

Theoretical and Experimental Sonochemistry Involving Inorganic Systems

Pankaj • Muthupandian Ashokkumar
Editors

Theoretical and Experimental Sonochemistry Involving Inorganic Systems

 Springer

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Foreword

I began my research into Sonochemistry over 30 years ago now and at that time it was for me an exploration of the unknown. In 1988 with my colleague Phil Lorimer we wrote the first book to carry in its title the word Sonochemistry with a subtitle “Theory applications and uses of ultrasound in chemistry”. In recent years, *Sonochemistry* has shown significant growth in a variety of fields no longer limited to chemistry with special attention being paid to materials science, environmental protection, food technology and therapy. Indeed the overall breadth of sonochemistry is expanding to such an extent that it now encompasses hybrid technologies involving combinations of ultrasound with electrochemistry, photochemistry and microwaves. In particular great attention has been focused on the synthesis of functional nano- and micro-particles involving both biological and inorganic materials.



The publication of new text books and monographs reflects the health of a subject and so it is with great pleasure that I write this Foreword for the book, *Theoretical and Experimental Sonochemistry Involving Inorganic Systems*, Edited by Professors Pankaj and Ashokkumar.

Theoretical and Experimental Sonochemistry Involving Inorganic Systems is a unique compilation of theoretical and experimental studies involving water based systems and chemical rather than biological species. This is really where sonochemistry began and so it is appropriate to have the more recent studies in aqueous systems brought together in one volume. When ultrasound is introduced into such systems the chemistry becomes quite fascinating as a result of the influence of acoustic cavitation both from the points of view of chemical and physical effects. This book contains chapters that deal with various aspects of sonochemical research

in aqueous solutions with a particular emphasis on inorganic systems. This will be an important text for all those interested in or directly involved with current sonochemistry research.

September 2010

Timothy J. Mason
Professor of Chemistry
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Preface

The themes of several books published in the field of sonochemistry revolve around physical and chemical aspects involving mainly organic chemistry or a combination of physics, chemistry and other areas. The sonochemical studies involving inorganic reactions, although numerous, are scarcely discussed and compiled in the existing literature. This prompted us to editing this book. This was welcomed and has been made successful by many contributors, as can be seen through various chapters of this book. Besides, the availability of a book devoted to inorganic systems in sonochemistry may also help undergraduate students, juvenile workers and senior researchers alike to learn about sonochemistry and publicize the sonochemistry research field to a much broader community.

The book offers a theoretical introduction in the first three chapters, provides recent applications in material science in the next four chapters, describes the effects of ultrasound in aqueous solutions in the following five chapters and finally discusses the most exciting phenomenon of sonoluminescence in aqueous solutions containing inorganic materials in subsequent two chapters, before ending with a few basic introductory experiments of sonochemistry and sonoluminescence in the concluding chapter.

Prof. Yasui discussed the fundamentals of acoustic cavitation and sonochemistry through the splitting of water to generate free radicals as a consequence of exceptionally high temperatures, pressures and mass flow conditions generated during acoustic cavitation in solutions. Dr. Gogate has discussed the design aspects of cavitation reactors and examined the effect of intensity and frequency of ultrasound, geometry of the reactor, physicochemical properties of liquids and the operational temperature on the intensity of cavitation for the maximization of process efficiencies. Later, Dr. Gogate and Prof. Pandit have described the phenomenon of hydrodynamic cavitation for the scale up operation of several physical, chemical and biological processes. Prof. Garcia has discussed the combined effects of electrochemistry and ultrasound for the production of gas, metal deposits and metal oxides, in addition to providing a summary of the fundamental aspects, experimental set-up and different applications of a rather new field of applied

sonoelectrochemistry. Prof. Okitsu has illustrated the synthesis of metal nanoparticles and the effects of dissolved gases, rate of reduction and the concentration of organic additives on the size and shapes of nanoparticles. To advance the portrayal further, Assistant Prof. Anandan and Prof. Ashokkumar have provided additional information on the sonochemical preparation of monometallic, bimetallic and metal loaded semiconductor nanoparticles. In continuation with these reviews, Associate Prof. Sonawane and Dr. Kulkarni have described the sonochemical synthesis of nanocalcium carbonate through the acoustic and hydrodynamic cavitations. Associate Prof. Sivakumar has summarized various kinds of simple and mixed oxides and sulphides obtained in the last few years through sonochemical processes. Prof. Pankaj has discussed the effect of ultrasound propagation in aqueous solutions in the atmospheres of inert and reactive gases and the precipitation behavior of hydroxides of several di- and tri-valent metal ions, besides reporting the results of nephelometric and conductometric studies of sonicated solutions of these metal ions. Prof. Pankaj and Dr. Chauhan further reported the redox characteristics of ferrous and ferric ions in aqueous solutions and a comparative account of the oxidizing power of permanganate and dichromate ions, under the influence of ultrasound. In the next two chapters, Mr Verma and Prof. Pankaj have advanced the description of sonophotocatalytic degradation of phenol and several amines and also found a very interesting improvement of such degradation in the presence of rare earth ions, co-added with the photocatalyst, titanium dioxide. Other conventional methods for the degradation of these species in aqueous solutions have been compared with the sonochemical treatment processes. To explain a relatively difficult but equally fascinating consequence of high intensity ultrasound, Prof. Choi has discussed the phenomenon of sonoluminescence from aqueous solutions containing inorganic ions, especially alkali metal atom emission in aqueous solutions in various environments and described the emission mechanism, supporting the gas phase origin of the emission. Finally, Dr. Brotchie, Prof. Grieser and Prof. Ashokkumar have discussed the role of salts in acoustic cavitation and the use of inorganic complexes as cavitation probes to infer invaluable quantitative information regarding the temperature and pressure at the time of cavitation bubble collapse. Few basic experiments of sonochemistry and sonoluminescence have also been described in the last segment of the book.

Besides the contributors of various chapters, we also wish to acknowledge the support and critical evaluation of the chapters by several professionals (cannot be named due to confidentiality) who reviewed the articles in a timely manner.

We sincerely hope that this book is immensely beneficial to graduate students and researchers to learn the fundamental aspects of cavitation and to launch new research activities in the sonochemistry research field. The readers will also realize that sonochemistry is not just limited to “chemistry” but has the potential to incorporate in other areas including physics, engineering, biochemistry and medicine.

