

# Theory of Sonochemistry

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## Abstract

Sonochemistry refers to ultrasound-initiated chemical processes in liquids. The interaction between bubbles and sound energy in liquids results in acoustic cavitation. This chapter presents the fundamental aspects of acoustic cavitation and theoretical aspects behind sonochemistry such as dynamics of bubble oscillation, rectified diffusion process that is responsible for the growth of cavitation bubbles, near adiabatic collapse of cavitation bubbles resulting in extreme reaction conditions and several chemical species generated within collapsing bubbles that are responsible for various redox reactions. Specifically, a detailed discussion on single bubble sonochemistry is provided.

### 1.1. Introduction

Ultrasound refers to sound waves beyond the frequency that can be detected by the human ear. Sound waves with a frequency of >20 kHz fall under this category. Ultrasound is divided into three main regions: low frequency (20-100 kHz), intermediate frequency (100 kHz-1 MHz) and high frequency (1-10 MHz) [1]; however, intermediate range is also sometime referred as high frequency. Ultrasound interacts with gas bubbles in liquids generating chemical reactions and strong physical forces that could be used for various processing applications and for promoting chemical reactions. The driving force for the generation of chemical and physical forces is acoustic cavitation, which generates extreme temperatures and pressures. The consequences of these extreme conditions generated include radical generation, light emission – sonoluminescence (SL), shock waves, microjets, microstreaming, shear forces and turbulence [1]. Due to these strong physical and chemical effects, various applications of acoustic cavitation have been developed for its commercial usage including wastewater treatment [2] and the formation of protein microbubbles which can be used for flavour encapsulation and drug delivery [3].

### 1.2. History

Cavitation phenomenon was first reported by Thornycroft and Barnaby [4] in 1895. In 1917, Rayleigh published the first mathematical model describing cavitation event in an incompressible liquid [5]. In 1930's Brohult [6] and other groups discovered that sonication can be used for the degradation of bio- and synthetic polymers. In 1935 Frenzel and Schulze [7] reported for the first time that light emission occurred in water when exposed to intense ultrasound. In 1944 Weiss [8] observed that the sonication of water leads to the generation of hydrogen and hydroxyl radicals and later in 1956, Parke and Taylor [9] provided the first experimental evidence for the formation of OH radicals in aqueous solutions. The first observations on chemical reactions in organic solutions were made in the early 1950s. It was found that methanol solutions containing diphenylpicryl hydracyl were decolourised, indicating the formation of free radicals [10]. Also, the first computer calculations modelling a cavitation bubble was published by Neppiras and Noltingk [11] in 1950. Makino et al. [12] used spin trapping agents and electron spin resonance measurements to verify the formation of H and OH radicals during the sonication of water. It was reported in 1987 by Henglein [13] that over 80% of primary radicals originally generated in the hotspot recombine to produce water molecules. Since 1930s, acoustic cavitation has gained popularity as it can be used for the enhancement of chemical reactions, emulsification of oils, degradation of chemical and biological pollutants, etc.

A number of books, review articles and book chapters have been published on acoustic cavitation and its applications are available in the literature. Fundamentals of an acoustic bubble have been discussed in detail by Leighton[14] in his book ‘The Acoustic Bubble’. Mason and Lorimer [15-17] have published various review articles and books dealing with different aspects of ultrasound such as theory of sonochemistry, applications of ultrasound in food technology, uses of ultrasound in chemical synthesis, physical aspects of sonochemistry. A review by Leong et al. focuses on the fundamentals of ultrasound-induced physical processes such as transient and stable cavitation, rectified diffusion, coalescence and sonoluminescence [18]. The current review provides an overview of various fundamental processes of acoustic cavitation with a particular emphasis on single bubble sonochemistry.

### 1.3. Acoustic cavitation

#### 1.3.1. Bubble formation

Acoustic cavitation is the phenomenon of formation, growth and violent collapse induced by the pressure fluctuations generated by sound waves in a liquid medium. If the intensity of ultrasound is enough to overcome the tensile strength of the medium, there occurs a point where intermolecular forces are not able to hold the molecular structure together. This point leads to the formation of a cavity in the medium. A large amount of energy is required to create a void or cavity. Equation 1 can be used to calculate the critical pressure ( $P_B$ ) required to create a cavity of radius,  $R_e$ .

$$P_B \sim P_h + \frac{0.77\sigma}{R_e} \quad \text{Equation 1.0}$$

$\sigma$  is surface tension of the liquid and  $P_h$  is hydrostatic pressure (could be approximated to atmospheric pressure under normal experimental conditions). The equation is valid when  $2\sigma R_e \ll P_h$  [19]. However, free gas bubbles and gas molecules trapped in solid impurities are inherently present in liquids, which can act as nuclei for cavitation. Hence, the actual pressure required is far less for cavitation to occur. Hence, in practical terms, acoustic cavitation refers to the growth of pre-existing gas nuclei followed by the collapse of “grown” bubbles.

There are different mechanisms associated with the formation of bubbles [14]. Firstly, gas molecules trapped in crevices of the container walls, motes or on hydrophobic dust particles [20] can act as bubble source. Harvey’s crevice model depicts how an air bubble can be nucleated from crevices. A gas pocket, trapped in a crevice, responds to alternating compression and the rarefaction cycles of the applied ultrasound. The gas pocket expands considerably during the negative pressure cycle. When the gas pocket grows sufficiently it gets detached from crevice leading to the formation of free a gas bubble in the liquid [21]. Dissolved gas in the liquid then fills the residual gas cavity under applied sound field and the cycle is repeated. The second mechanism is based on the skin model where inherently present bubble nuclei are stabilized against dissolution when their surface is completely covered with organic materials or surfactants [22]. It has also been suggested that such bubbles can be stabilized by hydrophobic impurities present in a liquid. These bubbles tend to grow in an acoustic field by coalescence or rectified diffusion [23, 24]. Recently Yasui et al. have introduced the dynamic equilibrium model for the stabilization of the bubbles covered with

the hydrophobic materials [25]. A chemical potential gradient that exists near the edge of hydrophobic material generates a dynamic equilibrium state [25]. Other mechanism for the nucleation is fragmentation of the active cavitation bubbles [26]. The shape instability of a bubble which is mostly induced by asymmetric collapse leads to the fragmentation of the bubble into several daughter bubbles which then act as new nuclei for cavitation [27-30].

