

## The cavitation induced Becquerel effect and the hot spot theory of sonoluminescence

**T. V. Prevenslik**

14B, Brilliance Court, Discovery Bay, Hong Kong

### **Abstract**

Over 150 years ago, Becquerel discovered the ultraviolet (UV) illumination of one of a pair of identical electrodes in liquid water produced an electric current, the phenomenon called the Becquerel effect. Recently, a similar effect was observed if the water surrounding one electrode is made to cavitate by focused acoustic radiation, which by similarity is referred to as the cavitation induced Becquerel effect. The current in the cavitation induced Becquerel effect was found to be semi-logarithmic with the standard electrode potential that is consistent with the oxidation of the electrode surface by the photo-decomposition theory of photoelectrochemistry. But oxidation of the electrode surface usually requires high temperatures, say as in cavitation. Absent high bubble temperatures, cavitation may produce vacuum ultraviolet (VUV) light that excites water molecules in the electrode film to higher  $\text{H}_2\text{O}^*$  energy states, the excited states oxidizing the electrode surface by chemical reaction. Solutions of the Rayleigh-Plesset (RP) equation during bubble collapse that include the condensation of water vapor show any increase in temperature or pressure of the water vapor by compression heating is compensated by the condensation of vapor to the bubble wall, the bubbles collapsing almost isothermally. Hence, the cavitation induced Becquerel effect is likely caused by cavitation induced VUV light at ambient temperature.

*Keywords:* cavitation; hot spot theory; sonoluminescence; photoelectrochemistry

Contact author: Thomas Prevenslik

Postal Address: 14B, Brilliance Court, Discovery Bay, Hong Kong

FAX: (852) 2987-8183

Email: [cavityqed01@yahoo.com](mailto:cavityqed01@yahoo.com)

## 1. Introduction

In 1839, Becquerel [1] discovered that electrical current flowed between a pair of electrodes if one electrode was illuminated with UV light, the phenomenon referred to as the Becquerel effect. Recently, electrical current was observed [2] between a pair of identical electrodes if one electrode was irradiated with focussed ultrasound, and because of similarity with the Becquerel effect is called the cavitation induced Becquerel effect.

In the cavitation induced Becquerel effect, the current is semi-logarithmic [3-4] with the standard electrode potential, a mathematical form consistent with the oxidation of the electrode in the photo-decomposition theory of photoelectrochemistry. But oxidation may only occur if cavitation produces high temperatures or VUV light.

High temperatures in cavitation are believed to produce the visible and UV photons observed in the phenomenon of sonoluminescence (SL). Many theories have been proposed to explain SL, but the hot spot theory [5] is generally accepted. By this theory, SL is caused by the incandescence produced during bubble collapse by the compressive heating of bubble gases. Currently, bubble gas temperature [6] from 20,000 to 30,000 K is predicted. In sonochemistry, the hot spot theory is thought [7] to produce temperatures as 'hot as the sun', i.e, about 5000 K, and thereby enhance chemical reaction rates of gaseous reactants.

The high bubble temperatures are usually determined with RP solutions [5-7] that treat the gas as non-condensable air while neglecting the pressure relief from the condensation of water vapor. But except for traces of air in the water, the bubble gas is fully water vapor, and therefore, the high temperatures computed are artifacts of the analysis assumptions. Recently, RP simulations [8] were performed that included condensation, but were based on condensation coefficients [9] based on falling drops for application to cloud formation in the atmosphere. For a condensation coefficient ( $\alpha = 0.075$ ), the bubble collapse temperature was found to vary between 5200 and 10,000 K.

But the condensation of vapor inside a bubble is very different than the condensation of water vapor on a drop in the atmosphere. The condensation coefficient may be defined at the sticking probability given as the fraction of vapor molecules colliding with the drop which condense, and once the molecules scatter, they are no longer available for subsequent collisions with the drop. In contrast, water molecules undergoing collisions with the bubble wall are always confined to the bubble, and if scattered are always available to stick to another location on the bubble wall. Therefore, the probability of water vapor sticking in the bubble is unity and far greater than the probability for vapor condensing on the falling drop. For the bubble, the condensation coefficient ( $\alpha = 1$ ) is equivalent (e.g., see [9,10]) to the accommodation coefficient ( $a_c = 1$ ).

