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Measurement of Temperature in Sonoplasma [†]

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Abstract: Stable plasma can be generated in a liquid hydrocarbon such as n-dodecane or benzene by simultaneous microwave and ultrasonic irradiation. The authors refer to this plasma as “sonoplasma” and distinguish it from “sonoluminescence” on the basis of the continuity of emission. The temperature in the plasma was obtained by measuring two specified emission intensities from the plasma, which reached approximately 5000 K. To analytically estimate the temperature, numerical simulations of the behavior of a single bubble in sound field, taking into account the absorption of microwave energy, were carried out. The temperature inside the bubble in n-dodecane reached approximately 8000 K. In benzene, the temperature inside the bubble, which continued expanding through absorption of microwave energy, exceeded 2000 K.

Key words: sonoplasma, ultrasonic irradiation, microwave, temperature, hydrocarbon, cavitation

1. Introduction

The application of plasma in material processing is becoming increasingly important in a variety of fields. Plasma chemical vapor deposition (plasma CVD) is well known to be an efficient method of growing diamond-like carbon (DLC) films[1-3)], fabricating coatings of silicon, titanium, alumina and other materials[4-6)], and synthesizing new carbon materials such as fullerenes and carbon nanotubes[7-9)]. Plasma CVD also enables the growth of artificial diamonds[10-12)]. As the growth rate of high-quality transparent diamond by plasma CVD[13-14)] is only about 1 μm/h, the fabrication of optical apertures by this method takes days, resulting in unacceptable costs.

The authors achieved the generation of plasma in a liquid by simultaneous ultrasonic and microwave irradiation, and referred to the plasma as “sonoplasma”[15)]. It is well known that ultrasonic irradiation generates a large number of bubbles (so-called acoustic cavitation) in liquids and these bubbles emit light as they collapse. The phenomenon is called “sonoluminescence” and is distinguished from “sonoplasma” by the duration of the emission. That is, light is emitted continuously from sonoplasma, whereas a burst of light is emitted from the collapsing bubbles. The plasma is generated by the absorption of microwave energy, not by energy focusing at the collapse of bubbles. Researchers[16-18)] have studied the mechanisms of the sonoluminescence, and pointed out that the temperature reaches about 5000 K and the pressure is above 100 MPa at the time of emission from the bubbles even though the environment remains constant.

We propose that sonoplasma be applied as a new technique to replace the gas-phase plasma applied in plasma CVD. As sonoplasma is only observed close to the top of the electrode, it is much more similar to plasma by glow discharge than that by arc discharge. As a result, although the plasma is applied to coating processes, the damage to the substrates and coatings by collisions of electrons with high energy may be less. As liquids are

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much denser than gases, the deposition rate is much higher in liquids. As liquid cooling can be expected, Deposition at much lower temperatures, which would allow the use of substrates that cannot withstand the temperatures necessary for plasma CVD, may be possible.

In this study, the temperature in the plasma is obtained experimentally as well as estimated analytically by simulations of the behavior of a single bubble in a sound field. The temperature is crucial to understanding the mechanisms of the plasma, and the establishment of a method to measure the temperature is important to plasma application.

2. Experimental Apparatus and Procedure

The experimental apparatus is shown in Fig. 1. The reactor vessel is a vacuum chamber made of quartz glass with an inner diameter of 55 mm, a height of 83 mm and a thickness of 2 mm. A horn-type transducer with a resonant frequency of 19.5 kHz (Kaijo Co., 6281A) is used for ultrasonic vibration. It faces downward from the top of the vessel. A microwave electrode faces upward from the bottom of the vessel. There is a space of 25 mm between the ultrasonic transducer and the microwave electrode. Microwaves with 2.45 GHz are transmitted from a microwave generator (Nihon Koshuha Co., MKN-152-3S9) to the electrode through a rectangular waveguide, and are irradiated into the test vessel after introduction from the electric field coupling electrode in the cavity resonator to the coaxial cable. The apparatus is designed to generate the maximum amplitude of the electric field at the top of the electrode by adjusting the length of the coaxial cable. The microwave power ranges from 50 W to 200 W.