Before discussing the growth of an acoustic cavitation bubble, the fundamental equations used to study the motion of bubbles in an acoustic field have been discussed in the following section.

### 1.3.2. Dynamics of bubble oscillation

This section focuses on the oscillation dynamics of a gas bubble in an acoustic field. Further details on this can be found in the book “The Acoustic bubble” by Leighton [14]. The Rayleigh–Plesset equation is used to examine the dynamics of a bubble oscillating at finite amplitudes [5, 14, 31]. The equation describes the motion of a spherical bubble to a time-varying pressure field in an incompressible liquid. When time  $t < 0$ , a bubble of radius  $R_0$  is at rest in an incompressible viscous liquid and hydrostatic pressure is  $p_0$  which is constant. However, at  $t > 0$  pressure  $p_t$  varies with time and is superimposed on  $p_0$ , so that the pressure of liquid at certain point from the bubble,  $p_\infty = p_0 + p_t$  which results in a change of bubble radius to some new value  $R_t$ . During this process, the liquid shell around the bubble acquires kinetic energy of

$$\frac{1}{2} \rho \int_R^\infty \dot{r}^2 4\pi r^2 dr \quad \text{Equation 1}$$

Where shell at radius  $r$  has thickness  $dr$ , mass =  $4\pi r^2 \rho dr$  ( $\rho$  = density of liquid) and  $\dot{r}$  is speed.

Using the liquid incompressibility condition,  $\dot{r}/\dot{R} = R^2/r^2$  (where  $R$  is radius of bubble when contracted,  $\dot{R}$  is the wall velocity) Equation 1 can be integrated to give  $2\pi\rho R^3\dot{R}^2$ . Equating this to the difference between the work done at certain point from the bubble by  $p_\infty$  and the work done by the pressure  $p_L$  in the liquid outside the bubble wall gives

$$\int_{R_0}^R (p_L - p_\infty) 4\pi R^2 dR = 2\pi R^3 \dot{R}^2 \quad \text{Equation 2}$$

Equation (4) is obtained after differentiating Equation (2) w.r.t  $R$ , noting that

$$\frac{\partial(\dot{R})^2}{\partial R} = \frac{1}{\dot{R}} \frac{\partial(\dot{R}^2)}{\partial t} = 2\ddot{R} \quad \text{Equation 3}$$

$$\frac{p_L - p_\infty}{\rho} = \frac{3\dot{R}^2}{2} + R\ddot{R} \quad \text{Equation 4}$$

Where  $\dot{R}$  is the velocity of the cavity,  $\ddot{R}$  is the acceleration of the cavity

The liquid pressure  $p_L$  for a pulsating bubble containing gas and vapour is given as,

$$p_L = \left( p_0 + \frac{2\sigma}{R_0} - p_v \right) \left( \frac{R_0}{R} \right)^{3\gamma} + p_v - \frac{2\sigma}{R} \quad \text{Equation 5}$$

Where,  $p_v$  is vapour pressure of the liquid,  $\sigma$  is surface tension,  $p_0$  is the ambient pressure,  $\gamma$  is the ratio of specific heat of gas at constant pressure to that of constant volume.

Substituting  $p_L$  from Equation 5 and  $p_\infty = p_0 + pt$  into Equation 3,

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho} \left\{ \left( p_0 + \frac{2\sigma}{R_0} - p_v \right) \left( \frac{R_0}{R} \right)^{3\gamma} + p_v - \frac{2\sigma}{R} - p_0 - pt \right\} \quad \text{Equation 6}$$

The effect of viscosity on the above equation was considered by Poritsy [32], who found that viscosity effects arises through boundary conditions and not through the Navier–Stokes equation and obtained Equation 7.

$$\ddot{R}R + \frac{3\dot{R}^2}{2} = \frac{1}{\sigma} \left\{ \left( p_0 + \frac{2\sigma}{R_0} - p_v \right) \left( \frac{R_0}{R} \right)^{3\gamma} + p_v - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} - p_0 - P(t) \right\} \quad \text{Equation 7}$$

where  $\eta$  is the viscosity of the liquid.

Equations 4, 6, and 7 are commonly known as ‘Rayleigh-Plesset’ equations and they indicate that the motion of a bubble under the acoustic field is non-linear.

A spherical bubble is subjected to the time varying pressure of amplitude  $p_A$  and circular frequency  $\omega$ . Therefore,

$$pt = -p_A \sin(\omega t) \quad \text{Equation 8}$$

Substituting Equation (8) into Equation (7) gives:

$$\ddot{R}R + \frac{3\dot{R}^2}{2} = \frac{1}{\sigma} \left\{ \left( p_0 + \frac{2\sigma}{R_0} - p_v \right) \left( \frac{R_0}{R} \right)^{3\gamma} + p_v - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} - p_0 + p_A \sin(\omega t) \right\} \quad \text{Equation 9}$$

Equation 9 is the fundamental equation used to describe the bubble motion at different frequencies. Over the past few decades the equation has been extended significantly to

account for damping effects, solution compressibility, condensation, non-linear evaporation etc. [33, 34].

### 1.3.3. Bubble growth

Bubbles inherently present in liquids tend to grow to a critical size (which is influenced by several parameters such as acoustic pressure, ultrasonic power and frequency, viscosity of medium, etc.) in an ultrasonic field. The ultrasound driven growth is due to “rectified diffusion” which is defined as “the slow growth of pulsating gas bubble due to an average flow of mass (dissolved gases and solvent vapour) into the bubble as a function of time. Crum [24] explained this “rectification of mass” in terms of two effects, viz., “area effect” and “shell effect”, schematically shown in Figure 1.

A gas bubble trapped in a liquid tends to expand when the surrounding liquid experiences negative pressure of the sound wave. At this stage, the low internal pressure of the bubble results in the evaporation of solvent molecules and diffusion of dissolved gases into the bubble from the surrounding liquid. Therefore, the rarefaction cycle leads to “intake” of gas and vapour molecules. The bubble is compressed when the surrounding liquid experiences the positive pressure (compression cycle) of the sound wave. At this stage, the internal pressure of the bubble is high, which leads to the expulsion of the gas/vapour molecules from the bubble into the surrounding liquid. Thus, the compression cycle leads to the “loss” of bubble mass. Since the bubble collapse is relatively fast and less surface area is available for mass transport, the amount of material that diffuses out of the bubble during compression cycle is always less than that diffuses into the bubble during expansion cycle leading to the net growth of bubble. This is known as the area effect.