But whether or not the analytical RP simulations predict high bubble temperatures, an isothermal collapse is nonetheless indicated on experimental grounds. Without a doubt, the bubble temperatures are less than about 690 K, as melting of the zinc electrode surface was not reported [2-4] in the cavitation induced Becquerel effect experiments. Moreover, it is a fact known to most undergraduate Chemistry students (e.g., see [11]) that reducing the volume of a 2 phase vapor-liquid system does not change its pressure and temperature, i.e., bubbles collapse isothermally at constant pressure. Hence, RP simulations giving high temperatures by assuming a bubble gas of non-condensable air [5-6] or using falling drop data for condensation coefficients [8] in the bubble can only be construed as erroneous. Bubble formation and vapor condensation in a 1D simulation using the syringe experiment [11] was performed at the UI 2001 Poster Session.

The purpose of this paper is to present RP simulations of bubble collapse that show the temperature and pressure of the water vapor in a collapsing bubble remain almost constant provided the water vapor is permitted to condense. A similar RP simulation [12] showed the bubble to collapse almost isothermally.

## 2. Theoretical Background

### 2.1 Bubble gases and relation to bubble radius

Liquid water contains a small fraction of air, at ambient temperature the solubility of air in water is about 0.0022% by weight. Thus, bubbles nucleated from the continuum in a single event, or by repeated events as in single bubble SL are comprised of water vapor in two-phase equilibrium with the liquid bubble wall, the bubbles containing only trace amounts of air. But as shown in Fig. 1, nucleation also leaves a spherical particle of liquid water molecules of radius  $R_c$  in the bubble, the particle separating from the bubble wall because of surface tension  $S$ , i.e.,  $R_c \sim 2 S / P_o$ , where  $P_o$  is ambient pressure. For water,  $S \sim 0.072$  N/m and  $R_c \sim 1.44$   $\mu\text{m}$ .

In a single nucleation event, the minimum bubble radius  $R_{min}$  always coincides with the particle radius  $R_c$  formed by surface tension in the continuum,  $R_{min} \sim R_c$ . However, in single bubble SL successive nucleation may not produce a particle if  $R_{min} > R_c$ . Single bubble SL is quantified by measurements [13] of the equilibrium radius  $R_o$ , where  $R_o > R_{min} > R_c$ . But the minimum radius  $R_{min}$  is not measured. Moreover, actual measurements of  $R_o$  are not made, but rather are inferred from video images illuminated by stroboscopic light. Thus, it is not clear whether the images are actual equilibrium bubble volumes or some larger volume of bubble break-up that is reflecting the stroboscopic light. For single bubble SL to be observed, the hot spot theory requires:  $1 < R_o < 7$   $\mu\text{m}$ ; whereas, the return of the bubble to the continuum requires,  $R_{min} = R_c$ .

### 2.2 RP equation and modification

In a spherical bubble, mass transfer of water vapor and air to the liquid water bubble walls may be assessed [14] with the RP equation. Neglecting surface tension and viscosity, the bubble radius  $R$  is given in terms of time  $t$  is,

$$P_B + P_a \sin(2\mathbf{p}ft + \mathbf{f}) - P_{atm} = \mathbf{r} \left[ R \frac{d^2 R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 \right] \quad (1)$$

where,  $P_B$  is the pressure beneath the surface of the bubble wall and  $P_{atm}$  is atmospheric pressure. The density  $\mathbf{r}$  of liquid water,  $\mathbf{r} \sim 1000 \text{ kg / m}^3$ . The acoustic pressure is simulated with an amplitude  $P_a$ , frequency  $f$ , and phase angle  $\mathbf{f}$ .

