of chemical reactions in liquid during cavitation. K.S. Suslick et al. [4,5] reported that the gas-temperature inside a bubble is 5200 K and that the liquid-temperature outside a bubble is 1900 K at a strong collapse of a bubble from the experimental determination of the first-order rate coefficients of sonochemical ligand substitution as a function of metal carbonyl vapor pressure. In their experiments [4,5], alkane carbonyls (0.01 M) were irradiated with a collimated beam of ultrasound at 20 kHz, in the presence of excess triphenylphosphine. The above results mean that chemical reactions take place not only in gas-phase inside a bubble but also in liquid-phase outside a bubble. They theoretically estimated the thickness of the liquid layer heated and the lifetime of the heated layer to be $\sim 0.2 \mu\text{m}$ and $\sim 2 \mu\text{s}$ respectively by a simple conduction model [4,5]. However, in their analysis [4,5], the latent heat of the intense vapor condensation is completely neglected. In the present study, it is taken into account, which affects the liquid temperature near bubble wall considerably at a strong collapse as is seen in section 4.3.

It should be noted that the liquid temperature near bubble wall has already been calculated in some theoretical studies of SBSL [6-8]. However, in

the studies[6-8], the latent heat of the intense vapor condensation is completely neglected, which affect the liquid temperature at bubble wall considerably at a strong collapse as is seen in section 4.3.

Some researchers[9-12] have already constructed models of bubble dynamics including effect of the latent heat of evaporation and condensation. However, the new model constructed in this paper differs from the previous models[9-12] in many points. In ref.[9], it is assumed that the vapor pressure inside a bubble(p_v) is at the equilibrium vapor pressure (p_v^*) at the temperature of the bubble wall, while in the present study non-equilibrium effect of evaporation and condensation is taken into account by the kinetic theory(see chapter 2 and 3). The non-equilibrium effect of evaporation and condensation is considerable on bubble dynamics and on the vapor pressure inside a bubble(p_v) as is clarified by S.Fujikawa and T.Akamatsu[10] and by the author(see chapter 2 and 3). In ref.[11], it is assumed that the temperature profile in the liquid near bubble wall is parabolic. The assumption is valid only as long as the bubble contents temperature increases monotonically[11]. In the present model, the temperature profile is assumed to be exponential (eqs.(4.6)(4.7) below) and the model works even when the bubble contents temperature decreases. However, for more accurate study, the heat conduction equation should be solved directly without assuming a profile of liquid temperature. In refs.[10,12], the formulations of bubble dynamics are more accurate than the present one. However, in refs.[10,12], numerical calcula-

tions for SL are not performed. In the present study, numerical calculations are performed under a condition of SBSL and that of non-light emission including the effect of the latent heat of non-equilibrium evaporation and condensation for the first time.

In section 4.2, the new model is described. In section 4.3, calculated results are shown in the two cases; a condition of SBSL and that of non-light emission. The comparisons are also shown between the calculated results and the experimental data [13] of radius-time curves.

4.2 Model

In this chapter, effect of variation of liquid-temperature is newly included in the previous model described in section 3.3. Followings are the description of the newly included effect: variation of liquid temperature at bubble wall.

Continuity of energy flux at the bubble wall is given by

$$\kappa_L \left. \frac{\partial T_L}{\partial r} \right|_{r=R} = \kappa \left. \frac{\partial T}{\partial r} \right|_{r=R} + \dot{m}L + (\dot{m}_{eva}e_{eva} - \dot{m}_{con}e_{con}) + \left. \frac{dm}{dt} \right|_{diff} (e_{air} - \Delta H_{air}) \quad (4.1)$$

where κ_L is the thermal conductivity of liquid water, $T_L(r)$ is the liquid temperature at radius r , L is the latent heat of evaporation or condensation, and ΔH_{air} is the heat of solution of air into water. κ_L , L and ΔH_{air} depend on the liquid temperature and the liquid pressure. The formulas of them are described in Appendix 4-A. In this model, $\left. \frac{\partial T_L}{\partial r} \right|_{r=R}$ is calculated by eq.(4.1).

The spatial distribution of the liquid temperature ($T_L = T_L(r)$) should

satisfy the following boundary conditions.

$$T_L(R) = T_{L,i} \quad (4.2)$$

$$\left. \frac{\partial T_L(r)}{\partial r} \right|_{r=R} = \left. \frac{\partial T_L}{\partial r} \right|_{r=R} \quad (4.3)$$

$$T_L(r \rightarrow \infty) = T_\infty \quad (4.4)$$

$$\left. \frac{\partial T_L(r)}{\partial r} \right|_{r \rightarrow \infty} = 0 \quad (4.5)$$

where T_∞ is the ambient liquid temperature. In the present model, the temperature profile in the liquid ($T_L = T_L(r)$) is assumed to be exponential.

When $(T_{L,i} - T_\infty) \left. \frac{\partial T_L}{\partial r} \right|_{r=R} < 0$

$$T_L(r) = (T_{L,i} - T_\infty) \exp \left(- \frac{\left. \frac{\partial T_L}{\partial r} \right|_{r=R}}{(T_\infty - T_{L,i})} (r - R) \right) + T_\infty \quad (4.6)$$

When $(T_{L,i} - T_\infty) \left. \frac{\partial T_L}{\partial r} \right|_{r=R} > 0$

$$T_L = A \exp(-B(r - C)^2) + T_\infty \quad (4.7)$$

where

$$A = (T_{L,i} - T_\infty) \exp(Be_1^2)$$

$$B = \frac{\left. \frac{\partial T_L}{\partial r} \right|_{r=R}}{2(T_{L,i} - T_\infty)} \frac{1}{e_1}$$

$$C = R + e_1$$

$$e_1 = e_0 \left| \frac{T_{L,i} - T_B}{\left. \frac{\partial T_L}{\partial r} \right|_{r=R}} \right|$$

where e_0 is a parameter. Both eqs.(4.6) and (4.7) satisfy the boundary conditions (eqs.(4.2)-(4.5)).

In the present model, a boundary layer is assumed in liquid phase near a bubble. The thickness of the layer (δ_L) is assumed as eqs.(4.8) and (4.9).

When $(T_{L,i} - T_\infty) \frac{\partial T_L}{\partial r} \Big|_{r=R} < 0$

$$\delta_L = \frac{T_\infty - T_{L,i}}{\frac{\partial T_L}{\partial r} \Big|_{r=R}} \quad (4.8)$$

When $(T_{L,i} - T_\infty) \frac{\partial T_L}{\partial r} \Big|_{r=R} > 0$

$$\delta_L = \frac{1}{\sqrt{B}} + e_1 \quad (4.9)$$

Variation of the liquid temperature at bubble wall ($T_{L,i}$) is calculated by

$$T_{L,i}(t + \Delta t) = T_{L,i}(t) + \frac{4\pi R^2 \Delta t \cdot j_1 - 4\pi(R + \delta_L)^2 \Delta t \cdot j_2}{\frac{4}{3}\pi \left((R + \delta_L)^3 - R^3 \right) \rho_{L,i} \cdot c_p} \quad (4.10)$$

where $j_1(j_2)$ is the energy flux at $r = R(r = R + \delta_L)$ per unit area and unit time, and c_p is the specific heat of liquid water at constant pressure. j_1 and j_2 are calculated by

$$j_1 = -\kappa_L \Big|_{r=R} \frac{\partial T_L}{\partial r} \Big|_{r=R} \quad (4.11)$$

$$j_2 = -\kappa_L \Big|_{r=R+\delta_L} \frac{\partial T_L}{\partial r} \Big|_{r=R+\delta_L} \quad (4.12)$$

Physical quantities of liquid depend on the liquid temperature (T_L) and the liquid pressure (p_L). Formulas of the quantities employed in the calculations are described in Appendix 4-A.