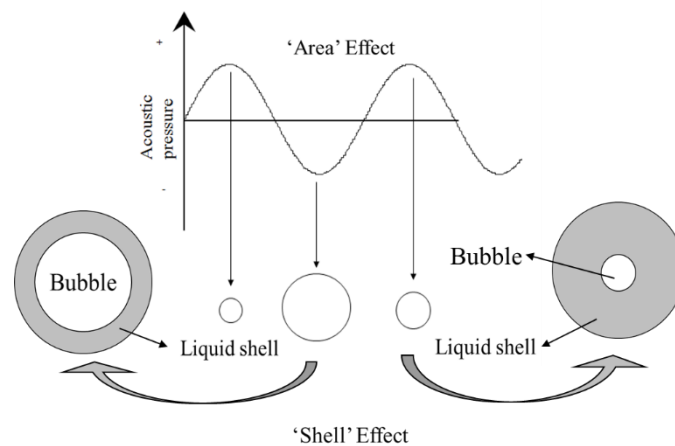


Figure 1: Schematic description of the growth of a bubble in an acoustic field by “area” and “shell” effects. (Adapted from [35]).

A change in the surface area of the bubble alone, however, is not sufficient to explain rectified diffusion. The concentration of dissolved gases and thickness of liquid shell around the bubble change during expansion and rarefaction cycle. During the compression half cycle, the bubble contracts and the shell thickness increases leading to a decrease in the concentration of gases within the shell. This generates a concentration difference between the gas at the interface and bulk. The rate of diffusion of gas in a liquid is proportional to the

gradient of the concentration of the dissolved gas. However, the gas concentration gradient lowers as the shell thickness increases, which lowers the mass transfer of the gas coming out of the bubble. When the bubble is in its expanded state, the liquid shell becomes thinner (relative to the size of the bubble) with a relatively higher gas concentration. Since the gas concentration inside the bubble is lower, material diffuses into the bubble from the surrounding liquid shell. Two factors i.e. gas concentration at the bubble wall and the shell thickness, work together when the bubble is in the expanded state and work against each other when the bubble is in the compressed state, thus resulting in a net bubble growth over time.

Crum [12] noted that both effects have to be considered to theoretically model the rectified diffusion process. The kinetics of the bubble growth and collapse is also a crucial factor, expected to control the rectified diffusion. Therefore, a mathematical solution for the growth of a gas bubble by rectified diffusion requires equations of bubble motion, diffusion equations and heat conduction equations for both the liquid and bubble [24]. Consideration of these factors makes it complicated. Both Hsieh and Plesset [36] and Eller and Flynn [37] have taken into account the motion of the bubble wall, and a diffusion equation for the concentration of gas dissolved in the liquid alone. The diffusion of gas in the liquid obeys Fick's law of mass transfer.

Eller and Flynn [37] had shown that rate of change of number of moles  $n$  of the gas in the bubble with the time is given as

$$\frac{dn}{dt} = 4\pi DR_0 C_0 \left[ \left\langle \frac{R}{R_0} \right\rangle + \left( \frac{\langle (R/R_0) \rangle}{\pi Dt} \right)^{\frac{1}{2}} \right] H \quad \text{Equation 10}$$

Where H is,

$$H = \frac{C_i}{C_0} - \left\langle \left( \frac{R}{R_0} \right)^4 \left( \frac{p_{g,m}}{p_\infty} \right) \right\rangle \left\langle \left( \frac{R}{R_0} \right)^4 \right\rangle \quad \text{Equation 11}$$

$C_i$  is the concentration of dissolved gas in the liquid far from the bubble and  $p_{g,m}$  the instantaneous pressure of the gas in the bubble,  $C_0$  is the saturation concentration of the gas in the liquid, D is the diffusivity of the gas, and  $\left\langle \left( \frac{R}{R_0} \right)^4 \left( \frac{p_{g,m}}{p_\infty} \right) \right\rangle$ ,  $\left\langle \left( \frac{R}{R_0} \right)^4 \right\rangle$  and  $\left\langle \frac{R}{R_0} \right\rangle$  are the time averages.

Crum later extended Equation 11 to obtain the rate of change of equilibrium bubble radius as a function of time, which is given as

$$\frac{dR_0}{dt} = \frac{Dd}{R_0} \left[ \left\langle \frac{R}{R_0} \right\rangle + R_0 \left( \frac{\langle (R/R_0) \rangle}{\pi Dt} \right)^{1/2} \right] \left( 1 + \frac{4\sigma}{3P_\infty R_0} \right)^{-1} \left( \frac{C_i}{C_0} - \left\langle \left( \frac{R}{R_0} \right)^4 \left( \frac{p_{g,m}}{p_\infty} \right) \right\rangle / \left\langle \left( \frac{R}{R_0} \right)^4 \right\rangle \right)$$

$$\text{Equation 12}$$

where,  $d = kTC_0/P_\infty$  (K is the universal gas constant, T is the temperature).

The threshold acoustic pressure growth of a gas bubble is obtained by setting  $dR_0/dt = 0$ , and results in the equation

$$P_A^2 = \frac{(\rho R_0^2 \omega_0^2)^2 [(1 - \omega^2/\omega_0^2)^2 + b^2(\omega^2/\omega_0^2)] (1 + 2\sigma/R_0 P_\infty - C_i/C_0)}{(3 + 4K)(C_i/C_0) - \left\{ \left[ \frac{3(\eta - 1)(3\eta - 4)}{4} \right] + (4 - 3\eta)K \right\} (1 + 2\sigma/R_0 P_\infty)}$$

Equation 13

Figure 2 represents the rectified diffusion threshold as a function of radius for the radius above and below the resonance values calculated using Equation 13.