In the RP equation, the collapse velocity is,  $V_{collapse} \sim dR / dt$ . However, the RP equation is only valid if  $P_B < (P_{air} + P_{vap})$ , where  $P_{air}$  and  $P_{vap}$  are the pressure of the air and vapor in the bubble. If  $P_B > (P_{air} + P_{vap})$ , the RP equation is no longer valid and  $V_{collapse}$  requires modification. Instability causes the surface of the bubble wall to break-up to form micro-jets [12,15] that penetrate the interior of the bubble as illustrated in Fig. 1.

The bubble surface may be described as an irregular spherical surface of an average diameter  $2R$  defined by the separation between the tips of diametrically opposite jets. In the numerical solution of the RP equation, the  $P_B$  pressure is computed from Eqn. (1), the bubble radius  $R^*$  at the instability defined by the condition:  $P_B = (P_{air} + P_{vap})$ . After instability, the collapse velocity  $V_{collapse}$  is determined by applying the Bernoulli equation to a 1D streamline between  $R^*$  and the tip of the micro-jet, the bubble radius given by,

$$R = R^* - \int V_{collapse} dt \quad (2)$$

where, 
$$V_{collapse} \sim \sqrt{\left( \frac{dR^*}{dt} \right)^2 + \frac{2}{\mathbf{r}} (P_B - P_{vap} - P_{air})} \approx \frac{dR^*}{dt}$$

and,  $dR^* / dt$  is the flow velocity computed from the RP equation at  $R^*$ . The pressure contribution to collapse velocity  $V_{collapse}$  may be neglected giving  $V_{collapse} \sim dR^* / dt$ . Hence, the average bubble radius  $R$  after instability,

$$R = R^* - \int \frac{dR^*}{dt} dt \quad (3)$$

### 2.3 Perfect gas law

The air  $P_{air}$  and water vapor  $P_{vap}$  pressures are related to the mass of air  $W_{air}$  and vapor  $W_{vap}$  in the bubble by the perfect gas law.

$$W_{air} = \frac{M_{air} P_{air} V}{RT} \quad \text{and} \quad W_{vap} = \frac{M_{vap} P_{vap} V}{RT} \quad (4)$$

where,  $M_{air}$  and  $M_{vap}$  are the molecular weights of air and vapor. The temperature  $T$  and volume  $V$  are the same for both gas and vapor. Since the temperature of the gas and vapor is not expected to depart far from ambient because of the dominance of the water vapor-liquid equilibrium in the bubble, the temperature  $T$  is assumed to be a constant,  $T = 20 \text{ C} \sim 300 \text{ K}$ . For a spherical bubble having a bubble radius  $R$ , the volume  $V = 4\pi R^3 / 3$ .

### 2.4 Hertz-Knudsen relation and mass loss

The Hertz-Knudsen relation [16] gives the air and water vapor mass loss from the bubble for small temperature changes between liquid and vapor. The flux  $dN_{vap} / dt$  of the number of water vapor molecules condensing on a unit area of the bubble wall is,

$$\frac{dN_{vap}}{dt} = \frac{\mathbf{a}_c}{\sqrt{2\mathbf{p}m_{vap}kT}} (P_{vap} - P_{vapo}) \quad (5)$$

where,  $\mathbf{a}_c$  is the accommodation coefficient.  $P_{vapo}$  is the vapor pressure of liquid water at temperature  $T$ , i.e., at  $T \sim 20 \text{ C}$ ,  $P_{vapo} \sim 2339 \text{ Pa}$ . Boltzman's constant  $k$  is,  $k = 1.38 \times 10^{-23} \text{ J/K}$ . The mass  $m_{vap}$  of the water vapor molecules is  $m_{vap} = M_{vap} / N_{avag}$ , where Avagadro's number  $N_{avag}$  is,  $N_{avag} = 6.023 \times 10^{26} / \text{kg-mole}$ . A similar relation may be written for the flux  $dN_{air} / dt$  of the non-condensable air molecules that stick to the liquid water bubble wall surface,