Agra, India
Melbourne, Australia
June 2010

Pankaj
Muthupandian Ashokkumar

About the Editors

Professor Pankaj is a graduate and Ph.D. from Lucknow University, India (1982) with specialization in Inorganic Chemistry and a victor of M Raman Nayer Gold Medal. From his initial work on the studies of solvent properties of non-aqueous solvents and later on the measurement of ultrasonic velocity, Prof. Pankaj switched over to sonochemical studies in aqueous solutions involving inorganic systems, after his European Community Post-Doctoral Fellowship (1990 – 91) at the Department of Physics, University of Surrey, UK. He has published ~50 papers in peer reviewed national and international journals and contributed chapters to 5 books. He is a recipient of grants from agencies such as UGC, AICTE, DST & DAE-BRNS. Prof. Pankaj is also the *Executive Editor* of the Journal of Indian Council Chemists and reviewer for several national and international journals like Canadian J Chemical Engineering; CLEAN – Soil, Air, Water; Ind. J. Chem. and Ind. J. Pure Appl. Ultrasonics. He is a Fellow of Ultrasonic Society of India and Indian Council of Chemists.



Professor Muthupandian Ashokkumar (Ashok) is a Physical Chemist who specializes in Sonochemistry, teaches undergraduate and postgraduate Chemistry and is a senior academic staff member of the School of Chemistry, University of Melbourne. Ashok is a renowned sonochemist who has developed a number of novel techniques to characterize acoustic cavitation bubbles and has made major contributions of applied sonochemistry to the Food and Dairy industry. His research team has developed a novel ultrasonic processing technology for improving the functional properties of dairy ingredients. Recent research also involves the ultrasonic synthesis of functional



nano- and biomaterials including protein microspheres that can be used in diagnostic and therapeutic medicine. He is an Editorial Board Member of *Ultrasonics Sonochemistry*, an international journal devoted to sonochemistry research. He has edited/co-edited several books and special issues for journals; published ~200 refereed papers in high impact international journals and books; and delivered over 100 invited/keynote/plenary lectures at international conferences and academic institutions. Ashok is the recipient of several prizes, awards and fellowships, including the Grimwade Prize in Industrial Chemistry. He is a Fellow of the Royal Australian Chemical Institute.

Acknowledgement

Prof. Ram Gopal, my Ph.D. supervisor had rightly said about 30 years back that science could not be pursued lifelong unless enjoyed, without me realizing that it is eventually coming to happen in my life too. Towards the end of my Ph.D. work, in early eighties, I read about ultrasound – a word which fascinated me and I drifted towards measuring ultrasonic velocity in non-aqueous solvents of high dielectric constant and their solutions, interpreting their variations in terms of thermodynamic parameters. But the real contact with sonochemistry was through Prof. R.C. Chivers, my supervisor for European Community Post Doctoral fellowship at the University of Surrey, UK, who fixed my appointment with Prof. T.J. Mason in early nineties, when sonochemistry was still in its infancy. However, limitations of finance, space and culture of working in an apprehensive small Indian University later was always only an impediment but, of course, never a barrier to my motivation. The initial sonochemical results of my students, different from conventional chemical reactions of aqueous wet chemistry always stimulated me to stick to this field.

The idea of writing a book on inorganic sonochemistry originated way back in 2000 but turned to reality only recently when discussed with Dr. Sonia Ojo from Springer UK. She thankfully introduced me to Prof. Muthupandian Ashokkumar, University of Melbourne, Australia, a very well known name in the area of sonochemistry and sonoluminescence, to accomplish the task. Furthermore, I would also like to acknowledge Mrs. Claudia Culierat from Springer UK for her instantaneous and supportive attention to all my queries related to editorial assistance.

With all humility, I acknowledge the initial strength derived for this book from Dr. Ashok Kumar, Head, Ultrasonics Division, National Physical Laboratory, New Delhi, besides the unwavering encouragement from Dr. G.C. Saxena, Ex VC, Awadh University, Faizabad and Dr. BR Ambedkar University, Agra and Prof. P. Muruthamuthu, Ex VC Madurai Kamraj University, Dr. G.N. Pandey, BRNS and Dr. A.K. Tripathi, BARC.

I cannot close the eyes to admit a very patient, silent and supportive co-operation of my compassionate wife, Dr. Hemlata Srivastava and two considerate sons, Abhijit Srivastav and Arpit Srivastava, who suffered seclusion and neglect due to my invariable involvement with the book for about 1 year. Last, but not the least my gratitude to all my friends and well wishers, who through their admiration or criticism added directly or indirectly to my strength and inspired vigorously to complete the task in the form as it is today.

Agra, India
June 2010

Prof. Pankaj

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Chapter 1

Fundamentals of Acoustic Cavitation and Sonochemistry

Kyuichi Yasui

Abstract Acoustic cavitation is the formation and collapse of bubbles in liquid irradiated by intense ultrasound. The speed of the bubble collapse sometimes reaches the sound velocity in the liquid. Accordingly, the bubble collapse becomes a quasi-adiabatic process. The temperature and pressure inside a bubble increase to thousands of Kelvin and thousands of bars, respectively. As a result, water vapor and oxygen, if present, are dissociated inside a bubble and oxidants such as OH, O, and H₂O₂ are produced, which is called sonochemical reactions. The pulsation of active bubbles is intrinsically nonlinear. In the present review, fundamentals of acoustic cavitation, sonochemistry, and acoustic fields in sonochemical reactors have been discussed.

1.1 Introduction

An acoustic wave (sound) is a propagation of pressure oscillation in medium such as air or liquid water with the sound velocity [1]. Ultrasound is inaudible sound and its frequency of pressure oscillation is above 20 kHz (20,000 oscillations per second) [2]. For convenience, an acoustic wave above 10 kHz in frequency is sometimes called an ultrasonic wave.

When the pressure amplitude of an acoustic wave in liquid or solid exceeds the ambient pressure (atmospheric pressure), the instantaneous pressure becomes *negative* during the rarefaction phase of an acoustic wave. *Negative* pressure is defined as the force acting on the surface of a liquid (or solid) element per surface area to expand the element [3, 4]. For example, consider a closed cylinder filled with liquid

K. Yasui (✉)

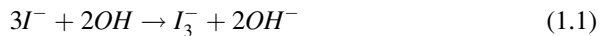
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with a movable piston. When a piston is pulled strongly, the liquid volume slightly increases. At this moment, the pressure in the liquid is *negative*. *Negative* pressure is possible only in liquid or solid.

When the instantaneous local pressure becomes *negative* in liquid irradiated by ultrasound, bubbles are generated because gas such as air dissolved in the liquid can no longer be dissolved in the liquid under *negative* pressure, which is called acoustic cavitation [5, 6]. For a static condition, vapor bubbles are generated when the static pressure is lower than the saturated vapor pressure, which is called boiling. In many cases of acoustic cavitation, the instantaneous local pressure should be negative because the duration of low pressure is short.