According to the variation of liquid temperature at bubble wall, the previous model described in section 3.3 is modified in two points. One is on the

equation of bubble radius(R).

$$\begin{aligned}
 & \left(1 - \frac{\dot{R}}{c_\infty} + \frac{\dot{m}}{c_\infty \rho_{L,i}}\right) R \ddot{R} + \frac{3}{2} \dot{R}^2 \left(1 - \frac{\dot{R}}{3c_\infty} + \frac{2\dot{m}}{3c_\infty \rho_{L,i}}\right) \\
 &= \frac{1}{\rho_{L,\infty}} \left(1 + \frac{\dot{R}}{c_\infty}\right) \left(p_B - p_s\left(t + \frac{R}{c_\infty}\right) - p_\infty\right) \\
 &+ \frac{\ddot{m}R}{\rho_{L,i}} \left(1 - \frac{\dot{R}}{c_\infty} + \frac{\dot{m}}{c_\infty \rho_{L,i}}\right) \\
 &+ \frac{\dot{m}}{\rho_{L,i}} \left(\dot{R} + \frac{\dot{m}}{2\rho_{L,i}} + \frac{\dot{m}\dot{R}}{2c_\infty \rho_{L,i}} - \frac{R}{\rho_{L,i}} \frac{d\rho_{L,i}}{dt} - \frac{\dot{m}R}{c_\infty \rho_{L,i}^2} \frac{d\rho_{L,i}}{dt}\right) \\
 &+ \frac{R}{c_\infty \rho_{L,\infty}} \frac{dp_B}{dt}
 \end{aligned} \tag{4.13}$$

where $\cdot$ denotes the time derivative ($\frac{d}{dt}$), c_∞ is the sound speed in the liquid at infinity, $\rho_{L,i}$ ($\rho_{L,\infty}$) is the liquid density at the bubble wall(at infinity), $p_B(t)$ is the liquid pressure on the external side of the bubble wall, $p_s(t)$ is a nonconstant ambient pressure component such as a sound field, and p_∞ is the undisturbed pressure. Derivation of eq.(4.13) is described in Appendix4-B.

The other is on the liquid pressure at bubble wall(p_B).

$$p_B(t) = p(t) - \frac{2\sigma}{R} - \frac{4\mu}{R} \left(\dot{R} - \frac{\dot{m}}{\rho_{L,i}}\right) - \dot{m}^2 \left(\frac{1}{\rho_{L,i}} - \frac{1}{\rho_g}\right) \tag{4.14}$$

where σ is the surface tension, μ is the liquid viscosity, and ρ_g is the density inside the bubble.

4.3 Results and Discussions

Calculations are performed in two cases: (1) a condition of the single-bubble sonoluminescence(SBSL), (2) a condition of non-light-emission. Both conditions are listed in Table 3-1-(b). The ambient liquid temperature(T_∞) and

the ambient pressure (p_∞) are chosen to be 20°C and 1 atm, respectively. At the condition, the speed of sound in liquid water (c_∞) and the liquid density ($\rho_{L,\infty}$) are $1483.0(\text{m/s})$ and $9.982 \times 10^2(\text{kg/m}^3)$, respectively. The specific heat of liquid water at constant pressure (c_p) is $c_p = 4.2(\text{J/g} \cdot \text{K})$. The accommodation coefficient for evaporation and condensation (α_M) is assumed to be $\alpha_M = 0.4$ [14,15]. It should be noted that in the previous chapters, α_M is assumed to be $\alpha_M = 0.04$. (Recently, S.Fujikawa and M.Maerefat[14] and M.Matsumoto[15] recommend the value $\alpha_M = 0.4$). $n = 3$ is assumed (see chapter 3), which determines the thickness of the thermal boundary layer inside a bubble ($n\lambda$). α_e in eq.(3.8) is assumed to be $\alpha_e = 1.0$ [10]. The parameter e_0 in eq.(4.7) is assumed to be $e_0 = 1 \times 10^{-3}$. The parameter (e_0) is determined as the calculated result fits well with the experimental data of radius-time curve[13] in case(1). (The radius-time curve at the rebound of a bubble after the strongest collapse strongly depend on the value e_0 .)

Calculations start from the time $t = 0(\mu\text{s})$ with the initial conditions that $R = R_0$, $\dot{R} = 0$, $T = T_B = T_{L,i} = T_\infty$, $p_B = p_\infty$, $\frac{dp_B}{dt} = 0$, $\dot{m} = \ddot{m} = 0$, $\frac{d\rho_g}{dt} = 0$, $p_s(0) = 0$. The initial number of vapor molecules ($n_{H_2O,0}$) and that of air molecules ($n_{air,0}$) in a bubble are listed in Table 3-1-(b) for both cases.

(A) A condition of SBSL (case(1))

Results of the calculation under a condition of SBSL (case(1)) are shown in Figs.4-1-(b~f) for three acoustic cycles. The time axes (the horizontal axes) in Figs.4-1-(a~f) are the same. All the physical quantities of a bubble

except n_{air} change with time periodically with the frequency of the acoustic field ($p_s(t)$) applied on the bubble (Fig.4-1-(a)) (n_{air} slightly decreases (almost constant)). In a steady condition, n_{air} should also change periodically with time. More accurate calculations of $n_{air}(t)$ is being prepared by the author.

Fig.4-1. Calculated variation of liquid temperature T_L (°C) versus time t (ms) for the acoustic field applied on the bubble. (a) The period of the acoustic field is 100 ms. (b) The period of the acoustic field is 200 ms. (c) The period of the acoustic field is 300 ms. (d) The period of the acoustic field is 400 ms. (e) The period of the acoustic field is 500 ms. (f) The period of the acoustic field is 600 ms. (g) The period of the acoustic field is 700 ms. (h) The period of the acoustic field is 800 ms. (i) The period of the acoustic field is 900 ms. (j) The period of the acoustic field is 1000 ms.

Fig.4-1 Calculated results for case(1) for three acoustic cycles. The time axes (the horizontal axes) are the same.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time.

Fig.4-1-(b) The bubble radius(R) as a function of time.

Fig.4-1-(c) The temperature inside the bubble(T) as a function of time with logarithmic vertical axis.

Fig.4-1-(d) The liquid-temperature at the bubble wall ($T_{L,i}$) as a function of time. The vertical axis is the same with that in Fig.4-1-(c).

Fig.4-1-(e) The number of molecules in the bubble as a function of time with logarithmic vertical axis. The line shows the total number of molecules (n_t), the dash-dotted line shows the number of vapor molecules (n_{H_2O}), and the dotted line shows the number of air molecules (n_{air}).

Fig.4-1-(f) The internal energy of the bubble(E) as a function of time with logarithmic vertical axis.

In Fig.4-1-(b), the bubble radius (R) is shown as a function of time. In Fig.4-1-(c), the temperature inside the bubble (T) is shown as a function of time with logarithmic vertical axis. Qualitative discussions on T as a function of time are given in chapter3. In Fig.4-1-(d), the liquid-temperature at the bubble wall ($T_{L,i}$) is shown as a function of time. The temperature axis (the vertical axis) is the same with that in Fig.4-1-(c). It is concluded from Fig.4-1-(d) that $T_{L,i}$ is almost identical to T_{∞} during bubble oscillations except at strong collapses. At strong collapses, $T_{L,i}$ increases to the same order of magnitude with that of the maximum temperature attained in the bubble. It is caused by the latent heat of intense condensation and by the thermal conduction from the heated interior of the bubble to the surrounding liquid. At strong collapses, intense vapor condensation takes place at bubble wall because the pressure inside the bubble increases dramatically. It is concluded that the latent heat of the intense vapor condensation should be taken into account in the calculations of the liquid temperature at bubble wall ($T_{L,i}$) at strong collapses, while it has been not in the previous studies of SBSL [2,6-8]. The calculated result means that chemical reactions take place not only inside a bubble (gas-phase) but also outside a bubble (liquid-phase). Strictly speaking, the boundary between gas-phase and liquid-phase may be ambiguous at the final stage of the strong collapse because the density of gas is very high. The "liquid" here means that actually liquid at least before the final stage of the strong collapse. The thickness and the life time of the liquid-

layer heated are estimated crudely by the present model to be in the order of $0.01 \sim 0.1 \mu m$ and $0.01 \sim 0.1 \mu s$, respectively. The pressure of the liquid-layer is estimated by the present model to vary in the range from $10^6 (Pa)$ to $10^9 (Pa)$ in the life time. (The pressure increases at first up to $10^9 (Pa)$, and decreases to $10^6 (Pa)$). The result supports the experimental conclusion by K.S.Suslick et al.[4,5] that liquid-phase reaction zone exists near bubble wall. The thickness estimated by the present model is comparable to or one order less than that estimated theoretically by K.S.Suslick ($\sim 0.2 \mu m$)[4,5]. However, the life time estimated by the present model is one or two orders of magnitude shorter than that estimated by K.S.Suslick ($\sim 2 \mu s$)[4,5].