$$\frac{dN_{air}}{dt} = \frac{\mathbf{a}_s}{\sqrt{2\mathbf{p}m_{air}kT}} (P_{air} - P_{airo}) \quad (6)$$

where,  $\mathbf{a}_s$  is the sticking coefficient. The  $P_{airo}$  pressure is similar to  $P_{vapo}$  in that both are pressures in the bubble just prior to collapse. The mass  $m_{air}$  of the air ( $\text{N}_2$  and  $\text{O}_2$ ) molecules

is  $m_{air} = M_{air} / N_{avag}$ . In an increment of time  $\Delta t$ , the mass  $\Delta W$  of vapor and air transferred to the bubble wall area  $A = 4\pi R^2$  is given by,

$$\Delta W_{vap} = 4p \frac{M_{vap}}{N_{avag}} \frac{dN_{vap}}{dt} R^2 \Delta t \quad \text{and} \quad \Delta W_{air} = 4p \frac{M_{air}}{N_{avag}} \frac{dN_{air}}{dt} R^2 \Delta t \quad (7)$$

The mass of vapor and air in the bubble at any time,

$$W_{vap} = W_{vapo} - \Delta W_{vap} \quad \text{and} \quad W_{air} = W_{airo} - \Delta W_{air} \quad (8)$$

where,  $W_{airo}$  is the mass of air in the bubble at nucleation, the mass  $W_{airo}$  contained in a spherical nucleation volume having a bubble radius  $R_o$  at atmospheric pressure  $P_{atm}$ . During isothermal expansion to the maximum bubble radius  $R_{max}$ , the air pressure  $P_{air}$  decreases to  $(R_o / R_{max})^3 P_{atm}$ . In contrast, the vapor pressure  $P_{vap}$  remains at  $P_{vapo}$  as the bubble expands, the vapor mass increasing to a value of  $W_{vapo}$  at the maximum bubble radius  $R_{max}$ .

## 2.5 Average molecular random velocity

Mass loss by collisions of air and vapor molecules with the bubble wall is delayed [15] by collisions with other molecules within the bubble. If the air molecules move in a random walk the average time  $t_{air}$  for an air molecule to move from the center of the bubble and collide with the wall at a radius  $R$  is given by,

$$t_{air} = \frac{R^2}{mfp V_{air}} \quad (9)$$

where,  $V_{air}$  is the RMS velocity and  $mfp$  is the mean free path of the air ( $N_2$ ,  $O_2$ ) molecule.

$$V_{air} = \sqrt{\frac{3kT}{m_{air}}} \quad \text{and} \quad mfp = \frac{kT}{\sqrt{2}p (P_{air} + P_{vap}) d^2} \quad (10)$$

where,  $d$  is the diameter of the air molecule, say  $d \sim 0.291$  nm. The average random velocity  $V_{r,air}$  is,

$$V_{r,air} \sim \frac{R}{t_{air}} = \frac{mfp V_{air}}{R} \quad (11)$$

Similar relations  $t_{vap}$ ,  $V_{vap}$ , and  $V_{r,vap}$  may be written for the water vapor molecules.

## 2.6 Mass of air, and diffusion of air molecules from the liquid bubble wall.

The mass  $W_{air}$  of air in the bubble is taken to be that contained in the volume of the nucleation site at ambient temperature and pressure. Typically, RP simulations in the hot spot theory [5-6] assume a spherical nucleation site with a radius  $R_o \sim 5 \mu\text{m}$ . But this overstates the air mass in the bubble, as a typical nucleation site comprises only an infinitesimally small annular space surrounding the particle of radius  $R_c$ . Only a few air molecules are present in the space, but even as the bubble grows additional air does not diffuse into the bubble from the liquid bubble wall. To justify this assertion, consider the characteristic diffusion time  $t_d$  for dissolved air at a concentration  $C_o$  in the liquid water bubble wall to diffuse [17] into a bubble of radius  $R$ ,