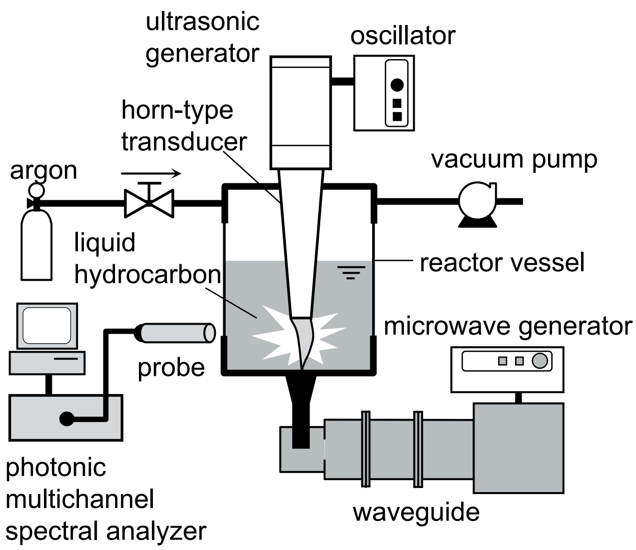

Fig. 1 Schematic diagram of the experimental apparatus. Sonoplasma is generated between a horn-type transducer and a microwave electrode.

Two kinds of liquid hydrocarbon at normal temperature were used: n-dodecane ($C_{12}H_{26}$), and benzene (C_6H_6). The gas pressure in the vessel was fixed at 50 hPa by adjusting the amount of argon gas flow. The emission spectrum of the sonoplasma was recorded with a multichannel spectral analyzer (Hamamatsu Photonics, PMA-11).

3. Temperature in Sonoplasma

In this study, the temperature of the plasma is not estimated by fitting of the blackbody radiation curve, because the continuous spectra from the plasma cannot be extracted from the experimentally measured spectra, which contain various components such as the continuous spectra from the electrode and the substrate. This is the reason why the intensities of the emissions due to the specified transition are measured to estimate the temperature of plasma. The gas temperature and electron temperature are almost identical in sonoplasma under the assumption of thermal equilibrium. Introducing the ratio of the two intensities of the spectral lines and

Einstein's A coefficients, which correspond to the transition probabilities of spontaneous photon emissions, the electron temperature is given by

$$\frac{I_{ij}}{I_{kl}} = \frac{\nu_{ij} A_{ij} g_i}{\nu_{kl} A_{kl} g_k} \exp\left(-\frac{E_i - E_k}{k_B T} \right), \quad (1)$$

where I is the intensity of emission due to the transition between two energy levels, ν is the frequency of the spectral lines, A is Einstein's A coefficient (0.6465 when H_α and 0.2062 when H_β) , g is the statistical weight of the energy level (6 when the energy levels before the both H_α and H_β emission), k_B is the Boltzmann constant, T is the electron temperature and the subscripts i, j, k and l indicate energy levels.

Figure 2 shows the emission spectrum of sonoplasma (a) in n-dodecane and (b) in benzene. Introducing two intensities at specific wavelengths such as H_α and H_β, the electron temperatures in n-dodecane and in benzene were respectively estimated to be 5300 K and 4700 K. Their observational errors are both within ±200 K.