Though the liquid temperature at bubble wall ($T_{L,i}$) increases considerably at strong collapses, the possibility of solidification suggested by R.Hickling[2] can not be excluded. Because the thickness of the heated layer is so small that low temperature region still exists outside the layer under very high pressure in the order of 1GPa.

In Fig.4-1-(e), the number of molecules in the bubble is shown as a function of time with logarithmic vertical axis. The line shows the total number of molecules ($n_t = n_{H_2O} + n_{air}$), the dash-dotted line shows the number of vapor molecules (n_{H_2O}), and the dotted line shows the number of air molecules in the bubble (n_{air}). It is seen that n_{H_2O} decreases dramatically by the intense condensation at the strong collapses.

In Fig.4-1-(f), the internal energy of the bubble (E) is shown as a function

of time with logarithmic vertical axis. Qualitative discussions on E as a function of time are given in chapter 3.

In Fig. 4-2, comparison is given between the calculated result and the experimental data [13] of radius-time curve for one acoustic cycle. The calculated result fits well with the experimental data (Strictly speaking, one fitting parameter (e_0) exists). However, in case (1), the present model no longer works at the strong collapses because the assumption of the spatial uniformity of pressure inside the bubble is no longer valid at the strong collapses as is seen in Table 4-1. The assumption is valid only when the Mach number of the bubble wall relative to the instantaneous speed of sound inside the bubble is much less than 1 ($M \ll 1$). In case (2), the assumption holds relatively well even at strong collapses as is seen in Table 4-1.

Fig.4-2 Comparison between the calculated result (line) and the experimental data[13] (open circles) of radius-time curve for one acoustic cycle for case (1).

Table 4-1

Calculated results at the strongest collapse of a bubble for both case(1) and case(2). M_{max} is the maximum Mach number of the bubble wall relative to the instantaneous speed of sound in the bubble. $\dot{R}_{(|\dot{R}|_{max})}$ is the velocity of the bubble wall when $|\dot{R}|$ has the maximum value.

	case(1)	case(2)
M_{max}	1.53	0.32
$\dot{R}_{(\dot{R} _{max})}(m/s)$	-1.49×10^3	-1.31×10^2

(B) A condition of non-light-emission (case(2))

Results of the calculation under a condition of non-light-emission (case(2)) are shown in Figs.4-3-(b~g) for three acoustic cycles. The time axes (the horizontal axes) in Figs.4-3-(a~g) are the same. (Additionally, the time axes in Figs.4-3 are the same with those in Figs.4-1.) All the physical quantities of a bubble except n_{air} change with time periodically with the frequency of the acoustic field($p_s(t)$) applied on the bubble (Fig.4-3-(a))(n_{air} slightly decreases(almost constant)). The pressure axis (the vertical axis) in Fig.4-3-(a) is the same with that in Fig.4-1-(a).

In Fig.4-3-(b), the bubble radius (R) is shown as a function of time. In Fig.4-3-(c), the temperature inside the bubble (T) is shown as a function of time with linear vertical axis. In Fig.4-3-(d), the liquid-temperature at the bubble wall($T_{L,i}$) is shown as a function of time. The temperature axis (the vertical axis) is the same with that in Fig.4-3-(c). It is concluded from Fig.4-3-(d) that $T_{L,i}$ is almost identical to T_∞ during bubble oscillations except at strong collapses as in case(1). At strong collapses, $T_{L,i}$ increases considerably due to the latent heat of intense condensation and the thermal conduction from the heated interior of the bubble to the surrounding liquid as in case(1). As in case(1), intense vapor condensation takes place at bubble wall at strong collapses as is seen in Fig.4-3-(e). It is concluded that the latent heat of the intense vapor condensation should be taken into account in the calculations of the liquid temperature at bubble wall ($T_{L,i}$) at strong collapses as in case(1).

Both the thickness and the life time of the liquid layer heated are crudely estimated by the present model to be in the same order of magnitude with those in case(1). As in case(1), existence of the heated liquid-layer near the bubble wall at strong collapses is confirmed theoretically by the present calculation. In this case, the pressure of the liquid-layer heated is estimated to be in the order of $10^7 \sim 10^8 (Pa)$.

In Fig.4-3-(f), the internal energy of the bubble(E) is shown as a function of time with the linear vertical axis. In Fig.4-3-(g), the pressure inside the bubble(p) is shown as a function of time with logarithmic vertical axis. The pressure (p) oscillates according to the oscillations of bubble radius (Fig.4-3-(b)). At strong collapses, the pressure inside the bubble (p) increases to the order of $10^8 (Pa)$ in this case.

In Fig.4-4, the comparison is given between the calculated result and the experimental data[13] of radius-time curve for one acoustic cycle. The calculated result fits well with the experimental data. (In this case, no fitting parameter exists because e_0 is determined in case(1)).

Fig.4-3 Calculated results for case(2) for three acoustic cycles. The time axes (the horizontal axes) are the same with those in Figs.4-1.

-(a) The pressure of the acoustic field ($p_s(t)$) employed in the calculation as a function of time. The vertical axis is the same with that in Fig.4-1-(a).

Fig.4-3-(b) The bubble radius(R) as a function of time.

Fig.4-3-(c) The temperature inside the bubble(T) as a function of time with linear vertical axis.

Fig.4-3-(d) The liquid-temperature at the bubble wall ($T_{L,i}$) as a function of time. The vertical axis is the same with that in Fig.4-3-(c).

Fig.4-3-(e) The number of molecules in the bubble as a function of time with logarithmic vertical axis. The line shows the total number of molecules (n_t), the dash-dotted line shows the number of vapor molecules (n_{H_2O}), and the dotted line shows the number of air molecules (n_{air}).

Fig.4-3-(f) The internal energy of the bubble(E) as a function of time with linear vertical axis.

Fig.4-3-(g) The pressure inside the bubble (p) as a function of time with logarithmic vertical axis.

Fig.4-4 Comparison between the calculated result (line) and the experimental data[13] (open circles) of radius-time curve for one acoustic cycle for case (2).

4.4 Conclusion

The liquid temperature at bubble wall ($T_{L,i}$) is numerically calculated, including effect of the latent heat of non-equilibrium evaporation and condensation at the bubble wall under a condition of the single-bubble sonoluminescence (SBSL) and that of non-light emission. In order to calculate $T_{L,i}$, a simple new model of bubble dynamics is constructed including effect of thermal conduction both inside and outside a bubble and that of non-equilibrium evaporation and condensation of water vapor at bubble wall. Calculated results fit well with the experimental data of radius-time curves. The results reveal that the liquid temperature at bubble wall ($T_{L,i}$) is almost identical to the ambient liquid temperature during bubble oscillations except at strong collapses. At strong collapses, $T_{L,i}$ increases to the same order of magnitude with that of the maximum temperature attained in the bubble. It is caused by the latent heat of intense vapor condensation and by the thermal conduction from the heated interior of the bubble to the surrounding liquid. At strong collapses, intense vapor condensation takes place because the pressure inside the bubble increases dramatically. It is concluded that the latent heat of the intense vapor condensation should be taken into account in the calculations of the liquid temperature near bubble wall at strong collapses, while it has been not in the previous studies of SBSL. The calculated result also means that chemical reactions take place not only inside a bubble (gas-phase) but also outside a bubble (liquid-phase).