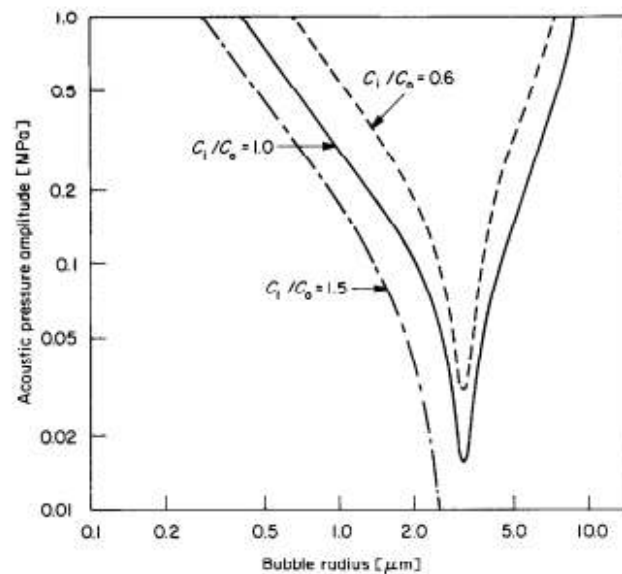


Figure 2: Rectified diffusion threshold as a function of gas bubble radius at different dissolved gas concentration ratios. The curves can be calculated by Equation 13, the acoustic frequency used was 1 MHz and the surface tension was 68 dyn/cm; the liquid is assumed to be water (Reprinted with permission from Elsevier [24], Copyright (1984)).

Later Fyrrillas and Szeri [38] developed a new mathematical analysis for describing the mass transportation during rectified diffusion. They extended the analysis to incorporate the effect of interfacial resistance to mass transfer caused by surfactants. Crum's experimental data was used to estimate the rectified diffusion growth of the cavitation bubbles. Lee et al. [39] and Leong et al. [18] have studied rectified diffusion growth in the presence of various surfactants. They have reported that acoustic streaming, caused due to surfactant adsorption, plays a major role in rectified diffusion growth of bubbles in addition to surface activity and the nature of head group of surfactants [18].



### 1.3.4. Bubble collapse

Rectified diffusion leads to the growth of the bubble to a critical (resonance) size, at which the natural bubble oscillation frequency matches that of the driving ultrasound frequency. A simple relationship between the frequency of ultrasound and the resonance radius of a bubble is given by Equation (14) called Minnaert's equation.

$$F \times R \approx 3 \quad \text{Equation 14}$$

(F = frequency in Hz, R = radius of the bubble in meters)

Yasui [26] suggests that resonance size is not a single value but consists of a range. While Equation 14 theoretically predicts the relationship between ultrasound frequency and resonance size of the bubble, experimental data to support this Equation is only recently reported. A pulsed ultrasound technique can be used to determine the resonance size range of sonoluminescence (SL) bubbles and sonochemically (SCL) active bubbles [40-43]. Brotchie et al. [44] have shown for sonochemically active bubbles that with increasing frequency the mean bubble size becomes smaller, and the distribution becomes narrower (Figure 3). SL and SCL have been discussed later in this chapter. Other experimental techniques used to measure the bubble size are laser light diffraction [45], active cavitation detection [46] and phase-Doppler [47].

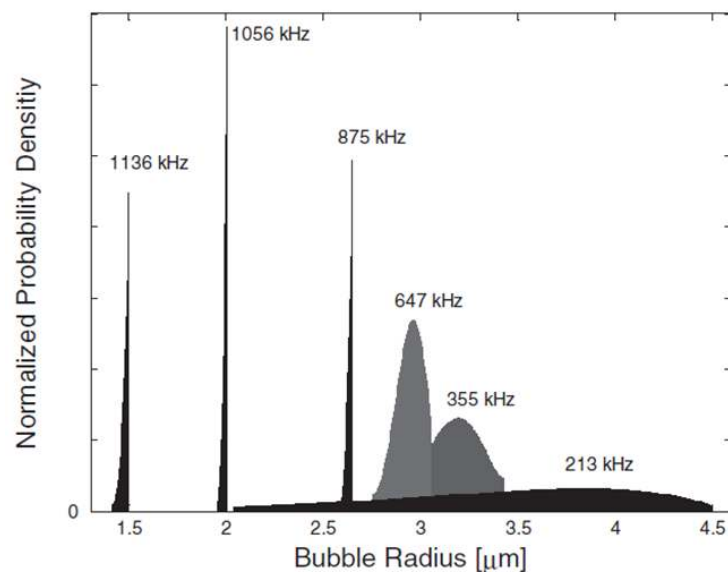


Figure 3: The bubble-size distributions for 213, 355, 647, 875, 1056, and 1136 kHz. For 875, 1056, and 1136 kHz data have been scaled down by a factor of 4. The acoustic power of all frequencies is  $1.5 \pm 0.4$  W (Reprinted with permission from American Physical Society [24]; Copyright (2009)).

Once a critical size is reached, the bubble grows to a maximum in a single acoustic cycle and implodes (collapses). The bubble implosion, from a thermodynamic consideration is important because a large change in bubble volume occurs. Since the bubble collapse happens in a very short time domain ( $\sim 1 \mu\text{s}$ ), the “work done” (PdV) leads to a “near” adiabatic heating of the contents of the bubble, which results in the generation of very high temperatures ( $> 5000$  K) and pressures ( $> 1000$  atm) within the bubble.

Rayleigh initially developed the fundamental equation dealing with the collapse of gas cavity in 1917 for an isothermal process, which can be easily extended for an adiabatic process. The model was proposed for a bubble of initial radius of  $R_m$  and when  $\dot{R} = 0$ , the cavity would collapse, rebound and oscillates between maximum radius  $R_{max}$  and minimum radius  $R_{min}$ .  $R = R_m$  and  $\dot{R} = 0$  in the beginning of the collapse. The pressure of gas inside the bubble is  $p_{g,m}$  and temperature is  $T_m$ . Assuming that there is no heat flow across the bubble wall, the gas pressure is given by Equation 15, which follows adiabatic law.

$$p_g = p_{g,m} \left( \frac{R_m}{R} \right)^{3\gamma} \quad \text{Equation 15}$$

Due to the presence of gases inside the bubble, the decrease in the potential energy will be equal to the sum of kinetic energy of the liquid and amount of work done in compressing the liquid when radius changes from  $R_m$  to  $R$ . The energy balance is given as,

$$- \int_{R_m}^R p_{\infty} 4\pi R^2 dR = 2\pi R^3 \dot{R}^2 \rho - \int_{R_m}^R p_L 4\pi R^2 dR \quad \text{Equation 16}$$