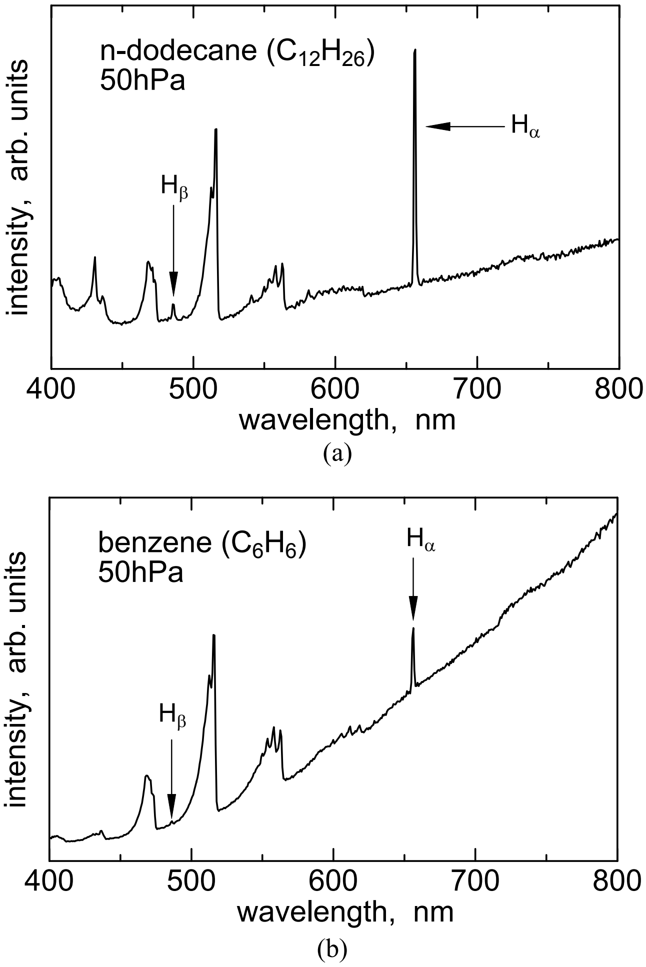

Fig. 2 Emission spectra from the sonoplasma (a) in n-dodecane and (b) in benzene at 50 hPa. Specified wavelengths H_α and H_β are 656.3 nm and 486.1 nm, respectively.

The intensities moderately increase with wavelength, as seen in Fig. 2. This increase is caused by emissions from carbides generated in the sonoplasma. At higher pressures, the liquids become discolored more quickly, and large amounts of sooty material were generated which diffused within the liquids in a few seconds. As a result, though the plasma occurs, it is difficult to measure the temperature at higher pressures.

4. Estimate of Temperature in a Forced Oscillation Bubble with Heat Generation

4.1 Simulation models

The plasma is being generated in the acoustic cavitation bubble. Since many cavitation bubbles occur in liquids, it is difficult to estimate the temperature and the pressure in the plasma by numerical analysis. Therefore, the behavior of a single bubble filled with mixed argon gas and vapor in a sound field is numerically analyzed. In addition, heat generation through absorption of the microwave energy is taken into account. As we know, dielectric absorption does not occur in liquid hydrocarbons such as n-dodecane and benzene. However, if some of the molecules of the hydrocarbon are ionized in a bubble, the microwave energy is absorbed within the bubble. The purpose of this simulation is to clarify the behavior of the bubble with the absorption of energy, therefore the mechanism of ionization of molecules is ignored, and the rate of absorption is assumed to be proportional to the amount of the hydrocarbon within the bubble.

As a state equation for the mixed gas in the bubble, the Redlich-Kwong equation[19] is employed,

$$p = \frac{R_g T}{v - b} - \frac{a}{\sqrt{T} v (v + b)} \tag{2}$$

$$a = \frac{R_g^2 T_{cm}^2}{9(2^{1/3} - 1) p_{cm}} \tag{3}$$

$$b = \frac{(2^{1/3} - 1) R_g T_{cm}}{3 p_{cm}} \quad , \tag{4}$$

where p is the total pressure, R_g is the gas constant, T is the temperature, and v is the molar volume. The critical temperature T_{cm} and the critical pressure p_{cm} of mixed gas are expressed as

$$T_{cm} = \left\{ \frac{\left[x_a \left(T_{ca}^{5/2} / p_{ca} \right)^{1/2} + x_v \left(T_{cv}^{5/2} / p_{cv} \right)^{1/2} \right]^2}{x_a \left(T_{ca} / p_{ca} \right) + x_v \left(T_{cv} / p_{cv} \right)} \right\}^{2/3} \tag{5}$$