$$t_d = \frac{\mathbf{r}_{air} R^2}{DC_o} \quad (12)$$

where,  $\mathbf{r}_{air}$  is the density of air,  $D$  is the diffusion constant for air in liquid water,  $\mathbf{r}_{air} \sim 1.2 \text{ kg/m}^3$ ,  $D \sim 2 \times 10^{-9} \text{ m}^2/\text{s}$ . At  $T \sim 20 \text{ C}$ , the Ostwald coefficient for air in water is about 0.0188 that corresponds to a concentration  $C_o \sim 0.022 \text{ kg of air / m}^3 \text{ of liquid water}$ , or 0.0022 % by weight. For a bubble collapsing from a maximum radius  $R_{max} \sim 40 \mu\text{m}$ , an average radius of  $20 \mu\text{m}$  gives the diffusion time  $t_d \sim 10 \text{ s}$ . Diffusion of air into the bubble may be neglected because the diffusion time  $t_d$  is long compared to the period  $\mathbf{t}$  of the acoustic vibration, i.e.,  $\mathbf{t} \sim f^{-1}$ , and for  $f = 26.5 \text{ kHz}$ ,  $\mathbf{t} \sim 40 \mu\text{s} \ll 10 \text{ s}$ . Not only is the amount of air in the bubble at the instant of nucleation insignificant, it remains so, as the bubble grows and collapses.

## 3. Analysis and results

The RP equation was solved for acoustic pressure amplitudes  $P_a \sim 1.3$  and  $1.6 P_{atm}$ , frequency  $f \sim 26.5 \text{ kHz}$ , and a phase angle  $\mathbf{f} \sim 45$  degrees. Bubble responses were initiated at a radius  $R_o \sim 5 \mu\text{m}$  and the minimum  $R_{min}$  bubble radii was limited to  $0.5 \mu\text{m}$ . The Hertz-Knudsen relation assumes an accommodation coefficient  $\mathbf{a}_c \sim 1$  for the condensation [9,10]



of water vapor. The sticking coefficient  $\mathbf{a}_s \sim 2/3$  for air on liquid water is based on the sticking coefficients for NO and SO<sub>2</sub> computed [18] by molecular dynamics. Fig. 2 shows the bubble radius  $R$  response for  $P_a \sim 1.3$  and  $1.6 P_{atm}$ , the maximum bubble radius  $R_{max}$  is about 80 and 53  $\mu\text{m}$ , respectively.

The  $P_a \sim 1.3$  and  $1.6 P_{atm}$  pressure and velocity solutions in the collapse from  $R_{max}$  to  $R_{min}$  are shown in Figs. 3 and 4, respectively. For clarity, only bubble collapse is shown, the collapse proceeding on the plots from right-to-left. Figs. 3(a) and 4(a) give pressure ratios  $P_{vap} / P_{vapo}$ ,  $P_{air} / P_{atm}$  and  $P_B / P_{vap}$  and Figs. 3(b) and 4(b) give velocities  $V_{collapse}$ , and  $V_{r,air}$  for air and  $V_{r,vap}$  for vapor. The instability ratio  $P_B / P_{vap}$  is used instead of  $P_B / (P_{air} + P_{vap})$  because  $P_{air} \ll P_{vap}$ .

The  $P_a \sim 1.3 P_{atm}$  solution shows an increase in  $P_B / P_{vap}$  as the bubble collapses from  $R_{max}$ , the instability observed to occur at a bubble radius  $R^* \sim 26 \mu\text{m}$ . The  $P_{vap} / P_{vapo}$  ratio at  $R_{min}$  is about 5 giving a vapor pressure  $P_{vap} \sim 12,000$  Pa, the temperature  $T$  of the water vapor increases to about 50 C, an insignificant amount. The maximum collapse velocity  $V_{collapse}$  is about 128 m/s. The  $P_{air} / P_{atm}$  ratio at  $R_{min}$  increases to about 0.07.