The difference between acoustic cavitation and boiling is the collapse of bubbles in acoustic cavitation. Under ultrasound, a generated bubble expands during the rarefaction phase and collapses during the compression phase. The speed of the bubble collapse increases to the sound velocity in liquid. Accordingly, the bubble collapse is a quasi-adiabatic process where “quasi” means that considerable thermal conduction takes place between the interior of a bubble and the surrounding liquid. The temperature and pressure inside a bubble increase to thousands of Kelvin and thousands of bars, respectively at the end of the bubble collapse [7]. Furthermore, a bubble emits a shock wave into the surrounding liquid just after the end of the bubble collapse [8-11]. This bubble collapse is absent in boiling.

As the temperature and pressure dramatically increase inside a bubble at the end of the collapse, water vapor and oxygen, if present, are dissociated inside a bubble and oxidants such as OH, O, and H₂O₂ are created [12, 13]. They dissolve into the liquid and solutes are oxidized by them. This is called sonochemical reaction. For example, potassium iodide (KI) in aqueous solution is oxidized by the irradiation of ultrasound ((1.1)), and the solution is gradually colored by the product (I₃⁻) as the irradiation time increases.



1.2 Acoustic Cavitation

1.2.1 *Transient and Stable Cavitation*

There are two types in acoustic cavitation. One is transient cavitation and the other is stable cavitation [14, 15]. There are two definitions in transient cavitation. One is that the lifetime of a bubble is relatively short such as one or a few acoustic cycles as a bubble is fragmented into daughter bubbles due to its shape instability. The other is that bubbles are active in light emission (sonoluminescence (SL)) or chemical reactions (sonochemical reactions). Accordingly, there are two definitions in stable cavitation. One is that bubbles are shape stable and have a long lifetime. The other is that bubbles are inactive in SL and chemical reactions. There exist

some bubbles which are both shape stable and active in SL or chemical reactions. They are classified into stable cavitation bubbles by the former definition and called “high-energy stable cavitation” bubbles. On the other hand, they are classified into transient cavitation bubbles by the latter definition and called “repetitive transient cavitation” bubbles. Whenever the terms transient and stable cavitation are used, it is necessary to indicate which definition is used, shape stability or activity.

In Fig. 1.1, the parameter space for transient and stable cavitation bubbles is shown in R_0 (ambient bubble radius) – p_a (acoustic amplitude) plane [15]. The ambient bubble radius is defined as the bubble radius when an acoustic wave (ultrasound) is absent. The acoustic amplitude is defined as the pressure amplitude of an acoustic wave (ultrasound). Here, transient and stable cavitation bubbles are defined by their shape stability. This is the result of numerical simulations of bubble pulsations. Above the thickest line, bubbles are those of transient cavitation. Below the thickest line, bubbles are those of stable cavitation. Near the left upper side, there is a region for bubbles of “high-energy stable cavitation” designated by “Stable (strong nf_0)”. In the brackets, the type of acoustic cavitation noise is indicated. The acoustic cavitation noise is defined as acoustic emissions from

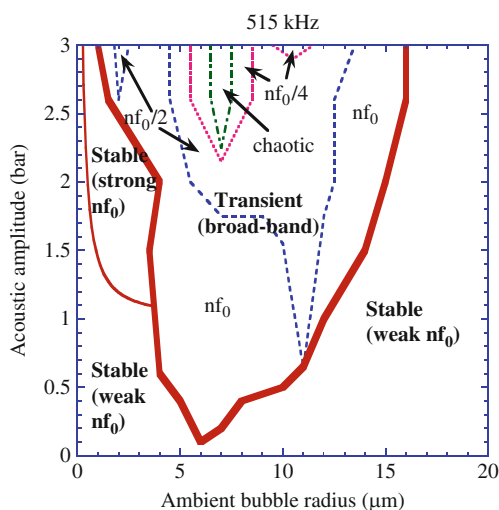


Fig. 1.1 The regions for “transient” cavitation bubbles and “stable” cavitation bubbles when they are defined by the shape stability of bubbles in the parameter space of ambient bubble radius (R_0) and the acoustic amplitude (p_a). The ultrasonic frequency is 515 kHz. The thickest line is the border between the region for “stable” cavitation bubbles and that for “transient” ones. The type of bubble pulsation has been indicated by the frequency spectrum of acoustic cavitation noise such as nf_0 (periodic pulsation with the acoustic period), $nf_0/2$ (doubled acoustic period), $nf_0/4$ (quadrupled acoustic period), and chaotic (non-periodic pulsation). Any “transient” cavitation bubbles result in the broad-band noise due to the temporal fluctuation in the number of bubbles. Reprinted from *Ultrasonics Sonochemistry*, vol. 17, K.Yasui, T.Tuziuti, J. Lee, T.Kozuka, A.Towata, and Y. Iida, Numerical simulations of acoustic cavitation noise with the temporal fluctuation in the number of bubbles, pp. 460–472, Copyright (2010), with permission from Elsevier

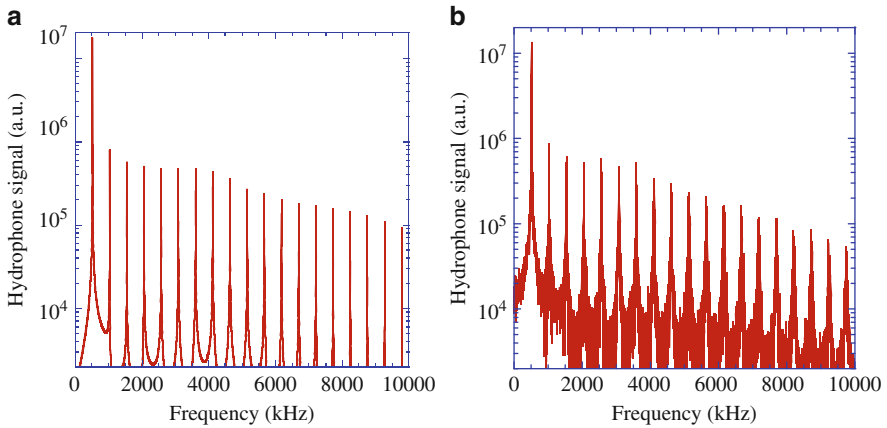


Fig. 1.2 Numerically simulated frequency spectra of the hydrophone signal due to acoustic cavitation noise. The driving ultrasound is 515 kHz in frequency and 2.6 bar in pressure amplitude. (a) For stable cavitation bubbles of 1.5 μm in ambient radius. (b) For transient cavitation bubbles of 3 μm in ambient radius. Reprinted from *Ultrasonics Sonochemistry*, vol. 17, K. Yasui, T. Tuziuti, J. Lee, T. Kozuka, A. Towata, and Y. Iida, Numerical simulations of acoustic cavitation noise with the temporal fluctuation in the number of bubbles, pp. 460–472, Copyright (2010), with permission from Elsevier