Appendix 4-A Physical Quantities of Liquid Water

Physical quantities of liquid water depend on the temperature (T_L) and the pressure (p_L). In the present calculations, following physical quantities of liquid water are calculated as a function of T_L and p_L ; density (ρ_L), saturated vapor pressure (p_v^*), thermal conductivity (κ_L), latent heat of evaporation (L), viscosity (μ), surface tension (σ), Henry's constant of air (K_H), diffusion coefficient of air (D_{air}), heat of solution of air (ΔH_{air}), and saturated air concentration (c_s).

(A) Density (ρ_L)

The density of liquid water at 1 atm ($\rho_{L,0}$) is given in ref.[16] as a function of temperature (T_L) in the range $0^\circ C \leq T_L \leq 150^\circ C$. When $T_L > 150^\circ C$ ($T_L < 0^\circ C$), the value at $T_L = 150^\circ C$ ($T_L = 0^\circ C$) is employed in the present calculations.

The density of liquid water at pressure p_L is calculated by eq.(4.A1)[17].

$$\rho_L(p_L) = \rho_{L,0} (1 + n\beta_0 (p_L - p_0))^{\frac{1}{n}} \quad (4.A1)$$

where n and β_0 are functions of temperature (T_L), and p_0 is 1 atm ($\rho_{L,0}$ is the density at pressure p_0). n and β_0 are calculated as a function of temperature (T_L) by interpolating the experimental values[17] by Gregory-Newton formula[18].

However, eq.(4.A1) is valid in the range $9.8 \times 10^4 (Pa) \leq p_L \leq 1.176 \times 10^9 (Pa)$. When $p_L < 9.8 \times 10^4 (Pa)$ ($p_L > 1.176 \times 10^9 (Pa)$), the value (ρ_L)

at $p_L = 9.8 \times 10^4 (Pa)$ ($p_L = 1.176 \times 10^9 (Pa)$) is employed in the present calculations.

(B) Saturated vapor pressure (p_v^*)

The saturated vapor pressure of water (p_v^*) is given by eq.(4.A2) as a function of T_L in the range $258.15(K) \leq T_L \leq 647.3(K)$ [19].

$$p_v^* = 133.322 \times \exp \left(A' - \frac{B'}{T_L + C'} \right) \quad (4.A2)$$

where p_v^* is in (Pa), T_L is in (K), $A' = 18.3036$, $B' = 3816.44$, and $C' = -46.13$ [19].

(C) Thermal conductivity (κ_L)

Empirical formula of the thermal conductivity of liquid water (κ_L) is given in ref.[20] as a function of T_L , p_L , and p_v^* in the range $p_v^* \leq p_L \leq 5 \times 10^7 (Pa)$ and $273.15(K) \leq T_L \leq 623.15(K)$.

(D) Latent heat of evaporation (L)

The latent heat of evaporation of water (L) is given by eq.(4.A3) as a function of T_L in the range $273.15(K) \leq T_L \leq 646.63(K)$ [21].

$$L = 2.44281 \times 10^5 \left(673.43 - \frac{9}{5} (T - 273.15) \right)^{0.358} \quad (4.A3)$$

where L is in (J/kg) and T_L is in (K).

In eq.(4.1), L is expressed in ($J/molecule$)(Multiplying eq.(4.A3) by $\frac{M_{H_2O}}{N_A}$, where M_{H_2O} is the molar weight of water in (kg/mol) and N_A is the Avogadro number in ($molecules/mol$)).

(E) Viscosity (μ)

The viscosity of liquid water (μ) is given by eq.(4.A4) as a function of p_L , T_L , and p_v^* in the range $p_v^* \leq p_L \leq 8 \times 10^7 (Pa)$ and $273.15(K) \leq T_L \leq 573.15(K)$ [20].

$$\mu = 2.414 \times 10^{-5} \times 10^{\frac{247.8}{T_L - 140}} \left(1 + 1.04673 (p_L - p_v^*) \times 10^{-11} (T_L - 305) \right) \quad (4.A4)$$

where μ is in $(Pa \cdot s)$, p_L and p_v^* are in (Pa) , and T_L is in (K) .

(F) Surface tension (σ)

The surface tension of liquid water (σ) at T_L is estimated by interpolating the experimental values[22] by Gregory-Newton formula[18].

(G) Henry's constant of air (K_H)

The solubility of air in liquid water at 1 atm (x_1) is given by eq.(4.A5) as a function of temperature (T_L) in the range $273.15(K) \leq T_L \leq 373.15(K)$ [23].

$$\ln x_1 = -104.208 + 137.296/\tau + 58.7394 \ln \tau - 5.7669\tau \quad (4.A5)$$

where x_1 is expressed in mole fraction, and $\tau = T_L(K)/100$.

Henry's constant of air (K_H) is given by eq.(4.A6)[23].

$$K_H = \frac{p_1}{x_1} \quad (4.A6)$$

where $p_1 = 1.01325 \times 10^5 (Pa)$.

(H) Diffusion coefficient of air (D_{air})

The diffusion coefficient of air in liquid water (D_{air}) is related to the viscosity of liquid water (μ) by eq.(4.A7)[24].

$$D_{air} = \frac{1.40 \times 10^{-8}}{\mu^{1.1} V_{air}^{0.6}} \quad (4.A7)$$

where D_{air} is in (m^2/s), μ is in (*centipoise*) ($1 \text{ centipoise} = 10^{-3}(Pa \cdot s)$), and V_{air} is the molar volume of air in (cm^3/mol).

In the present calculations, $V_{air} = 30.3(cm^3/mol)$ is employed[24].

(I) Heat of solution of air (ΔH_{air})

The heat of solution of air into water (ΔH_{air}) is given by eq.(4.A8) as a function of T_L in the range $273.15(K) \leq 373.15(K)$ [23].

$$\Delta H_{air} = -1.37296 \times 10^4 R_g + 5.87394 \times 10 R_g T_L - 5.7669 \times 10^{-2} R_g T_L^2 \quad (4.A8)$$

where ΔH_{air} is in (J/mol) and R_g is the gas constant in ($J/mol \cdot K$) ($R_g = 8.31451(J/mol \cdot K)$). When $\Delta H_{air} < 0$, solution of air into water is the exothermic process.

(J) Saturated air concentration (c_s)

The saturated air concentration at bubble wall ($c_{s,i}$) is calculated by eq.(4.A9)[25].

$$c_{s,i} = \frac{10^3 \rho_{L,i} N_A p_{air}}{M_{H_2O} K_B} \quad (4.A9)$$

where $c_{s,i}$ is in ($molecules/m^3$), and p_{air} is the partial pressure of air in the bubble in (Pa).

In the present calculations, air concentration far from the bubble (c_0) is calculated by eq.(3.18).

*) Out of the range of each equation ($B \sim J$), the value is estimated by the method described in (A) in the present calculations.

Appendix 4-B. Derivation of Eq.(4.13)

Equation of bubble radius (eq.(4.13)) is derived by the method described in Appendix 2-B. The only different point from the description in Appendix 2-B is the boundary condition (eq.(4.B1)).

$$\rho_{L,i} \left(\left(\frac{\partial \varphi}{\partial r} \right)_R - \dot{R} \right) = -\dot{m} \quad (4.B1)$$

where φ is the velocity potential of the liquid.