The  $P_a \sim 1.6 P_{atm}$  solution shows an increase in  $P_B / P_{vap}$  as the bubble collapses from  $R_{max}$ , the instability observed to occur at a bubble radius  $R^* \sim 40 \mu\text{m}$ . The  $P_{vap} / P_{vapo}$  ratio at  $R_{min}$  is about 10 giving a vapor pressure  $P_{vap} \sim 23,000$  Pa, the temperature  $T$  of the water vapor increases to about 64 C, almost isothermal. The maximum collapse velocity  $V_{collapse}$  is about 150 m/s. The  $P_{air} / P_{atm}$  ratio at  $R_{min}$  increases to about 0.09.

#### 4. Discussion

The RP solutions show the two-phase equilibrium for water tends to maintain the water vapor at ambient temperature and pressure as the bubble volume vanishes. The air in the bubble does indeed increase in temperature and pressure as the bubble collapses. But any increase in air temperature is insignificant because the air undergoes numerous

collisions with water vapor molecules that are being maintained at ambient temperature. The RP solutions presented here are consistent with the physics of water vapor-liquid equilibrium, i.e., pressure and temperature remain constant with changes in volume. Hence, any compression heating of the vapor tends to be compensated by the condensation of water vapor to the bubble wall. Indeed, the average random velocities of the air and vapor molecules generally exceed the collapse velocity of the bubble wall, thereby permitting the bubble contents to collect on the bubble walls and not be available for compression heating.

Water vapor-liquid equilibrium precludes any increase in pressure of the vapor state during bubble collapse at least until the bubble walls collide. Upon collision, high-pressure shocks develop in the liquid state. However, the temperature of the air entrained in the liquid water at the instant of collision does not increase because of the massive cooling by the surrounding water molecules. Unequivocally, bubble collapse produces high pressure at ambient temperature, and although for different reasons is consistent with Rayleigh's intuitive assumption [19] of an isothermal bubble collapse in 1917.

## **5. Conclusions**

High bubble temperatures do not occur in bubble collapse. In fact, bubble collapse occurs almost isothermally at ambient temperature. Electrical current in the cavitation induced Becquerel effect is most likely caused by the chemical oxidation of the electrode surface by excited  $\text{H}_2\text{O}^*$  states from VUV light produced in cavitation at ambient temperature.