acoustic cavitation. Every pulsating bubble under ultrasound radiates a secondary acoustic wave, which is the origin of the acoustic cavitation noise. “Strong nf_0 ” means that strong harmonics components are to be observed in the frequency spectrum of acoustic cavitation noise (Fig. 1.2a) [15]. In Fig. 1.2a, the harmonics components are seen as sharp peaks. From the other space in Fig. 1.1 for stable cavitation bubbles designated by “stable (weak nf_0)”, the harmonics components are very weak as the bubble pulsation is much milder. From transient cavitation bubbles, broad-band noise is to be observed as well as the harmonics components (Fig. 1.2b). The broad-band noise is the continuum component in the frequency spectrum of the acoustic cavitation noise. According to Ref. [15], temporal fluctuation in the number of bubbles results in the broad-band noise. In transient cavitation, bubbles occasionally fragment into daughter bubbles, coalesce each other, and are nucleated, which results in the temporal fluctuation in the number of bubbles. Some bubbles pulsate with the period of $2T$ or $4T$ where T is the acoustic period, which results in the subharmonic and ultraharmonic components in the acoustic cavitation noise. The relationship between the type of cavitation and the acoustic cavitation noise is listed in Table 1.1. Some bubbles pulsate non-periodically as designated by “chaotic”, which also results in the broad-band noise without any peaks. However, its contribution to the total broad-band noise is minor at least under the condition studied in Fig. 1.1 [15].

From Fig. 1.1, it is seen that stable cavitation bubbles are tiny bubbles of a few μm in ambient radius or relatively large bubbles of about 10 μm or more in radius at 515 kHz. The range of ambient radius for transient cavitation bubbles becomes

Table 1.1 The relationship between the type of cavitation bubbles and that of the cavitation noise spectrum in the parameter space shown in Fig. 1.1. “Chaotic (initial transient)” means non-periodic pulsation only at the initial transient stage although the pulsation becomes periodic at the steady-state. Reprinted from *Ultrasonics Sonochemistry*, vol. 17, K.Yasui, T. Tuziuti, J. Lee, T. Kozuka, A. Towata, and Y. Iida, Numerical simulations of acoustic cavitation noise with the temporal fluctuation in the number of bubbles, pp. 460–472, Copyright (2010), with permission from Elsevier

Type	Pulsation	Noise spectrum
Stable (Low energy)	Periodic (period T)	Weak nf_0
(High energy)	Periodic (period T)	Strong nf_0
Transient	Periodic (period T)	nf_0 + broad-band
	Periodic (period 2T)	$nf_0/2$ + broad-band
	Periodic (period 4T)	$nf_0/4$ + broad-band
	Chaotic (steady-state)	Broad-band
	Chaotic (initial transient)	Broad-band

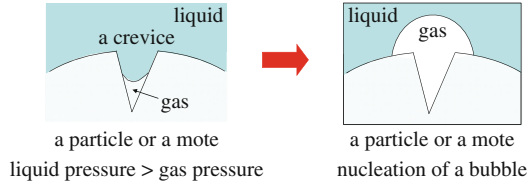
wider as the acoustic amplitude increases and ultrasonic frequency decreases [16]. Roughly speaking, stable cavitation bubbles are more frequently seen when acoustic amplitude is lower and ultrasonic frequency is higher [17]. In other words, transient cavitation bubbles are more frequently seen when acoustic amplitude is higher and ultrasonic frequency is lower. It is possible to control the population of stable cavitation bubbles relative to that of transient ones by the addition of a surfactant to the liquid because coalescence of bubbles is strongly retarded by a surfactant and the ambient radius of bubbles becomes sufficiently small for stable cavitation bubbles as described in 1.3.4 [15, 18, 19].

There is another experimental method to distinguish between transient and stable cavitation bubbles. According to the experiment of Guan and Matula [20], light emission (sonoluminescence (SL)) from a pulsating bubble is completely quenched in the presence of methanol in liquid water after about 8000 acoustic cycles. It is because quenching requires the repetitive injection of alcohol molecules into a pulsating bubble resulting in the accumulation of hydrocarbon products within the bubble. It means that only stable cavitation bubbles which have a long lifetime exhibit complete SL quenching in the presence of alcohol. In other words, transient cavitation bubbles do not exhibit complete SL quenching. Thus, by the experimental observation of SL quenching by the addition of alcohol, transient and stable cavitation bubbles can be distinguished [17]. It should be noted that transient and stable cavitation are defined here by the lifetime of bubbles (shape stability).

1.2.2 Nucleation of Bubbles

How is a bubble created in acoustic cavitation? There are three mechanisms in nucleation of a bubble in acoustic cavitation [14]. One is the nucleation at the surface of solids such as a liquid container, motes or particles in liquid, if present. Nucleation takes place especially at crevices of motes, particles or a liquid container (Fig. 1.3).

Fig. 1.3 Nucleation of a bubble from a crevice



In a crevice, the surface of a gas pocket is concave and the surface tension of a gas pocket *reduces* the pressure inside a pocket. It means that a gas pocket is stabilized against dissolution into the liquid because the partial pressure of dissolved gas in the liquid is possibly higher than that in a gas pocket. When the liquid is irradiated by ultrasound, a gas pocket in a crevice expands during the rarefaction phase of ultrasound and gas diffuses into the pocket from the surrounding liquid as the pressure inside a pocket further decreases. During the compression phase of ultrasound, a gas pocket shrinks and the gas pressure increases in a pocket. It results in the diffusion of gas out of a pocket into the liquid. Nevertheless, a gas pocket grows as the amount of gas diffusing into the pocket during the expansion is larger than that diffusing out of the pocket during the compression. This is because the surface area of a pocket is larger during expansion than that during compression (the area effect). Furthermore, the boundary layer for gas diffusion in the liquid is thinner during expansion than that during compression because the volume of the boundary layer is nearly constant and the surface area is larger during expansion (the shell effect). It results in the higher rate of diffusion during expansion because the gradient in concentration of the gas in the liquid is larger. Finally, a gas bubble is created from a crevice when the gas pocket sufficiently grows. The presence of particles in liquid reduces the threshold acoustic pressure for cavitation due to the above mechanism [21–23].

The second mechanism for nucleation is the initially present bubble nuclei which are stabilized against dissolution by the coverage of its surface with surfactants slightly present in the liquid as impurities. Without surfactants, bubbles with radius smaller than $1\ \mu\text{m}$ should dissolve within a few seconds in the absence of ultrasound unless the liquid is supersaturated with gas [24]. It is because the gas pressure inside a bubble is larger than the partial pressure of the dissolved gas in the liquid due to surface tension of a bubble (The excess pressure of the gas inside a bubble is $\Delta p = 2\sigma/R$, where σ is the surface tension and R is the bubble radius). Thus the gas inside a bubble gradually dissolves into the surrounding liquid. On the other hand, bubbles larger than $1\ \mu\text{m}$ in radius should float to the liquid surface by a buoyant force. Nevertheless, bubble nuclei (tiny bubbles of a few μm in radius) have been experimentally observed in liquids even in the absence of an acoustic wave (ultrasound) [6]. It suggests that such bubble nuclei are stabilized by surfactants which strongly retard the mass (gas) diffusion across the bubble surface. Under ultrasound, these stabilized nuclei grow by coalescence and gas diffusion, which initiates acoustic cavitation.