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Chapter 5

Chemical Reactions in a Bubble

Abstract

Rates of chemical reactions in an air bubble are calculated numerically under a condition of the single-bubble sonoluminescence (SBSL). In the calculations, effect of non-equilibrium evaporation and condensation of water vapor at the bubble wall and that of thermal conduction both inside and outside the bubble are taken into account. Numerical calculations reveal that appreciable amount of OH , H_2O_2 , HO_2 , O_3 , H_2 , H , and O molecules are created in a bubble under the condition of SBSL. The amount of chemical products containing nitrogen such as NO_x , NH_x , and HNO_x is much less than that of the above products. Numerical calculations also reveal that no chemical reactions take place under a condition of non-light emission. Connection with sonoluminescence is also discussed.

5.1 Introduction

In 1994, R.Hiller et al.[1] reported that the intensity of SBSL increases dramatically by the addition of the noble gas into a nitrogen bubble. The bubble motion is also stabilized dramatically by the addition of the noble gas[1]. The spectrum of SBSL also strongly depends on the nature of the gas inside the bubble: Xenon yields a spectral peak at about 300 nanometers, whereas the helium spectrum is so strongly ultraviolet that its peak is obscured by the cutoff of water[1]. These experimental facts suggest that chemical effects may affect the bubble dynamics and the emission of light(SBSL). Thus in the present chapter, rates of chemical reactions in an air bubble are numerically calculated under a condition of SBSL. The method of the calculations is described in section 5.2.

The calculation of the rates of chemical reactions is also important in the study of chemiluminescence in a bubble. Before the discovery of SBSL by D.F.Gaitan[2], sonoluminescence from bubbly water has long been studied both experimentally and theoretically since 1933[3-5]. Such sonoluminescence is called "multi-bubble sonoluminescence" (MBSL). In the present stage, the mechanism of light emission is unclear both for MBSL and SBSL[5]. Even it is unclear whether the mechanism of MBSL and that of SBSL are the same one or not[3]. However, many theoretical suggestions on the mechanism have been given both for MBSL and SBSL[3-9]. For MBSL, the light emission is often attributed to chemiluminescence[4,6]. For example,

$H + OH \rightarrow H_2O + h\nu$ is often considered [6]. The light emission from OH radicals is also often considered: $OH^* \rightarrow OH + h\nu$ [6]. By the present calculations of the rates of chemical reactions, the above possibilities are examined in the case of SBSL.

Rates of chemical reactions in a bubble have been already calculated numerically by V.Kamath et al.[10] in case of an argon bubble. However, in their study[10], evaporation and condensation of water vapor at bubble wall are completely neglected. They affect bubble dynamics quite considerably as is shown in the previous chapters. At strong collapses of a bubble, the number of water molecules in a bubble changes drastically by the intense condensation, which affects the rates of chemical reactions by the change of their concentration. Additionally, the latent heat of the intense condensation alters the liquid temperature at bubble wall as is shown in the previous chapter. It results in the change of the temperature inside a bubble, which affects the reaction rates. In the present study, these effects are correctly taken into account, while they are not in ref.[10]. This is the most important improvement in the present study compared to that in ref.[10]. There are three other important improvements in the present study compared to ref.[10]. One is the calculations for an air bubble in the present study, while an argon bubble is treated in ref.[10]. Thus, in the present study, chemical reactions involving nitrogen are also taken into account. It is preferred because most of the SBSL experiments were performed for an air bubble.

Another is that the physical condition employed in the present calculation is completely the same one with that in the SBSL experiments by B.P.Barber et al.[11], while it is not the case in ref.[10]. The other is the employment of van der Waals equation of state for the gas inside a bubble rather than the perfect gas law employed in ref.[10].

5.2 Model

Rates of chemical reactions in an air bubble are numerically calculated in combination with the model of bubble dynamics constructed in chapter4. In the model, effect of non-equilibrium evaporation and condensation of water vapor at the bubble wall and that of thermal conduction both inside and outside the bubble are taken into account. The difference between the present model and that in chapter4 is only the inclusion of the effect of chemical reactions inside a bubble in the present model.

Followings are the description of the chemical kinetics. In Tables 5-1 and 5-2, the chemical kinetic model used in the present calculations is shown. Here we consider a simple reaction (γ).

where a, b, m, n are the number of molecules contributing to one reaction (γ) of the species A, B, M, N , respectively. The forward reaction rate per unit volume and unit time ($r_{\gamma f}$) is calculated by eq.(5.1)[10,12].

$$r_{\gamma f} = k_{\gamma f} [A]^a [B]^b \quad (5.1)$$

where

$$k_{\gamma f} = A_{\gamma f} T^{\beta_{\gamma f}} \exp(-C_{\gamma f}/T) \quad (5.2)$$

where $A_{\gamma f}$, $\beta_{\gamma f}$, and $C_{\gamma f}$ are given in Table 5-1. $[A]$ is the concentration of the species A . The backward reaction rate per unit volume and unit time ($r_{\gamma b}$) is calculated in the same manner.

$$r_{\gamma b} = k_{\gamma b} [M]^m [N]^n \quad (5.3)$$

where

$$k_{\gamma b} = A_{\gamma b} T^{\beta_{\gamma b}} \exp(-C_{\gamma b}/T) \quad (5.4)$$

where $A_{\gamma b}$, $\beta_{\gamma b}$, and $C_{\gamma b}$ are given in Table 5-1.

Table 5-1

The chemical kinetic model used in the calculations[10,12]. The constants k_f and k_b are used in the calculation of the forward and backward reaction rates, respectively, according to eqs.(5.1)-(5.4). The concentration of each species are expressed in moles per m^3 . (Thus, A_f (or A_b) is expressed in $(m^3/mol \cdot s)$ for a two-body reaction(in $(m^6/mol^2 \cdot s)$ for a three-body reaction)). β is dimensionless, and C is in (K) . For some of the backward reactions, the constants are not listed. Those backward reactions are neglected in the present calculations. ΔH_f is the enthalpy change in the forward reaction in (kJ/mol) at 1atm and 1000(K) except the reactions No.56,57,65,67(in the cases, the values at 1atm and 298(K) are listed). When $\Delta H_f < 0$, the forward reaction is exothermic.

No.	Reaction	A_f	β_f	$C_f(K)$	A_b	β_b	$C_b(K)$	$\Delta H_f(kJ/mol)$
1	$H + O_2 \rightarrow O + OH$	1.92×10^3	0	8270	7.18×10^5	0.36	-342	69.17
2	$O + H_2 \rightarrow H + OH$	5.08×10^{-2}	2.67	3166	2.64×10^{-2}	2.65	2245	8.23
3	$OH + H_2 \rightarrow H + H_2O$	2.18×10^2	1.51	1726	1.02×10^3	1.51	9370	-64.35
4	$OH + OH \rightarrow H_2O + O$	2.1×10^2	1.4	200	2.21×10^3	1.4	8368	-72.59
5	$H_2 + M \rightarrow H + H + M$	4.58×10^{13}	-1.4	52500	2.45×10^8	-1.78	480	444.47
	Coef. H_2 :2.5, H_2O :16.0							
6	$O + O + M \rightarrow O_2 + M$	6.17×10^3	-0.5	0	1.58×10^{11}	-0.5	59472	-505.40
	Coef. H_2 :2.5, H_2O :16.0							
7	$O + H + M \rightarrow OH + M$	4.72×10^6	-1.0	0	4.66×10^{11}	-0.65	51200	-436.23
	Coef. H_2O :5.0							

(continued)