$$p_{cm} = \frac{T_{cm}}{x_a \left(T_{ca} / p_{ca} \right) + x_v \left(T_{cv} / p_{cv} \right)} \tag{6}$$

where T_c, p_c and x are the critical temperature, the critical pressure, and mole fraction, respectively. The subscripts a and v represent argon gas and vapor, respectively. The components of the mixed gas are argon and vapor of a hydrocarbon such as n-dodecane or benzene. Any chemical reactions are neglected. Therefore,

$$x_a + x_v = 1 . \tag{7}$$

An equation of the thermal energy, which is solved to obtain the temperature, is expressed by

$$\varepsilon = \frac{3}{2} x_a R_g T + 3 x_v R_g T - \frac{3a}{2b\sqrt{T}} \ln \frac{v + b}{v} , \tag{8}$$

where ε is the specific thermal energy. The dynamics of the gas inside a spherical bubble is described by the compressible Navier-Stokes equations, which represent the conservation of mass, momentum, and energy.

$$\frac{\partial \rho_a}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho_a u \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho D_m \frac{\partial x_a}{\partial r} \right) \tag{9}$$

$$\frac{\partial \rho_v}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho_v u \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho D_m \frac{\partial x_v}{\partial r} \right) \tag{10}$$

$$\frac{\partial (\rho u)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho u^2 \right) = - \frac{\partial p}{\partial r} \tag{11}$$

$$\frac{\partial}{\partial t} \left(\frac{\rho \varepsilon}{M_m} + \frac{\rho u^2}{2} \right) + \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 u \left(\frac{\rho \varepsilon}{M_m} + \frac{\rho u^2}{2} + p \right) \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 k \frac{\partial T}{\partial r} \right) + \rho_v q \tag{12}$$

Here, ρ is the density of the mixed gas (equal to $\rho_a + \rho_v$), r is the radial distance from the center of the bubble, u is the radial velocity, D_m is the mutual diffusion coefficient, M_m is the converted molar weight of the mixed gas and k is the thermal conductivity in the mixed gas. q is the heat generated from the vapor.

As the equation for the motion of the liquid-bubble interface, the Keller equation is employed:

$$\left(1 - \frac{\dot{R}}{c} - \frac{\dot{m}}{c \rho_l} \right) R \ddot{R} + \frac{3}{2} \left(1 - \frac{\dot{R}}{c} - \frac{2\dot{m}}{3c\rho_l} \right) \dot{R}^2 = \frac{1}{M_l \rho_l} \left(p_{ex} - p_{sur} \right) + \frac{R}{c M_l \rho_l} \frac{dp_b}{dt} - \frac{\ddot{m} R}{\rho_l} \left(1 - \frac{\dot{R}}{c} - \frac{\dot{m}}{c \rho_l} \right) - \frac{\dot{m} \dot{R}}{\rho_l} \left(1 - \frac{\dot{m}}{2 \dot{R} \rho_l} - \frac{\dot{m}}{2 c \rho_l} \right) , \tag{13}$$

where R is the radius of the bubble, $\dot{m}$ is the flux of the vapor at the interface, c is the speed of sound in liquid,

ρ_l is the density of liquid, M_l is the molecular weight of the liquid, p_{ex} is the liquid pressure on the external side of the interface, and p_{sur} is the ambient pressure with the sound field. The equation takes into account the compressibility of liquid and the effect of evaporation and condensation. The liquid pressure on the external side of the interface and the ambient pressure with the sound field are expressed by

$$p_{ex} = p - \frac{2\sigma}{R} - \frac{4\mu\dot{R}}{R} - \dot{m}^2\left(\frac{1}{\rho_l} - \frac{1}{\rho}\right) \tag{14}$$