The third mechanism for nucleation is the fragmentation of active cavitation bubbles [16]. A shape unstable bubble is fragmented into several daughter bubbles which are new nuclei for cavitation bubbles. Shape instability of a bubble is mostly induced by an asymmetric acoustic environment such as the presence of a neighboring bubble, solid object, liquid surface, or a traveling ultrasound, or an asymmetric liquid container etc. [25–27] Under some condition, a bubble jets many tiny bubbles which are new nuclei [6, 28]. This mechanism is important after acoustic cavitation is fully started.

1.2.3 Growth of a Bubble

There are two mechanisms in growth of a bubble in acoustic cavitation [14]. One is coalescence of bubbles. The other is the gas diffusion into a bubble due to the area and shell effects described before. This is called rectified diffusion.

The coalescence of bubbles is driven by the two mechanisms. One is the attractive radiation force between bubbles called secondary Bjerknes force. The other is the other radiation force called the primary Bjerknes force which drives active bubbles to the pressure antinode of a standing wave field. It should be noted, however, too strong acoustic wave repels bubbles from the pressure antinode as described in the next section [29, 30].

The bubble growth rate due to rectified diffusion strongly depends on acoustic amplitude and frequency. For a very weak driving such as 0.2 bar at 20 kHz, the bubble growth rate is in the order of a few μm per 100s for the initial radius of 35 μm [31, 32]. For a much stronger driving such as 2 bar at 30 kHz, it ranges from 10 to a few hundred μm per second depending on the initial radius [33]. It decreases as ultrasonic frequency increases for the same acoustic pressure amplitude.

Relative importance of coalescence and rectified diffusion in the bubble growth is still under debate. After acoustic cavitation is fully started, coalescence of bubbles may be the main mechanism of the bubble growth [16, 34]. On the other hand, at the initial development of acoustic cavitation, rectified diffusion may be the main mechanism as the rate of coalescence is proportional to the square of the number density of bubbles which should be small at the initial stage of acoustic cavitation. Further studies are required on this subject.

1.2.4 Radiation Forces on a Bubble (Primary and Secondary Bjerknes Forces)

Both the primary and secondary Bjerknes forces are originated from the pressure gradient across a bubble [35].

$$\vec{F}_B = -\langle V(t) \nabla p(\vec{x}, t) \rangle \quad (1.2)$$

where \vec{F}_B is the primary or secondary Bjerknes force, $V(t)$ is the instantaneous bubble volume, $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$ in xyz-coordinate, $p(\vec{x}, t)$ is the instantaneous local pressure at position \vec{x} , and $\langle \rangle$ denotes the time average. For the primary Bjerknes force, $p(\vec{x}, t)$ is the driving ultrasound. On the other hand, for the secondary Bjerknes force, $p(\vec{x}, t)$ is the acoustic wave radiated by a neighboring bubble.

When the driving ultrasound is a standing wave, $p(\vec{x}, t)$ is expressed as follows for the primary Bjerknes force.

$$p(\vec{x}, t) = p_a \cos(\vec{k} \cdot \vec{x}) \sin \omega t \quad (1.3)$$

where p_a is the acoustic pressure amplitude, \vec{k} is the wave vector, and ω is the angular frequency. Then, the primary Bjerknes force (\vec{F}_{PB}) is given by the following equation.

$$\vec{F}_{PB} = p_a \vec{k} \sin(\vec{k} \cdot \vec{x}) \langle V(t) \sin \omega t \rangle \quad (1.4)$$

When the bubble pulsation is in phase with the driving ultrasound, a bubble is attracted to the pressure antinode of a standing wave field. For a very low driving such as less than 0.1 bar in acoustic amplitude, bubble pulsation is nearly linear and this condition coincides with smaller ambient radius than the linear resonance radius. For active bubbles, pulsation is strongly nonlinear, and the situation is more complex. For example, at 20 kHz, an active bubble of smaller ambient radius than the linear resonance radius is repelled from the pressure antinode when the acoustic pressure amplitude is larger than about 1.8 bar [29, 30]. This is because a bubble continues expanding even during the compression phase of ultrasound due to the inertia of the surrounding liquid. To active bubbles (“transient cavitation bubbles” by the definition based on activity of bubbles), the linear theory can not be applied.

In a traveling wave of ultrasound, most active bubbles are pushed toward the direction of the wave propagation by the primary Bjerknes force. Furthermore, there is a fluid flow in the direction of the wave propagation called acoustic streaming [36]. Acoustic streaming is caused by the attenuation of a traveling wave resulting in the net radiation force in the direction of the wave propagation. The attenuation is caused by both viscosity of the liquid and the cavitation bubbles. Furthermore, moving bubbles driven by the primary Bjerknes force drag the surrounding fluid. The resulting fluid flow is called quasi acoustic streaming [37].

While the secondary Bjerknes force is always attractive if the ambient radius is the same between bubbles, it can be repulsive if the ambient radius is different [38]. The magnitude as well as the sign of the secondary Bjerknes force is a strong function of the ambient bubble radii of two bubbles, the acoustic pressure amplitude, and the acoustic frequency. It is calculated by (1.5).

$$\vec{F}_{1 \rightarrow 2} = \frac{\rho}{4\pi d^2} \langle \ddot{V}_1 V_2 \rangle \vec{e}_r \quad (1.5)$$

where $\vec{F}_{1 \rightarrow 2}$ is the secondary Bjerknes force acting on bubble 2 from bubble 1, ρ is the liquid density, d is the distance between the bubbles 1 and 2, \ddot{V}_1 is the second time derivative of the volume of bubble 1, V_2 is the volume of bubble 2, $\langle \rangle$ denotes the time average, and \vec{e}_r is the radial unit vector directed from bubble 1 to bubble 2. For a very low driving (such as less than 0.1 bar in acoustic amplitude) or for very large bubbles, the bubble pulsation is nearly linear and bubbles with the ambient radii both less (more) than the linear resonance radius pulsate in phase resulting in the attractive secondary Bjerknes force [14]. On the other hand, when the ambient radius of a bubble is less than the linear resonance radius and that of the other bubble is more than it, it is repulsive. For active bubbles, however, the bubble pulsation is strongly nonlinear and the situation is much more complex [38]. The theory for linear pulsation of bubbles should not be applied to active bubbles as already noted [39].