8	$H + OH + M \rightarrow H_2O + M$ Coef. $H_2:2.5, H_2O:16.0$	2.25×10^{10}	-2.0	0	1.96×10^{18}	-1.62	59700	-508.82
9	$H + O_2 + M \rightarrow HO_2 + M$ Coef. $H_2:2.5, H_2O:16.0$	2.00×10^3	0	-500	2.46×10^9	0	24300	-204.80
10	$HO_2 + H \rightarrow H_2 + O_2$	6.63×10^7	0	1070	2.19×10^7	0.28	28390	-239.67
11	$HO_2 + H \rightarrow OH + OH$	1.69×10^8	0	440	1.08×10^5	0.61	18230	-162.26
12	$HO_2 + O \rightarrow OH + O_2$	1.81×10^7	0	-200	3.1×10^6	0.26	26083	-231.85
13	$HO_2 + OH \rightarrow H_2O + O_2$	1.45×10^{10}	-1.0	0	2.18×10^{10}	-0.72	34813	-304.44
14	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.0×10^6	0	700	4.53×10^8	-0.39	19700	-175.35
15	$H_2O_2 + M \rightarrow OH + OH + M$ Coef. $H_2:2.5, H_2O:16.0$	1.2×10^{11}	0	22900	9.0×10^{-1}	0.90	-3050	217.89
16	$H_2O_2 + H \rightarrow H_2O + OH$	3.2×10^8	0	4510	1.14×10^3	1.36	38180	-290.93
17	$H_2O_2 + H \rightarrow H_2 + HO_2$	4.82×10^7	0	4000	1.41×10^5	0.66	12320	-64.32
18	$H_2O_2 + O \rightarrow OH + HO_2$	9.55	2	2000	4.62×10^{-3}	2.75	9277	-56.08
19	$H_2O_2 + OH \rightarrow H_2O + HO_2$	1.00×10^7	0	900	2.8×10^7	0	16500	-128.67
20	$O_3 + M \rightarrow O_2 + O + M$	2.48×10^8	0	11430	4.1	0	-1057	109.27
21	$O_3 + O \rightarrow O_2 + O_2$	Coef. $N_2:1.5, O_2:1.64$			Coef. $O_2:1.63, N_2:1.4, H_2O:3.75, H_2O:15$			
22	$O_3 + OH \rightarrow O_2 + HO_2$	5.2×10^6	0	2090	-	-	-	-396.14
23	$O_3 + HO_2 \rightarrow O_2 + O_2 + OH$	7.8×10^5	0	960	-	-	-	-164.95
24	$H + O_3 \rightarrow HO_2 + O$	1×10^5	0	1410	-	-	-	-121.92
25	$H + O_3 \rightarrow OH + O_2$	9×10^6	0.5	2010	-	-	-	135.65
		1.6×10^7	0	0	-	-	-	-96.20

(continued)

40	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	1.4×10^5	0	1600	2.9×10^{-3}	0	-400	17.26
41	$NO + NO_3 \rightarrow NO_2 + NO_2$	4.1×10^8	0	481	3.9×10^5	0	12000	-99.61
42	$NO + O_3 \rightarrow NO_2 + O_2$	8.9×10^5	0	1330	-	-	-	-201.87
43	$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$	1.2×10^2	0	2100	-	-	-	-
44	$NO_2 + O_3 \rightarrow O_2 + NO_3$	5.9×10^6	0	3500	4.3×10^{-3}	0	9000	-102.26
45	$NO_3 + M \rightarrow NO + O_2 + M$ ($M \neq NO_2$)	6×10^8	-1.5	4300	-	-	-	17.26
46	$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$	6.1×10^6	0	3000	-	-	-	-82.35
47	$N + OH \rightarrow NO + H$	4.1×10^7	0	0	-	-	-	-202.54
48	$O_3 + N \rightarrow NO + O_2$	1.2×10^6	0.5	1200	-	-	-	-529.5
49	$NO + HO_2 \rightarrow NO_2 + OH$	3×10^6	0.5	1200	-	-	-	-37.59
50	$NO + H + M \rightarrow HNO + M$	5.4×10^3	0	-300	3×10^{10}	0	24500	-216.11
51	$HNO + H \rightarrow H_2 + NO$	Coef. $H_2:1.8, N_2O:2.2, H_2O:6.1$			-	-	-	-
52	$HNO + OH \rightarrow H_2O + NO$	4.8×10^6	0	0	1.4×10^7	0	27630	-228.35
53	$NO_2 + H \rightarrow NO + OH$	3.6×10^7	0	0	2.4	0	0	-292.71
54	$N_2O + H \rightarrow N_2 + OH$	3.5×10^8	0	740	-	-	-	-125.10
		7.6×10^7	0	7600	2.5×10^6	0	39000	-267.32

**) The reaction 43 is a fraction of the reaction 42.

***) In the reaction 45, $M = NO_2$ case is already listed in the reaction 40.

(continued)

55	$\text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$	1.65×10^4	-0.08	-806	-	-	-	-208.02
56	$\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	Coef. $\text{H}_2:2.3$ 10^7	0	1650	-	-	-	-169.95
57	$\text{HNO}_3 + \text{M} \rightarrow \text{NO}_2 + \text{OH} + \text{M}$	1.6×10^9	0	15400	5.0×10^5	0	0	206.25
58	$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$	8×10^4	0	0	Coef. $\text{N}_2:2$ 1.4×10^{-8}	0	0	-77.86
59	$\text{NH}_3 + \text{M} \rightarrow \text{H} + \text{NH}_2 + \text{M}$	9.2×10^9	0	42400	4.5×10^8	0	-11185	440.00
60	$\text{NH}_3 + \text{H} \rightarrow \text{H}_2 + \text{NH}_2$	1×10^6	0	3140	-	-	-	-4.47
61	$\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$	1.5×10^6	0	3020	6×10^4	0	2500	3.77
62	$\text{NH}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NH}$	3×10^4	0.679	650	-	-	-	-110.51
63	$\text{NH}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NH}_2$	2×10^7	0	1503	-	-	-	-68.82
64	$\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{H}_2 + \text{N}_2\text{H}_3$	1.3×10^7	0	1260	-	-	-	-117
65	$\text{N}_2\text{H}_4 + \text{O} \rightarrow \text{H}_2\text{O} + \text{N}_2\text{H}_2$	7.1×10^7	0	600	-	-	-	-381.61
66	$\text{N}_2\text{H}_4 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{N}_2\text{H}_3$	10^7	0	1010	-	-	-	-134
67	$\text{NH}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{NH}$	4×10^6	0	2800	3.3	0	0	-41.69

Table 5-2

The chemical kinetic model used in the calculations[12]. For the reactions listed in this table, pressure dependence of the reaction rates are taken into account by eqs.(5.5)-(5.7). The upper line for each reaction shows the constants for k_0 , and the lower line shows the constants for k_∞ . For some of the backward reactions, the constants for k_∞ are not listed. For those backward reactions, pressure dependence of the reaction rates are neglected. The concentration of each species are expressed in moles per m^3 . β is dimensionless, and C is in (K). ΔH_f is the enthalpy change in the forward reaction in (kJ/mol) at 1atm and 1000(K).