$$p_{sur} = p_0 - p_{sa}\sin\varpi t\cos\omega\frac{R}{c}, \tag{15}$$

where σ is the surface tension, μ is the liquid viscosity, p_0 is the disturbed pressure, p_{sa} is the amplitude of sound pressure, and ω is the angular frequency of the acoustic wave. The heat and mass transfer at the interface, such as those by thermal condensation, evaporation, or diffusion of argon as a noncondensable gas, are given as

$$-k\left.\frac{\partial T}{\partial r}\right|_{r=R}^{in} + L\dot{m} + H\dot{m}_a = -k_l\left.\frac{\partial T}{\partial r}\right|_{r=R}^{ex} \tag{16}$$

$$\dot{m} = \frac{\alpha_M}{\sqrt{2\pi M_l R_g T_s}}\left(\Gamma p_v - p_{sat}\right) \tag{17}$$

$$\Gamma = e^{-\Omega^2} - \Omega\sqrt{\pi}\,\mathrm{erfc}(\Omega) \tag{18}$$

$$\Omega = -\frac{\dot{m}}{p_v}\sqrt{\frac{M_l R_g T_s}{2}} \tag{19}$$

$$\dot{m}_a = D\left.\frac{\partial C}{\partial r}\right|_{r=R}^{ex} + s_0\frac{p_a}{p_0}\dot{m} \tag{20}$$

$$C\Big|_{r=R}^{ex} = s_0\frac{p_a}{p_0}\rho_l, \tag{21}$$

where k_l is the thermal conductivity of liquid, L is the specific latent heat, H is the specific heat of solution, α_M is an accommodation coefficient for the condensation or evaporation. Details of this analytical model for the condensation or evaporation are described in refs. 20 and 21. M_l is the molecular weight of the liquid, T_s is the temperature at the interface, p_v is the partial pressure of vapor, p_{sat} is the saturated pressure, $\dot{m}_a$ is the flux of argon gas at the interface, D is the diffusion coefficient of argon in liquid, C is the concentration of argon in liquid, s_0 is the solubility at p_0, and p_a is the partial pressure of argon gas.

4.2 Simulation results

All calculations are initiated under the conditions that T_0=298 K, p_0=1 atm, and R_0=50 μm. The behavior of bubbles in ultrasound was observed using a stroboscope. This method was reported by Kozuka *et al.* [22] The instantaneous images of the bubbles were captured using a charge coupled device (CCD) camera. Since the radii of the bubbles in n-dodecane periodically changed between 35 μm and 55 μm in the images, we adopt 50 μm as the initial bubble radius. The partial pressure of vapor initially equals the saturated pressure, and the total pressure in a bubble is derived from $p_0 + 2\sigma/R_0$. The initial concentration of argon in the liquids is 20% of saturation solubility. The frequency and amplitude of sound pressure are 19.5 kHz and 1.3 atm, respectively. We adopt 0.1 as the accommodation coefficient for condensation or evaporation (α_M).

Figure 3(a) shows the calculated results for the motion of a single bubble, the temperature, and the pressure inside the bubble in n-dodecane. The rates of heat generation by absorption of the microwave energy for a vapor molecule in the bubble are 6×10^5 eV/s and 1.1×10^6 eV/s. Both the dotted lines and the dash-dotted lines in Fig. 3

represent a bubble with heat generation through the absorption of microwave energy. These results can be compared with the results obtained for the case without heat generation.

The bubble in n-dodecane repeatedly expands and contracts under all conditions. The frequencies of contraction of the bubble with absorption are not always in synchronization with the acoustic frequencies. The temperature increases with increasing absorption rate, and reaches approximately 8000 K when the bubble size is minimum. These temperature values are within the same range and order of experimental results. The difference between the maximum and the minimum of the pressure increases with increasing absorption rate.