The work done can be expressed as

$$- \int_{R_m}^R p_L dV = \frac{1}{\gamma - 1} \frac{4\pi R_m^3}{3} p_{g,m} \left\{ \left( \frac{R_m}{R} \right)^{3\gamma - 1} - 1 \right\} \quad \text{Equation 17}$$

Therefore, Equation (16) becomes

$$\int_{R_m}^R p_{\infty} 4\pi R^2 dR = 2\pi R^3 \dot{R}^2 \rho - \frac{1}{\gamma - 1} \frac{4\pi R_m^3}{3} p_{g,m} \left\{ \left( \frac{R_m}{R} \right)^{3\gamma - 1} - 1 \right\} \quad \text{Equation 18}$$

If in Equation (18), vapour pressure and surface tension are negligible and external pressure is constant, the energy equation described by Noltingk and Neppiras for the collapse becomes,

$$\frac{3\rho\dot{R}}{2} = p_{\infty} \left\{ \left( \frac{R_m}{R} \right)^3 - 1 \right\} - p_{g,m} \frac{1}{1 - \gamma} \left\{ \left( \frac{R_m}{R} \right)^3 - \left( \frac{R_m}{R} \right)^{3\gamma} \right\} \quad \text{Equation 19}$$

This equation can be solved for calculating  $R_{max}$  and  $R_{min}$  when the velocity  $\dot{R}$  of the bubble wall is zero.

$$p_{\infty}(\gamma - 1) \left\{ \left( \frac{R_m}{R} \right)^3 - 1 \right\} = p_{g,m} \left\{ \left( \frac{R_m}{R} \right)^{3\gamma} - \left( \frac{R_m}{R} \right)^3 \right\} \quad \text{Equation 20}$$

Where  $R = R_{max}$  or  $R_{min}$

When  $R = R_{max}$  and if  $R = R_{min} \ll R_m$  the Equation 20 reduces to

$$p_{g,m} \left( \frac{R_m}{R_{min}} \right)^{3(\gamma - 1)} = p_{\infty}(\gamma - 1) \quad \text{Equation 21}$$

As  $PV^\gamma$  and  $TV^{(\gamma-1)}$  are constant during the reversible adiabatic compression, the maximum pressure  $P_{max}$  and maximum temperature attained during collapse  $T_{max}$  can be obtained from Equation 21 and is given as

$$P_{max} = p_{g,m} \left( \frac{R_m}{R_{min}} \right)^{3\gamma} \approx p_{g,m} \left( \frac{p_\infty(\gamma - 1)}{p_{g,m}} \right)^{\frac{\gamma}{\gamma-1}} \quad \text{Equation 22}$$

$$T_{max} = \left( \frac{R_m}{R_{min}} \right)^{3\gamma-1} \approx T_m \left( \frac{p_\infty(\gamma - 1)}{p_{g,m}} \right) \quad \text{Equation 23}$$

Equation 23 for calculating the  $T_{max}$  tends to overestimate the collapse temperature because it does not take into account the heat leaking from the bubble into the surrounding fluid or the thermal conductivity of the gases or the energy consumed in the decomposition of the vapour/gas within the bubble. Figures 4 & 5 show the results of the numerical simulation of the pulsation of an isolated spherical air bubble in water irradiated with 300 kHz and 3-bar, calculated by Yasui et al.[48] using the bubble dynamics equations. The temperature at the end of the bubble collapse (Rayleigh collapse) increased up to 5100 K (Figure 5a) whereas pressure reaches to  $6 \times 10^9$  Pa (Figure 5b).

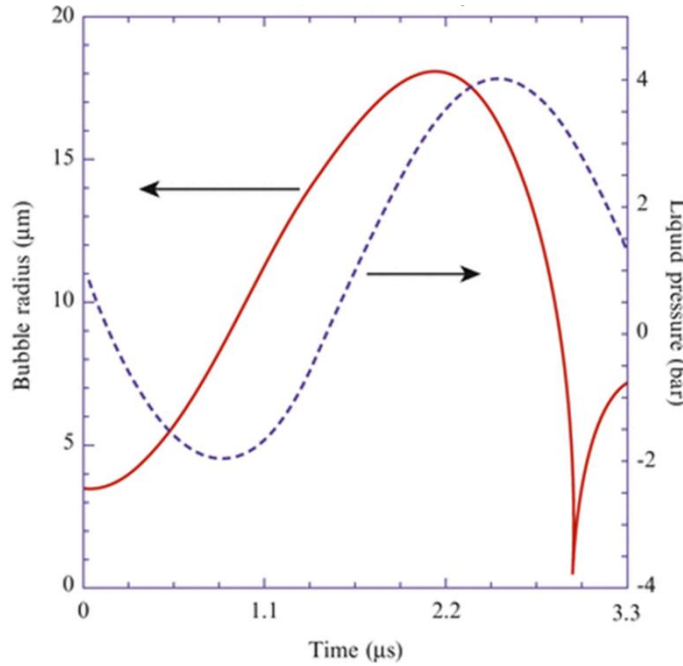


Figure 4: The result of the numerical simulation of the bubble radius as a function of time for one acoustic cycle (3.3  $\mu\text{s}$ ) when the frequency and pressure amplitude of an ultrasonic wave are 300 kHz and 3 bars, respectively. The ambient radius of an isolated spherical air bubble is 3.5  $\mu\text{m}$ . The dotted line is the acoustic pressure (plus the ambient pressure) as a function of time (Reprinted with permission from AIP Publishing LLC [48]; Copyright (2007)).