1.2.5 Bubble Radial Dynamics

Bubble radial dynamics is well described by the Rayleigh-Plesset equation or its modified version such as Keller and Herring equations [40]. The Rayleigh-Plesset equation is derived as follows [14]. Consider a liquid volume surrounding a pulsating bubble such that the liquid volume is much larger than the bubble volume and that the radius of the liquid volume is much smaller than the acoustic wavelength. The kinetic energy (E_K) of the liquid volume is given by (1.6).

$$E_K = \frac{1}{2} \rho \int_R^{R_L} \dot{r}^2 4\pi r^2 dr = 2\pi\rho R^3 \dot{R}^2 \quad (1.6)$$

where ρ is the liquid density, R_L is the radius of the liquid volume, R is the instantaneous bubble radius, r is the radial distance from the bubble center, the dot denotes the time derivative, and the liquid incompressibility condition ($\dot{r}/\dot{R} = R^2/r^2$) as well as the condition $R \ll R_L$ has been used. The work done by a pulsating bubble (W_{bubble}) to the surrounding liquid is given by (1.7).

$$W_{bubble} = \int_{R_0}^R 4\pi r^2 p_B dr \quad (1.7)$$

where R_0 is the ambient bubble radius, and p_B is the liquid pressure at the bubble wall. If the liquid is incompressible, the liquid volume does some work to the surrounding liquid (W_{liquid}) as it moves outward associated with the bubble expansion.

$$W_{liquid} = \int_{R_0}^R 4\pi r^2 p_{\infty} dr \quad (1.8)$$

where p_{∞} is the pressure at the surface of the liquid volume including the acoustic pressure. The conservation of energy requires the following relationship.

$$W_{bubble} = E_K + W_{liquid}. \quad (1.9)$$

Differentiation of (1.9) with respect to R results in the following equation.

$$\frac{p_B - p_{\infty}}{\rho} = \frac{3\dot{R}^2}{2} + R\ddot{R} \quad (1.10)$$

where the following relationship has been used.

$$\frac{\partial(\dot{R}^2)}{\partial R} = \frac{1}{R} \frac{\partial(\dot{R}^2)}{\partial t} = 2\ddot{R} \quad (1.11)$$

The liquid pressure at the bubble wall (p_B) is related to the gas pressure inside a bubble (p_g) as follows [14].

$$p_B = p_g - \frac{2\sigma}{R} - \frac{4\mu\dot{R}}{R} \quad (1.12)$$

where σ is the surface tension, and μ is the liquid viscosity. The pressure at the surface of the liquid volume is the sum of the acoustic pressure ($p_s(t)$) and the ambient static pressure (p_0). Then the Rayleigh-Plesset equation is derived from (1.10).

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho} \left(p_g - \frac{2\sigma}{R} - \frac{4\mu\dot{R}}{R} - p_0 - p_s(t) \right) \quad (1.13)$$

In this equation, liquid has been assumed as incompressible. In the following Keller and Herring equations, the liquid compressibility has been taken into account to the first order of \dot{R}/c_{∞} , where c_{∞} is the sound velocity in the liquid far from a bubble [41].

$$\begin{aligned} & \left(1 - (\lambda + 1) \frac{\dot{R}}{c_{\infty}} \right) R\ddot{R} + \frac{3\dot{R}^2}{2} \left(1 - \frac{1}{3}(3\lambda + 1) \frac{\dot{R}}{c_{\infty}} \right) \\ & = \frac{1}{\rho} \left(1 + (1 - \lambda) \frac{\dot{R}}{c_{\infty}} \right) \left[p_B - p_s \left(t + \frac{R}{c_{\infty}} \right) - p_0 \right] + \frac{R}{c_{\infty}\rho} \frac{dp_B}{dt} \end{aligned} \quad (1.14)$$

where $\lambda = 0$ or 1 for Keller or Herring equation, respectively, and $p_s(t + \frac{R}{c_\infty})$ is the instantaneous acoustic pressure at time $t + \frac{R}{c_\infty}$. As a similar equation, Gilmore equation has also been widely used [41].

1.2.6 Inertial Collapse (Rayleigh Collapse)

Now the bubble collapse is discussed using the Rayleigh-Plesset equation. After the bubble expansion, a bubble collapses. During the bubble collapse, important terms in the Rayleigh-Plesset equation are the two terms in the left hand side of (1.13). Then, the bubble wall acceleration is expressed as follows.

$$\ddot{R} = -\frac{3\dot{R}^2}{2R} \quad (1.15)$$

Thus, it is always negative. It means that the speed of the bubble collapse increases with time (The negative bubble-wall velocity further decreases). As the speed of the bubble collapse increases, the magnitude of the bubble wall acceleration increases according to (1.15). It means that the speed of the bubble collapse automatically increases more and more with time. This is caused by the inertia of the surrounding liquid ingoing into a collapsing bubble as well as the spherically shrinking geometry. Such a bubble collapse is called inertial collapse or Rayleigh collapse [40].

It has been shown theoretically that the speed of the bubble collapse is limited by the sound speed in the liquid at the bubble wall [42]. The sound speed is a function of pressure and density of the liquid as follows.

$$c_{L,B} = \sqrt{7.15(p_B + B)/\rho_{L,i}} \quad (1.16)$$

where $c_{L,B}$ is the sound speed in the liquid at the bubble wall, $B = 3.049 \times 10^8$ Pa, and $\rho_{L,i}$ is the liquid density at the bubble wall. The sound speed ($c_{L,B}$) increases as the bubble collapses up to about 3000 m/s (about two times of the ambient sound speed (1500 m/s) in water), which is the upper limit for the speed of the bubble collapse.

Finally, the bubble collapse stops when the pressure inside a bubble (p_g) in the right hand side of (1.13) dramatically increases as the density inside a bubble nearly reaches that of a condensed phase (A bubble is almost completely occupied by the van der Waals hard-cores of gas and vapor molecules at that moment). At the same time, the temperature and pressure inside a bubble dramatically increase.