Figure 3(b) shows the calculated results for the motion of a single bubble, the temperature, and the pressure inside the bubble in benzene. The absorption rates of microwave energy for a vapor molecule in the bubble are 5×10^4 eV/s and 1×10^5 eV/s. In benzene, a bubble absorbing sufficient microwave energy no longer contracts, and the temperature continues to rise to more than 2000 K. The difference between the maximum and the minimum pressure decreases in relation to the absorption rate.

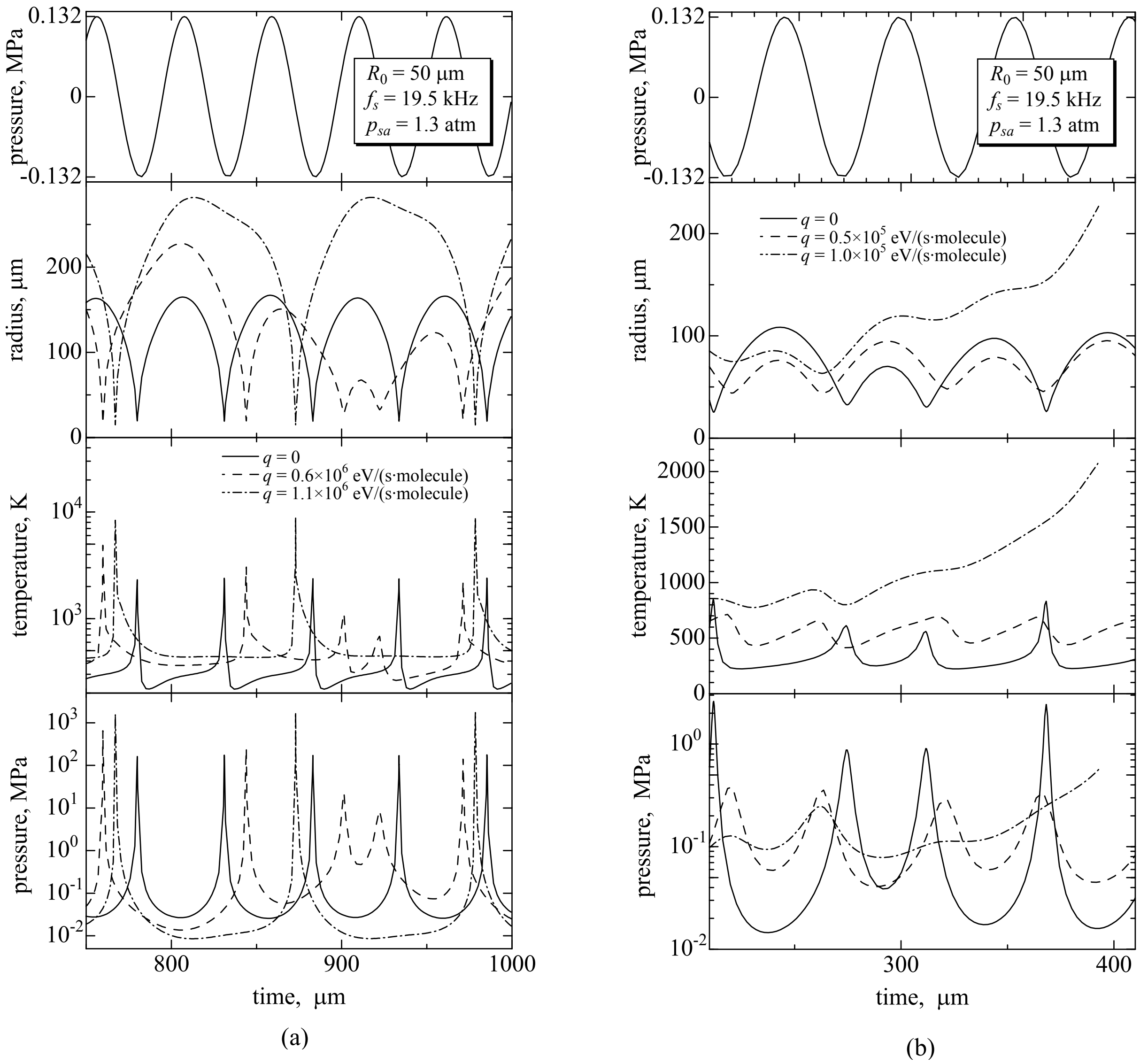

Fig. 3 Calculated results for bubble radius, temperature, and pressure inside the bubble in (a) n-dodecane and (b) benzene at the acoustic frequency of 19.5 kHz and acoustic pressure amplitude of 1.3 atm. Initial bubble size was 50 mm. Both the dotted lines and the dash-dotted lines represent the absorption of the microwave energy and the solid line represents no absorption.

Figure 4 shows the temperature inside the minimum-size bubble in n-dodecane as a function of the rate of the heat generation. When the rate of the heat generation is less than 1.1×10^6 eV/s, The temperature is approximately between 2000 K and 3500 K. The temperature sharply increases at 1.1×10^6 eV/s, and reaches approximately 8000 K. Because the temperature is sensitively affected by the synchronization of the contraction of the bubble with the acoustic frequency, fluctuations of the temperature are seen in Fig. 4. The temperature of the bubble contracting regularly is higher than that of the bubble contracting irregularly (see Fig. 3). This results lead to the qualitative