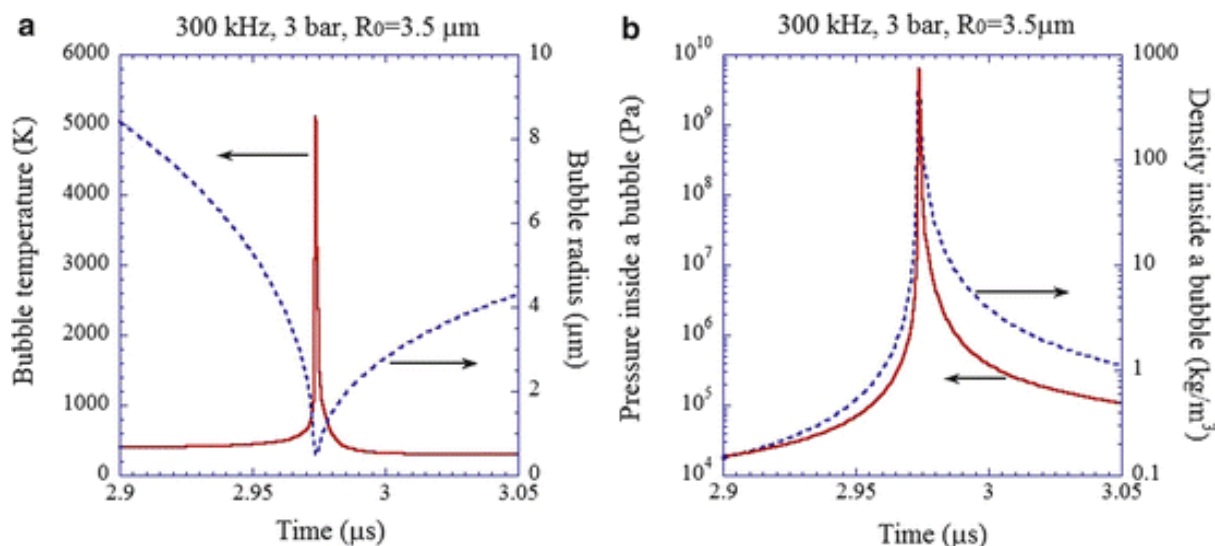


Figure 5: The results of the numerical simulation. (a) The bubble radius (*dotted line*) and the temperature inside a bubble (*solid line*). (b) The pressure (*solid line*) and the density (*dotted line*) inside a bubble with logarithmic vertical axes. (Reprinted with permission from AIP Publishing LLC [48]; Copyright (2007)).

Similar are the results shown by Merouani et al. (Figure 6) [49]. The temperature and pressure calculated inside a bubble increase suddenly at the end of the bubble collapse up to 4600 K and 1400 atm ( $\sim 140$  MPa), respectively.

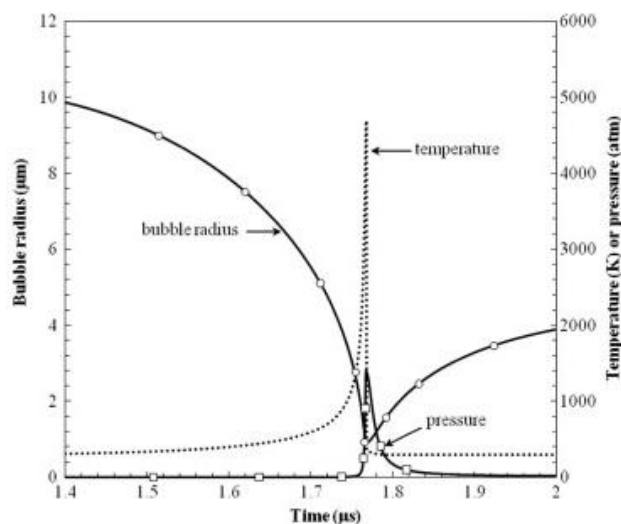


Figure 6: Bubble radius and temperature and pressure inside a bubble as function of time during the collapse phase of the bubble. The horizontal axis is only for 0.6  $\mu\text{s}$ . A maximum bubble temperature and pressure of about 4600 K and 1400 atm ( $\sim 140$  MPa), respectively are achieved at the end of the collapse. (Reprinted with permission from Elsevier [49]; Copyright (2014)).

A number of techniques have been developed for the experimental determination of the  $T_{\text{max}}$ . Misík et al. [50], using kinetic isotope effect of the sonolysis of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures, found

that the cavitation temperatures determined were dependent on the specific spin trap used and are in the range of 1000–4600 K. Mean temperatures in different regions of a “hot spot” were postulated by Suslick et al. [51], using comparative rate thermometry in alkane solutions. They have proposed a gas phase zone within the collapsing cavity with an estimated temperature and pressure of  $5200 \pm 650$  K and 500 atm, respectively, and a thin liquid layer immediately surrounding the collapsing cavity with an estimated temperature of 1900 K [51].

Henglein studied the sonolysis of methane to estimate the bubble core temperature [52]. The method is termed as methyl radical recombination (MRR) method. Sonication of methane leads to the reaction in the liquid medium:



The temperature dependence of the rate constants involved during the formation of ethane and ethylene (Reactions 5 & 6) is shown in Figure 7. The rate constant for the formation of ethylene increases with an increase in temperature whereas that for the formation of ethane has negligible dependence on the temperature. Figure 7 also shows the dependence of ratio of  $k_{\text{ethylene}}/k_{\text{ethane}}$  ( $= \text{yield}_{\text{ethylene}}/\text{yield}_{\text{ethane}}$ ) as a function of temperature which can be used to estimate the bubble temperature. Temperatures in the range of 1930 K to 2720 K have been estimated using this method.

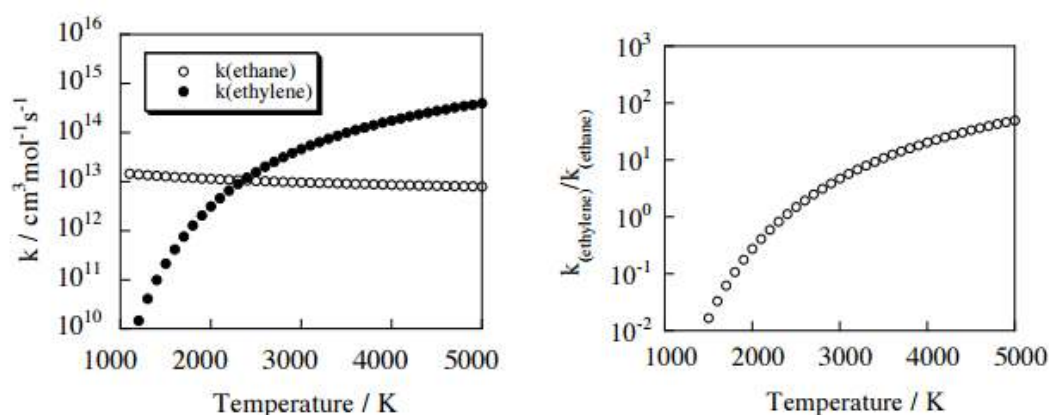


Figure 7: The rate constants for the formation of ethane and ethylene as a function of temperature (left) and temperature dependence of the ratio,  $k_{\text{ethylene}}/k_{\text{ethane}}$  (right) (Reprinted with permission from Elsevier [52]; Copyright (1990)).