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## FIGURE CAPTIONS

Fig. 1. RP equation modified for instability

Fig.2 Bubble radius  $R$  response for  $P_a \sim 1.3$  and  $1.6 P_{atm}$

Fig. 3.  $P_a \sim 1.3 P_{atm}$  solution. (a) pressure ratios. (b) velocities

Fig. 4.  $P_a \sim 1.6 P_{atm}$  solution. (a) pressure ratios. (b) velocities

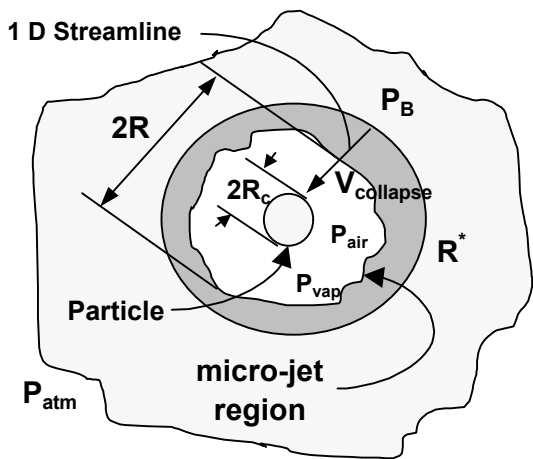


Fig. 1

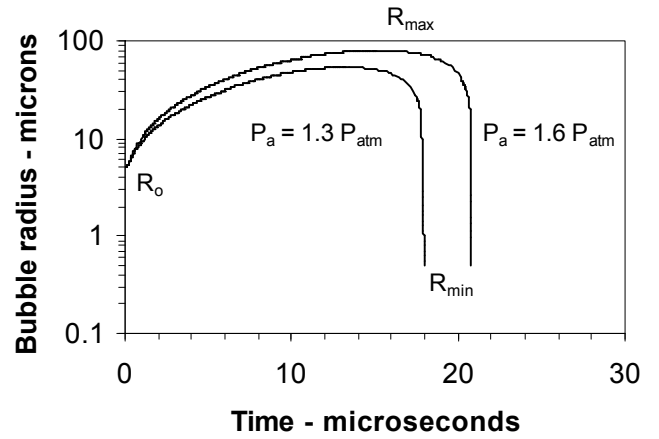


Fig. 2

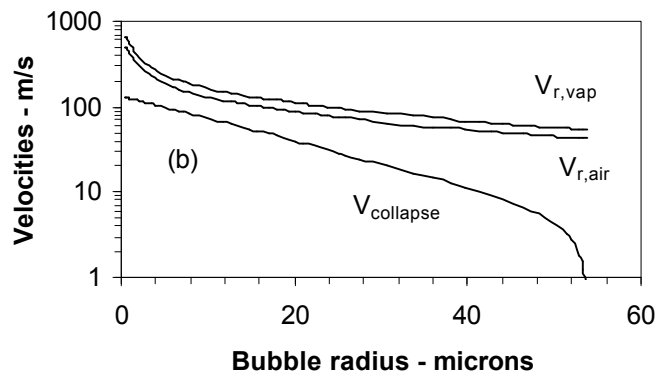
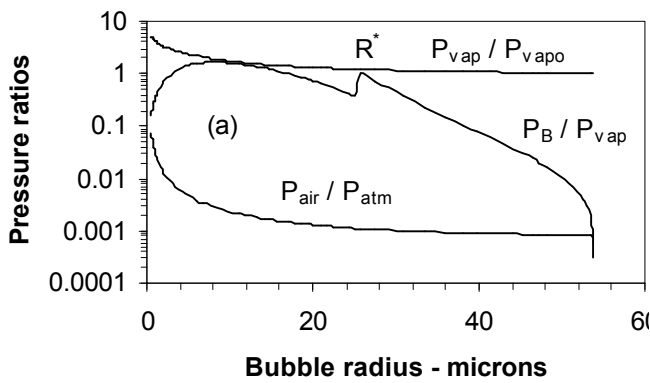


Fig. 3

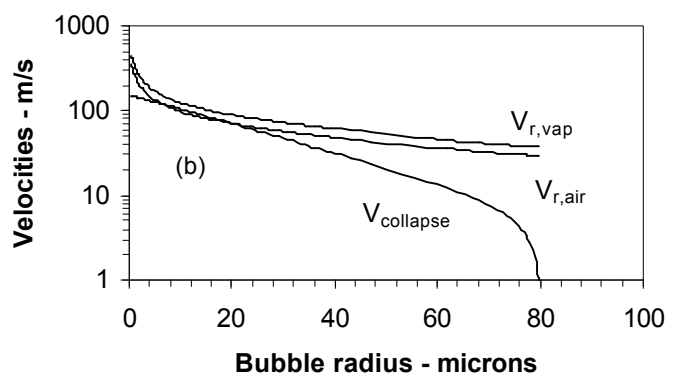
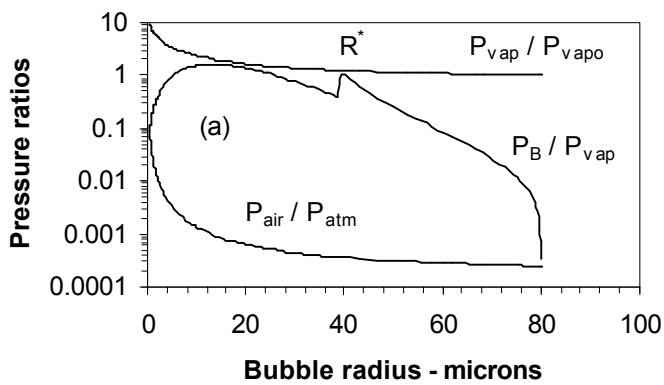


Fig. 4