discussion that not only the rate of heat generation, which is dependent on the intensity of the microwave irradiation, but also the behavior of the bubble with the sound pressure significantly affect the control of the temperature in the bubble. When the rate of heat generation of a vapor molecule within the bubble exceeds 1.3×10^6 eV/s, the bubble becomes unstable and rapidly expands. The dependability of the numerical method is limited to bubble radii of less than 300 μm.

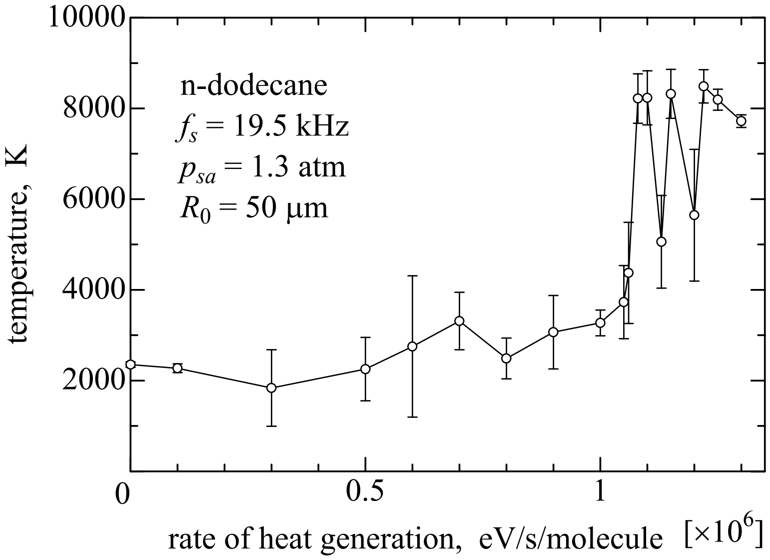

Fig. 4 The temperature inside the minimum-size bubble in n-dodecane as a function of heat generation.

5. Conclusions

The authors attempted to generate stable plasma in a liquid through simultaneous microwave and ultrasonic irradiation and determined the temperature in the plasma by measuring the emission spectra from the plasma. We numerically simulated the behavior of a single bubble in an acoustic field, taking into account the absorption of microwave energy, to estimate the temperature analytically. The conclusions are as follows.

(1) Sonoplasma temperatures of approximately 5300 K in n-dodecane and 4700 K in benzene were experimentally obtained.

(2) A bubble in n-dodecane repeatedly expands and contracts at a frequency that is not always in synchronization with acoustic frequency. The temperature inside the bubble reaches approximately 8000 K at its minimum radius.

(3) A bubble with sufficient absorption of microwave energy in benzene no longer contracts, and temperature inside the bubble exceeds 2000 K.

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