Tauber et al. estimated the temperature in the range of 2300 K and 3600 K using the MRR method by studying the sonolysis of n-butanol [53]. Grieser and coworkers [54, 55] noted that cavitation bubble temperature is affected by the surface activity of alcohols used to generate methyl radicals.

#### 1.4. Physical & chemical effects generated by acoustic cavitation

The sudden violent collapse of a cavitation bubble gives rise to a number of physical and chemical effects in the liquid such as microstreaming, agitation, turbulence, microjetting, shock waves, generation of radicals, sonoluminescence etc. [19]. Shock waves are produced when the bubble collapse symmetrically [19]. However, when the bubble collapse unsymmetrically (mostly at a boundary), it leads to the formation of a jet in the liquid (Figure 8) [56] due to the uneven acoustic field around the bubble.

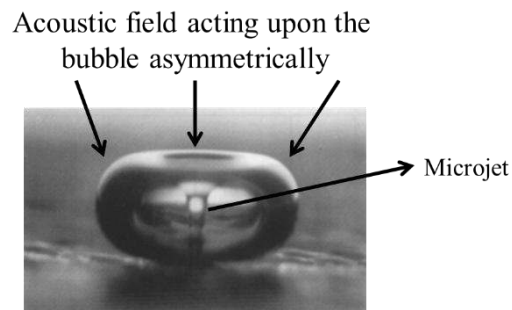


Figure 8: Microjet formation when a bubble collapses near solid surface; Adapted from [57].

The microjets have velocities of the order of 100 m/s. The effect of shock waves and microstreaming together with the transition from high to low flow velocities away from the bubble surface generates extensive amount shear stresses [57]. The generation of very high temperatures on bubble collapse leads to local heating. The heat generated can raise the temperature of the core of the bubbles to thousands of degrees for a short period (micro- to nanoseconds). Such extreme thermal conditions lead to light emission from the bubbles, referred to as sonoluminescence [58]. It was first observed in 1933 by Marinesco and Trilliant [59]. Frenzel and Schultes [7] and Griffing and Sette [60] were the first to detect sonoluminescence using photomultipliers with accurate temporal resolution. Sonoluminescence can be divided in to two categories [61]. A large number of cavitation bubbles generates multibubble sonoluminescence (MBSL). Single bubble sonoluminescence (SBSL) refers to emission observed from a stably oscillating single bubble in a liquid. The change in radius of a single bubble within one acoustic cycle is shown in Figure 9 [1, 61-63]. The relative scattered intensity is proportional to radius of the bubble. Using a stroboscopic technique, images of an oscillating bubble were recorded and shown in Figure 9. SL emission could also be observed at the end of bubble collapse.

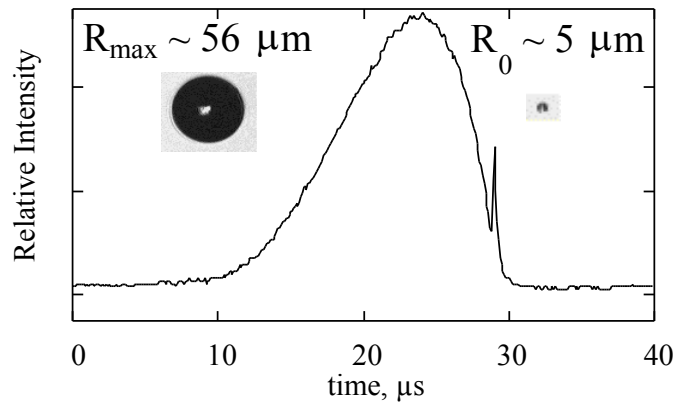


Figure 9: Relative scattered light intensity, proportional to the size of the bubble, as a function of time. Bubble growth is a relatively slow process compared to the collapse. The spike observed near end of collapse phase is the SL emission, Adapted from [1].

The intensity of SL depends on the nature of liquid medium [64, 65], amount of dissolved gases [66, 67], hydrostatic pressure [68], acoustic pressure amplitude [9, 60], and acoustic frequency [60, 69]. Different theoretical models have been proposed for SL. One model is based on inward moving shock waves during bubble collapse: it is believed that light is emitted from the bubble centre where plasma is created by the shock-wave convergences [70-72]. Another is quasiadiabatic compression model, where a bubble is heated by the quasiadiabatic compression [73, 74]. Both SBSL and MBSL originates from quasiadiabatic compression [62, 75]. However, Yasui has proposed that sonoluminescence is originated by the heat generated from whole of the bubble rather than a local point [62, 74] and has constructed a theoretical model for SL. Yasui has suggested that SL is due to both electron-ion radiative recombination and electron atom Bremsstrahlung [75]. The mechanism behind the SL observed from the noble gas bubbles is usually radiative recombination of electrons and ions and electron-atom bremsstrahlung [62].

The intensity of light emission from cavitation bubbles can be increased significantly by adding a small amount of luminol in aqueous alkaline solutions. This emission is referred to as sonochemiluminescence (SCL) [76-79], which arise due to the reaction between OH radicals and luminol. Thus, SCL indicates chemically active region in a reactor. Ashokkumar et al. [78, 79] have shown that two groups of cavitation bubbles exist. One group of bubbles reach higher temperatures for SL to occur and the 2<sup>nd</sup> group causing chemical reactions (Figure 10). It can be seen in the figure that SL occurs only in a small region closer to the liquid/water interface. It was speculated that these bubbles experience relatively larger acoustic force due to the reflected waves at the air/liquid interface. It can also be observed that chemical activity could be observed throughout the reactor from cavitation bubbles that reach a relatively lower temperature enough to cause chemical reactions (OH radical generation).