No.	Reaction	A_f	β_f	$C_f(K)$	A_b	β_b	$C_b(K)$	$\Delta H_f(kJ/mol)$
68	$N_2O + M \rightarrow N_2 + O + M$	5.0×10^3	0	29000	1.4×10	0	10400	169.36
		Coef. $O_2:2, N_2:2, N_2O:10$						
69	$NO_2 + M \rightarrow NO + O + M$	1.3×10^{11}	0	30000	3.3×10^3	0	11300	
		1.1×10^{10}	0	33000	1.1×10^3	0	-940	311.14
				Coef. $N_2:1.4, NO_2:2.1, H_2O:6.1$				
70	$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$	2×10^{14}	0	36170	1.7×10	0	860	48.82
		1.8×10^{11}	0	5550				
		Coef. $N_2:1.4, NO_2:3, N_2O_4:3$						
71	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	1×10^{16}	0	6600				
		1.3×10^{13}	0	9700	2×10^5	0	-481	82.87
72	$NO_2 + O + M \rightarrow NO_3 + M$	5.7×10^{14}	0	10600	4.6×10^5	0	-481	
		2.3×10^4	0	0	2.5×10^3	0	0	-211.52
		1.1×10^7	0	0				
73	$N_2H_4 + M \rightarrow NH_2 + NH_2 + M$	4×10^9	0	20600	10^4	0	0	237.95
		8×10^{13}	0	27700				

For the reactions listed in Table 5-2, the dependence of $k_{\gamma f}$ ($k_{\gamma b}$) on the pressure inside the bubble is also taken into account. In this case, the reaction rate per unit volume and unit time ($r_{\gamma' f}$) is calculated by eq.(5.5) for an unimolecular reaction(γ')[17].

where M is the collision partner, which acts only as catalysis in the reaction.

$$r_{\gamma' f} = k_{\gamma' f} [A] \quad (5.5)$$

where

$$k_{\gamma' f} = \frac{k_{\gamma' f \infty}}{1 + k_{\gamma' f \infty} / (k_{\gamma' f 0} [M])} \quad (5.6)$$

where $k_{\gamma' f \infty}$ and $k_{\gamma' f 0} [M]$ are the value of $k_{\gamma' f}$ when $[M] \rightarrow \infty$ and $[M] \rightarrow 0$, respectively. $k_{\gamma' f \infty}$ and $k_{\gamma' f 0}$ are calculated by the constants listed in Table 5-2 in the same manner with eq.(5.2). For an unimolecular reaction, $A_{\gamma' f \infty}$ and $A_{\gamma' f 0}$ in Table 5-2 are expressed in (s^{-1}) and ($m^3/mol \cdot s$), respectively. For a three-body reaction(γ''), the reaction rate per unit volume and unit time($r_{\gamma'' f}$) is calculated by eq.(5.7).

where M is the third body, which acts only as catalysis in the reaction.

$$r_{\gamma'' f} = k_{\gamma'' f} [A][B] \quad (5.7)$$

where $k_{\gamma'' f}$ is calculated in the same manner with eq.(5.6). $k_{\gamma'' f \infty}$ and $k_{\gamma'' f 0}$ are calculated by the constants listed in Table 5-2 in the same manner with

eq.(5.2). For a three-body reaction, $A_{\gamma''f\infty}$ and $A_{\gamma''f0}$ listed in Table 5-2 are expressed in $(m^3/mol \cdot s)$ and $(m^6/mol^2 \cdot s)$, respectively.

The number of each species(n_α) changes with time due to chemical reactions. (For H_2O and *air*, the number of molecules mainly changes by evaporation or condensation and diffusion, respectively).

$$n_\alpha(t + \Delta t) = n_\alpha(t) + \frac{4}{3}\pi R^3 \Delta t (\Sigma(\text{production}) - \Sigma(\text{destruction})) \quad (5.8)$$

where the first sum in the right hand side of eq.(5.8) contains the contributions of all reactions producing α , and the second one contains those of all reactions consuming α . For example, when $\alpha = A$ in the reaction (γ), $ar_{\gamma f}$ contributes to the second sum in eq.(5.8). (In this stage, $ar_{\gamma f}$ should be expressed in $(molecules/m^3 \cdot s)$). In Tables 5-1 and 5-2, M denotes the collision partner or the third body in a three-body reaction, which acts only as catalysis in the reaction. The listed values in Tables 5-1 and 5-2 are those for $M = Ar$. In case of the other species($M \neq Ar$), the value $A_{\gamma f}$ (or $A_{\gamma b}$) for $M = Ar$ should be multiplied by the coefficient listed in the table. For unlisted species, the value $A_{\gamma f}$ (or $A_{\gamma b}$) for $M = Ar$ is employed in the present calculations.

According to the effect of chemical reactions in a bubble, the model of bubble dynamics constructed in chapter4 is modified in two points. One is the contribution of the reaction heat to the change of the internal energy of a bubble(ΔE).

$$\begin{aligned}
\Delta E(t) &= -p(t) \cdot \Delta V(t) + 4\pi R^2 \Delta t (\dot{m}_{eva} e_{eva} - \dot{m}_{con} e_{con}) \\
&\quad + 4\pi R^2 \Delta t \left. \frac{dm}{dt} \right|_{diff} e_{air} + 4\pi R^2 \Delta t \cdot \kappa \left. \frac{\partial T}{\partial r} \right|_{r=R} \\
&\quad + \frac{4}{3} \pi R^3 \Delta t \sum_{\gamma} (r_{\gamma b} - r_{\gamma f}) \Delta H_{\gamma f}
\end{aligned} \tag{5.9}$$

where $\Delta H_{\gamma f}$ is the enthalpy change in the forward reaction (when $\Delta H_{\gamma f} < 0$, the reaction is exothermic). The last term in eq.(5.9) is the heat of chemical reactions inside the bubble.

Another is the total number of gas and vapor molecules in the bubble (n_t).

$$n_t = \sum_{\alpha} n_{\alpha} \tag{5.10}$$

where α denotes species of the gas or vapor;

$\{\alpha\} = \{N_2, O_2, Ar, H_2O, OH, H_2O_2, HO_2, O_3, H_2, H, O, N, N_2O, NO, NO_2, N_2O_4, N_2O_5, NO_3, NH, NH_2, NH_3, N_2H_2, N_2H_3, N_2H_4, HNO, HNO_2, HNO_3\}$. n_{α} is the number of molecules of the species α in the bubble. n_{air} is defined as $n_{air} = n_{N_2} + n_{O_2} + n_{Ar}$ in the present calculations.

5.3 Results and Discussions

Calculations are performed in two cases: (1) a condition of the single-bubble sonoluminescence(SBSL), (2) a condition of non-light-emission. Both con-

ditions are listed in Table 3-1-(b). Calculations start from the time $t = 57.5(\mu s)$ and $t = 54.4(\mu s)$ for case(1) and case(2), respectively. The initial values of $R, \dot{R}, T, n_{H_2O}, n_{N_2}, n_{Ar}, p_B, \frac{dp_B}{dt}, \dot{m}, \ddot{m}, \frac{d\rho_g}{dt}, T_B, \frac{dT_B}{dt}, T_{L,i}, \frac{d\rho_{L,i}}{dt}$ are the values calculated by the model in chapter4 starting from $t = 0(\mu s)$, in which effect of chemical reactions are neglected. The initial number of chemical products(n_α) are chosen to be zero($n_\alpha = 0$). The ambient liquid temperature(T_∞) and the ambient pressure (p_∞) are chosen to be $20^\circ C$ and 1 atm, respectively. In the present calculations, the temperature dependence of the accomodation coefficient for evaporation and condensation (α_M) is taken into account according to the results of the molecular dynamics simulation by M.Matsumoto[13]. Details are described in Appendix 5-A. As in the calculations in chapter4, $n = 3$ is assumed, which determines the thickness of the thermal boundary layer inside a bubble ($n\lambda$). α_e in eq.(3.8) is assumed to be $\alpha_e = 1.0$ [14]. The parameter e_0 in eq.(4.7) is assumed to be $e_0 = 1 \times 10^{-3}$ as in the previous chapter.

Fig.5-1 Calculated results under the condition of SBSL(case(1)) for one acoustic cycle. The time axis(the horizontal axis) is the same one for all the figures.

-(a) The pressure of the acoustic field($p_s(t)$) employed in the calculation.

Fig.5-1-(b) The bubble radius(R). The line is the calculated values and the open circles are the experimental data[11].

Fig.5-1-(c) The temperature inside the bubble(T) with logarithmic vertical axis.

Fig.5-1-(d) The density inside the bubble(ρ_g) with logarithmic vertical axis.

Fig.5-1-(e) The number of molecules in the bubble with logarithmic vertical axis. The line is the total number of molecules in the bubble(n_t), the dotted line is the number of air molecules(n_{air}), the dash-dotted line is the number of vapor molecules(n_{H_2O}), and the dashed line is the number of OH radicals(n_{OH}) inside the bubble.