In Fig. 1.4a, an example of the radius-time curve for a stably pulsating bubble calculated by the modified Keller equation is shown for one acoustic cycle [43]. After the bubble expansion during the rarefaction phase of ultrasound, a bubble strongly collapses, which is the inertial or Rayleigh collapse. After the collapse, there is a bouncing radial motion of a bubble. In Fig. 1.4b, the calculated flux of OH

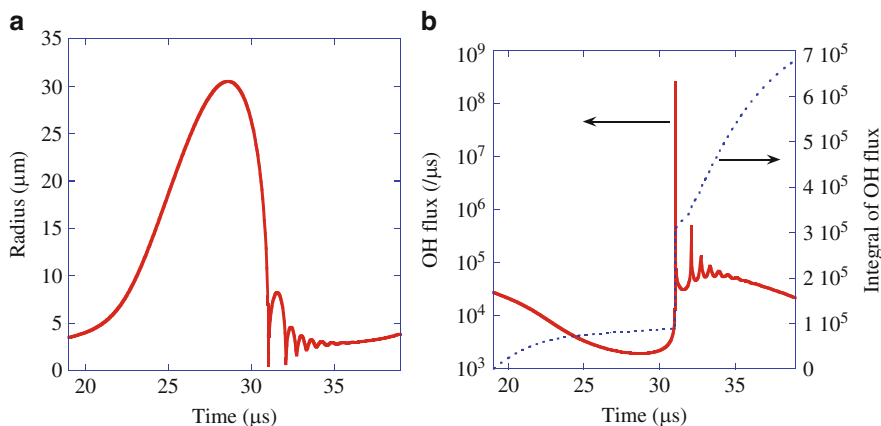


Fig. 1.4 The calculated results for one acoustic cycle when a bubble in water at 3 °C is irradiated by an ultrasonic wave of 52 kHz and 1.52 bar in frequency and pressure amplitude, respectively. The ambient bubble radius is 3.6 μm. **(a)** The bubble radius. **(b)** The dissolution rate of OH radicals into the liquid from the interior of the bubble (solid line) and its time integral (dotted line). Reprinted with permission from Yasui K, Tuziuti T, Sivakumar M, Iida Y (2005) Theoretical study of single-bubble sonochemistry. *J Chem Phys* 122:224706. Copyright 2005, American Institute of Physics

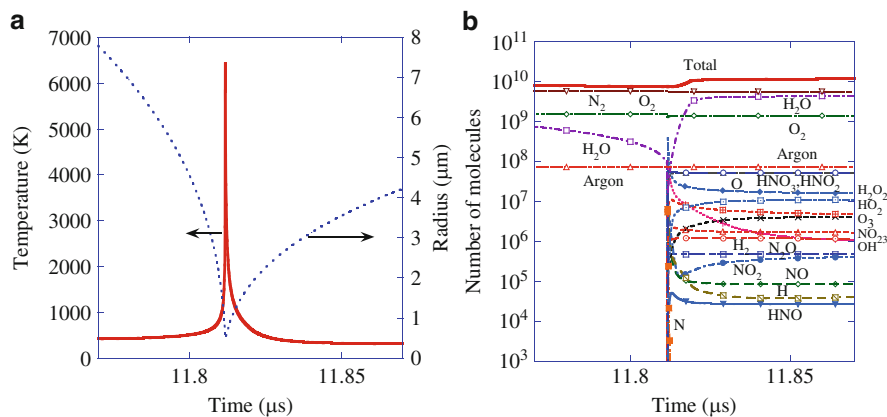


Fig. 1.5 The calculated results for an air bubble at around the end of the inertial collapse only for 0.1 μs. **(a)** The bubble radius and the temperature inside a bubble. **(b)** The number of molecules inside a bubble. Reprinted with permission from Yasui K, Tuziuti T, Sivakumar M, Iida Y (2005) Theoretical study of single-bubble sonochemistry. *J Chem Phys* 122:224706. Copyright 2005, American Institute of Physics

radicals from a bubble is shown as a function of time for one acoustic cycle [43]. OH radicals are created at each strong collapse, which diffuses out of a bubble into the surrounding liquid especially at the end of the strong collapse. In Fig. 1.5, the details of the inertial or Rayleigh collapse are shown [43]. In Fig. 1.5a, the bubble

radius and the temperature inside an air bubble are shown as a function of time only for 0.1 μs at around the end of the collapse. The temperature dramatically increases at the end of the collapse to 6500 K. As a result, water vapor, oxygen and nitrogen are dissociated inside a bubble and many chemical species are created as shown in Fig. 1.5b. The production of oxidants inside a bubble such as OH, O, and H_2O_2 is one of the major origins of sonochemical reactions. In other words, the inertial or Rayleigh collapse is essential for sonochemistry.

1.3 Sonochemistry

1.3.1 Single-Bubble Sonochemistry

In most of the experiments of sonochemical reactions, there are a lot of cavitation bubbles in liquid, which is called a multibubble system. It is a complicated system because bubbles interact with each other and the local acoustic field temporally changes because moving bubbles attenuate and scatter an acoustic wave. Bubbles frequently coalesce each other, fragment into daughter bubbles, grow by rectified diffusion, shrink by gas diffusion, and spatially move due to radiation forces. New bubbles are also created. The bubble pulsation as well as the acoustic wave propagation is strongly nonlinear [44, 45]. The motions of bubbles are also complex [35]. Thus, as a first step, we shall consider a much simpler system; a single-bubble system. The single-bubble system is that a single bubble is trapped at the pressure antinode of a standing wave field [40]. It can be stably driven when the acoustic pressure is lower than the threshold for the shape instability of a bubble. The acoustic pressure should also be lower than the threshold for the bubble repulsion from the pressure antinode (about 1.8 bar at 20 kHz). The light emission from a stable bubble in the single-bubble system has been intensively studied, which is called single-bubble sonoluminescence (SBSL) [40]. The light emission of SBSL in water is due to several light emission processes in weakly ionized gases inside a bubble such as electron-atom bremsstrahlung which is the light emission from free electrons accelerated by collisions with neutral atoms [46–48]. It is not an electric discharge but thermal plasma in which free electrons are created by high temperature and pressure inside a bubble. On the other hand, the mechanism of SBSL in sulfuric acid, which is much brighter than that in pure water, has not yet been solved [49].

Hatanaka et al. [50], Didenko and Suslick [51], and Koda et al. [52] reported the experiment of chemical reactions in a single-bubble system called single-bubble sonochemistry. Didenko and Suslick [51] reported that the amount of OH radicals produced by a single bubble per acoustic cycle was about $10^5 \sim 10^6$ molecules at 52 kHz and 1.3 \sim 1.55 bar in ultrasonic frequency and pressure amplitude, respectively. The result of a numerical simulation shown in Fig. 1.4 [43] is under the condition of the experiment of Didenko and Suslick [51]. The amount of OH

radicals calculated by the numerical simulation sufficiently agrees with the experimental data. It indicates that the theoretical model used in the numerical simulation is sufficiently accurate at least under the condition.

According to Didenko and Suslick [51], the amount of nitrite ions (NO_2^-) produced by a bubble per acoustic cycle was about $10^6 \sim 10^7$ molecules. Koda et al. [52] also reported a similar value.

1.3.2 Optimal Bubble Temperature for Oxidant Production

Using a chemical kinetics model for flames, numerical simulations of chemical reactions inside an air bubble have been performed under various conditions. The theoretical model of a bubble including the chemical kinetics model has been validated through a study of single-bubble sonochemistry [43]. It has been clarified by numerical simulations that there exists an optimal bubble temperature for the production of oxidants inside an air bubble such as OH, O, H_2O_2 , and O_3 [53, 54]. The optimal temperature is about 5,500 K because at higher temperature oxidants are strongly consumed inside an air bubble by oxidizing nitrogen (Fig. 1.6a). On the other hand, for an oxygen bubble, the amount of oxidants increases as the bubble temperature increases as oxidants are not consumed inside an oxygen bubble (Fig. 1.6b).