Fig.5-1-(f) The number of H_2O_2 molecules inside the bubble (dotted line). In Figs.5-1-(e~i), the line shows the total number of molecules inside the bubble(n_t). The vertical axes are the same throughout Figs.5-1-(e~i).

Fig.5-1-(g) The number of O_3 molecules inside the bubble (dash-dotted line).

Fig.5-1-(h) The number of HO_2 (dash-dotted line) and O molecules (dotted line) inside the bubble.

Fig.5-1-(i) The number of H_2 (dash-dotted line) and H molecules (dotted line) inside the bubble.

(A) A condition of SBSL (case(1))

Results of the calculations under a condition of SBSL(case(1)) are shown in Figs.5-1-(b ~ i) for one acoustic cycle. In Fig.5-1-(a), the acoustic field($p_s(t)$) applied on the bubble is shown as a function of time. In Fig.5-1-(b), the bubble radius(R) is shown as a function of time. The calculated values(line) fit well with the experimental data[11] (open circles). In Fig.5-1-(c), the temperature inside the bubble(T) is shown as a function of time with logarithmic vertical axis. Qualitative discussions on T as a function of time are given in chapter3. In Fig.5-1-(d), the density inside the bubble(ρ_g) is shown as a function of time with logarithmic vertical axis. The density increases dramatically at collapses of the bubble as is expected. In Fig.5-1-(e), the number of molecules in the bubble is shown as a function of time with logarithmic vertical axis. The line shows the total number of molecules(n_t), the dash-dotted line shows the number of vapor molecules(n_{H_2O}), the dotted line shows the number of air molecules ($n_{air} = n_{N_2} + n_{O_2} + n_{Ar}$), and the dashed line shows the number of OH radicals(n_{OH}) in the bubble. It is seen from the figure that appreciable amount of OH radicals are created in the bubble at the strong collapse. OH radicals are soon consumed after their creations because of their high reactivity. The half width of the number of OH radicals(n_{OH}) is in the order of 10^3 (ps), which is two orders of magnitude larger than the pulse width of SBSL(≤ 50 (ps)[15,16]). Even the half width of the number of excited OH molecules (n_{OH^*}) is in the order of 10^2 (ps) when n_{OH^*} is assumed

to be proportional to $n_{OH} \exp(-E_a/kT)$, where $E_a \sim 6 \times 10^{-19}(J)$ and k is the Boltzmann constant (E_a corresponds to the energy quantum of the light ($h\nu$) of the OH line($\lambda = 310nm$)[10]). However, in the present model, shock formation inside the bubble is completely neglected. The half width of n_{OH} may be shortened by the shock wave inside the bubble. Thus the possibility of $OH^* \rightarrow OH + h\nu$ as the source of SBSL should not be discarded.

The reaction rate of $H + OH \rightarrow H_2O$ also has a peak at around at $R \sim R_{min}$. The half width of the reaction rate is in the order of 10^2 (ps). The number of the reaction($H + OH \rightarrow H_2O$) in one strong collapse is in the order of 10^4 , while $10^5 \sim 10^6$ photons are emitted during one strong collapse[15,17]. However, the possibility of $H + OH \rightarrow H_2O + h\nu$ as the source of SBSL should be discussed further by taking into account the effect of shock formation inside the bubble.

In Fig.5-1-(f), the number of H_2O_2 molecules($n_{H_2O_2}$) is shown as a function of time. In Figs.5-1-(e~i), the vertical axes are the same. In Figs.5-1-(e~i), the line shows the total number of molecules in the bubble(n_t). It is seen from Fig.5-1-(f) that the number of H_2O_2 molecules ($n_{H_2O_2}$) decreases at first at the strong collapse and that it increases again to the almost the same value with that created in the previous strong collapse. Strictly speaking, $n_{H_2O_2}$ increases slightly after the strong collapse as is seen in Fig.5-1-(f). Thus in the time scale of 1(s) or more, the increase of $n_{H_2O_2}$ may affect the bubble motion because 10^4 or more strong collapses take place in

1(s). However, H_2O_2 is quite soluble in water. Thus effect of the solution of H_2O_2 into the surrounding water should also be taken into account in the discussions of the increase of $n_{H_2O_2}$. In Fig.5-1-(g), the number of O_3 molecules(n_{O_3}) is shown as a function of time. It is seen from the figure that n_{O_3} changes with time in the same manner with $n_{H_2O_2}$. For quantitative discussions, the solution of O_3 into the surrounding water should be taken into account as in the H_2O_2 case. In Fig.5-1-(h), the number of HO_2 molecules(n_{HO_2}) (dash-dotted line) and that of O atoms(n_O)(dotted line) are shown as a function of time. O atoms are created at the strong collapse and are consumed at the second collapse of the bubble. The number of HO_2 molecules increases slightly at the strong collapse. The increase of n_{HO_2} should be quantitatively discussed by taking into account the solution of HO_2 into the surrounding water as the H_2O_2 and O_3 cases. In Fig.5-1-(i), the number of H_2 molecules(n_{H_2}) (dash-dotted line) and that of H atoms(n_H) (dotted line) are shown as a function of time. H atoms are created at the strong collapse and are consumed soon. The number of H_2 molecules(n_{H_2}) increases slightly at the strong collapse. For quantitative discussions of n_{H_2} , the solution of H_2 into the surrounding water should be taken into account.

The calculated results also reveal that the amount of chemical products containing nitrogen such as N , N_2O , NO , NO_2 , N_2O_4 , N_2O_5 , NO_3 , NH , NH_2 , NH_3 , N_2H_2 is much less than that of the chemical products shown in Figs.5-1-(e~i). HNO_2 molecules are most created in the chemical products containing

nitrogen($n_{HNO_2} \sim 10^3$). The second is NO ($n_{NO} \sim 10^3$). The amount of the other products containing nitrogen is even much less than that of HNO_2 and NO . It is also clarified that the chemiluminescence reactions involving nitrogen listed in table5-1(the reaction No.27, 29,43) are all negligible.

(B) A condition of non-light emission (case(2))

Numerical calculations reveal that no chemical reactions take place under the condition of non-light-emission(case(2)). Because the temperature inside the bubble increases only up to 600(K) in this case.

5.4 Conclusion

Rates of chemical reactions inside a bubble are numerically calculated in combination with the model of bubble dynamics constructed in chapter4. The numerical calculations reveal that the appreciable amount of OH , H_2O_2 , HO_2 , O_3 , H_2 , H and O molecules are created in a bubble under a condition of SBSL. The amount of chemical products containing nitrogen such as NO_x , NH_x and HNO_x is much less than that of the above products. For quantitative discussions on the number of chemical products inside a bubble, effect of their solution into the surrounding water and that of shock formation inside the bubble should be taken into account. In the study of the mechanism of light emission(SBSL), effect of shock formation inside a bubble is particularly important.

Appendix 5-A. The Accomodation Coefficient (α_M)

In the present calculations, α_M is estimated by eqs.(5.A1)~(5.A3) as a function of the liquid temperature at the bubble wall($T_{L,i}$), which is derived by interpolating the calculated values by the molecular dynamics simulations[13].

When $T_{L,i} \leq 350(K)$

$$\alpha_M = 0.35$$

(5.A1)

When $350(K) \leq T_{L,i} \leq 500(K)$

$$\alpha_M = 0.35 - 0.05k^{(1)} - 0.05k^{(2)} + 0.025k^{(3)}$$

(5.A2)

where

$$k^{(m)} = k(k-1) \cdots (k-(m-1))$$

$$k = \frac{T_{L,i}(K)}{50} - 7$$

When $500(K) \leq T_{L,i}$

$$\alpha_M = 0.05$$

(5.A3)

It should be noted that α_M was assumed to be independent on temperature($\alpha_M \equiv 0.4$) in the calculations in the previous chapters.

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