Experimentally, Brotchie et al. [55] have shown that the range of ambient radius of sonoluminescing (SL) bubbles in which the temperature is relatively high

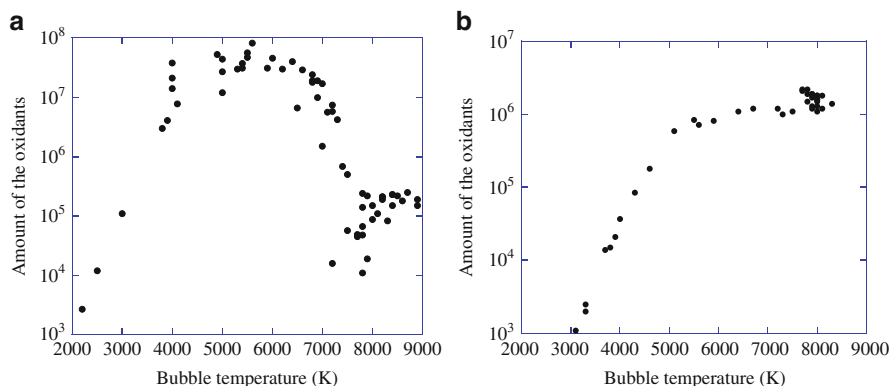


Fig. 1.6 The correlation between the bubble temperature at the collapse and the amount of the oxidants created inside a bubble per collapse in number of molecules. The calculated results for various ambient pressures and acoustic amplitudes are plotted. The temperature of liquid water is 20 °C. (a) For an air bubble of 5 μm in ambient radius at 140 kHz in ultrasonic frequency. (b) For an oxygen bubble of 0.5 μm in ambient radius at 1 MHz. Reprinted with permission from Yasui K, Tuziuti T, Iida Y, Mitome H (2003) Theoretical study of the ambient-pressure dependence of sonochemical reactions. *J Chem Phys* 119:346–356. Copyright 2003, American Institute of Physics

completely differs from that of chemically active bubbles which produce oxidants and glow by chemiluminescence in an aqueous luminol solution saturated with air. It suggests that the temperature inside chemically active bubbles is lower than that inside SL bubbles for an air bubble. It agrees with the results of the numerical simulations described above. The experimental method to measure the range of ambient radius of SL bubbles (or sonochemiluminescing (SCL) bubbles in an aqueous luminol solution) is based on the dissolution of bubbles during the pulse-off time of pulsed ultrasound [19]. Bubbles with larger ambient radius need longer pulse-off time for complete dissolution. As the pulse-off time increases, the SL (or SCL) intensity decreases because more bubbles dissolve during the pulse-off time and the number of bubbles decreases. From the dependence of the SL (or SCL) intensity on the pulse-off time, the range of ambient radius of SL (or SCL) bubbles is deduced [19].

1.3.3 Three Sites for Chemical Reactions

There are three sites for chemical reactions for a cavitation bubble as shown in Fig. 1.7 [56]. One is the interior of a bubble. Another is the interface region at around the bubble surface. The other is the liquid region outside the interface region. The liquid region is at the ambient temperature where chemical species with a relatively long lifetime such as H_2O_2 diffusing out of the interface region chemically react with solutes. In the interface region, the temperature dramatically increases due to the thermal conduction from the heated interior of a bubble where radicals with a relatively short lifetime such as OH and O react with solutes or radicals themselves. However, the actual temperature in the interface region is not known while several authors have estimated it [57–59]. Some researchers have suggested that in the interface region there is supercritical water [60]. Surfactants absorbed at the bubble surface can dissociate at the interface region due to both heat and radical attack [61]. In the interior of a bubble, volatile solutes which evaporate into the region are dissociated by high temperature [62].

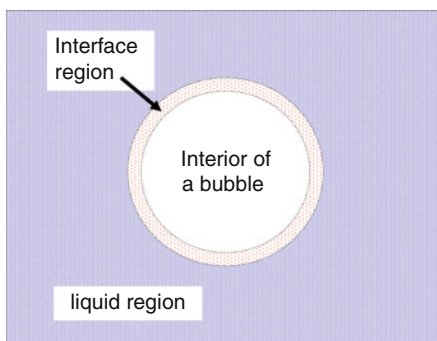


Fig. 1.7 Three sites for chemical reactions for a cavitation bubble

As stated above, more studies are required in future with regard to the interface region. What is the temperature and pressure in the interface region? What is the lifetime of OH radicals and O atoms in the interface region [63]? Is there supercritical water in the region?

1.3.4 Size of Active Bubbles

In some literature, there is a description that a bubble with linear resonance radius is active in sonoluminescence and sonochemical reactions. However, as already noted, bubble pulsation is intrinsically nonlinear for active bubbles. Thus, the concept of the linear resonance is not applicable to active bubbles (That is only applicable to a linearly pulsating bubble under very weak ultrasound such as 0.1 bar in pressure amplitude). Furthermore, a bubble with the linear resonance radius can be *inactive* in sonoluminescence and sonochemical reactions [39]. In Fig. 1.8, the calculated expansion ratio (R_{\max}/R_0 , where R_{\max} is the maximum radius and R_0 is the ambient radius of a bubble) is shown as a function of the ambient radius (R_0) for various acoustic amplitudes at 300 kHz [39]. It is seen that the ambient radius for the peak in the expansion ratio decreases as the acoustic pressure amplitude increases. While the linear resonance radius is 11 μm at 300 kHz, the ambient radius for the peak at 3 bar in pressure amplitude is about 0.4 μm . Even at the pressure amplitude of 0.5 bar, it is about 5 μm , which is much smaller than the linear resonance radius.

In Fig. 1.9, the results of numerical simulations at 300 kHz and 3 bar in ultrasonic frequency and pressure amplitude, respectively are shown as a function of ambient radius [39]. In Fig. 1.9a, the temperature inside a bubble at the end of the bubble collapse is shown with the molar fraction of water vapor inside a bubble.

Fig. 1.8 The calculated expansion ratio (R_{\max}/R_0) as a function of ambient bubble radius for various acoustic amplitudes at 300 kHz. Both the horizontal and vertical axes are in logarithmic scale. Reprinted with permission from Yasui K, Tuziuti T, Lee J, Kozuka T, Towata A, Iida Y (2008) The range of ambient radius for an active bubble in sonoluminescence and sonochemical reactions. J Chem Phys 128:184705. Copyright 2008, American Institute of Physics