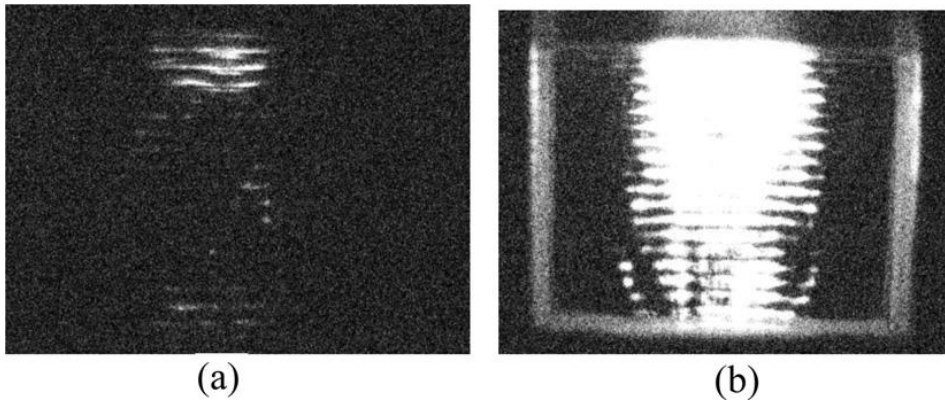


Figure 10: Sonoluminescence from water and (b) sonochemiluminescence from an aqueous solution containing luminol; frequency = 170 kHz; power = 12W (Reprinted with permission from John Wiley and Sons [78]; Copyright (2010)).

The speculation that SL bubbles reach relatively higher temperatures is supported by the experimental data published later. A comparison between the size distributions of SL emitting and sonochemistry producing cavitation bubbles was studied by Brotchie et al. [44]. They have shown that SL emitting bubbles are larger than sonochemically active bubbles (Figure 11) [44].

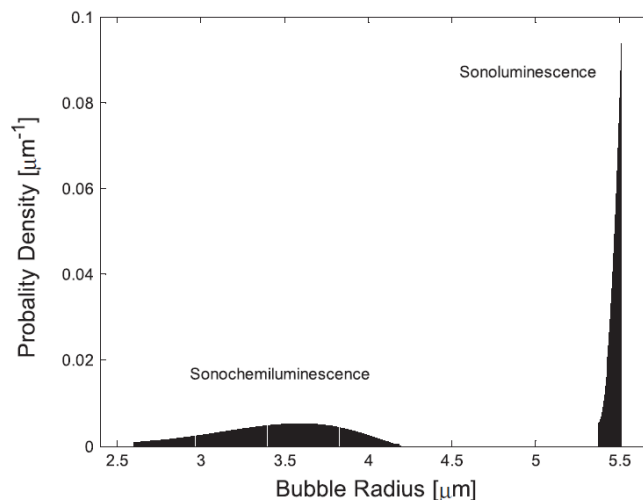
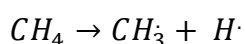


Figure 11: Bubble radius distribution of SL and SC bubbles. Frequency: 575 kHz (Reprinted with permission from American Physical Society [44]; Copyright (2009))

Another consequence of the extreme conditions of ultrasound is that it leads to a variety of chemical reactions (formation of highly reaction radical species). When the argon saturated liquid is sonicated formation of  $H^\cdot$  and  $OH^\cdot$  radicals (Reaction 2) takes place as majority of bubble content is water vapours.  $H^\cdot$  radicals are reducing in nature whereas  $OH^\cdot$  radicals are oxidising in nature.



Reaction 1



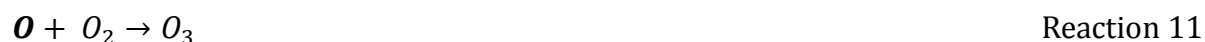


A number of techniques have been used to confirm the formation and quantification of radical species. ESR spin traps and chemical dosimeters have been used for the quantification of the radical produced during sonication [50,80, 81]. Another method is the reaction between terephthalic acid and OH $\cdot$  radicals which leads to the formation of fluorescent hydroxyterephthalic acid [81, 82]. The intensity of fluorescence can be utilized to quantify the amount of OH $\cdot$  radicals generated during cavitation. A simple method called ‘Weissler’ method can be used to quantify OH Radicals, which is based on the oxidation of iodide ions [1, 83]. In this method, OH $\cdot$  radicals react to produce hydrogen peroxide (Reaction 7) which can oxidize iodide ions to molecular iodine (Reaction 8). When excess of iodide ions are present, molecular iodine is converted into the triiodide complex (Reaction 9). Triiodide has absorption maximum at 353 nm which can be used to quantify the amount of iodine, and hence the amount of OH $\cdot$  radicals generated.



## 1.5. Single bubble sonochemistry

In air-saturated water, a variety of radicals and molecular products such as H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub>, O, O<sub>3</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>, and OH radicals (Reactions 2, 7, 10-15) are generated (Figure 12c).



The quantification of primary radicals and molecular products in multibubble systems has been extensively studied [26, 44, 55, 84-88]. Such information for a single bubble system has

also been theoretically studied [48, 49, 89]. Only in the past decade, experimental details on the amount of radicals and molecular products generated for single bubble systems became available [62, 76, 90].

Yasui et al. [89] have numerically calculated chemical reaction yield for a single cavitation bubble. In Figure 12a, the changes in bubble radius and temperature inside a bubble are shown. It is seen that the temperature inside a bubble increases at the end of bubble collapse up to 6500 K, which is much lower than that measured in argon saturated bubble because the molar specific heat of nitrogen and oxygen is larger than that of argon. Figure 12b shows the number of different molecules produced inside a bubble. The bubble content mostly consists of nitrogen, oxygen, and water vapour and main chemical products obtained in this case are  $\text{HNO}_3$ ,  $\text{HNO}_2$ , O, and  $\text{H}_2\text{O}_2$ . Figure 12c shows the intensity of the light emitted from a bubble. SL is only emitted at the end of the bubble collapse having pulse width of about 60 ps. The number of photons emitted is equal to  $1.53 \times 10^4$ , which was found to be 20% less than that of in the case of argon saturated bubble as the SL intensity is affected by the amount and nature of the dissolved gases. Yasui observed that these results were consistent with the experimental observation by Matula and Crum [91].

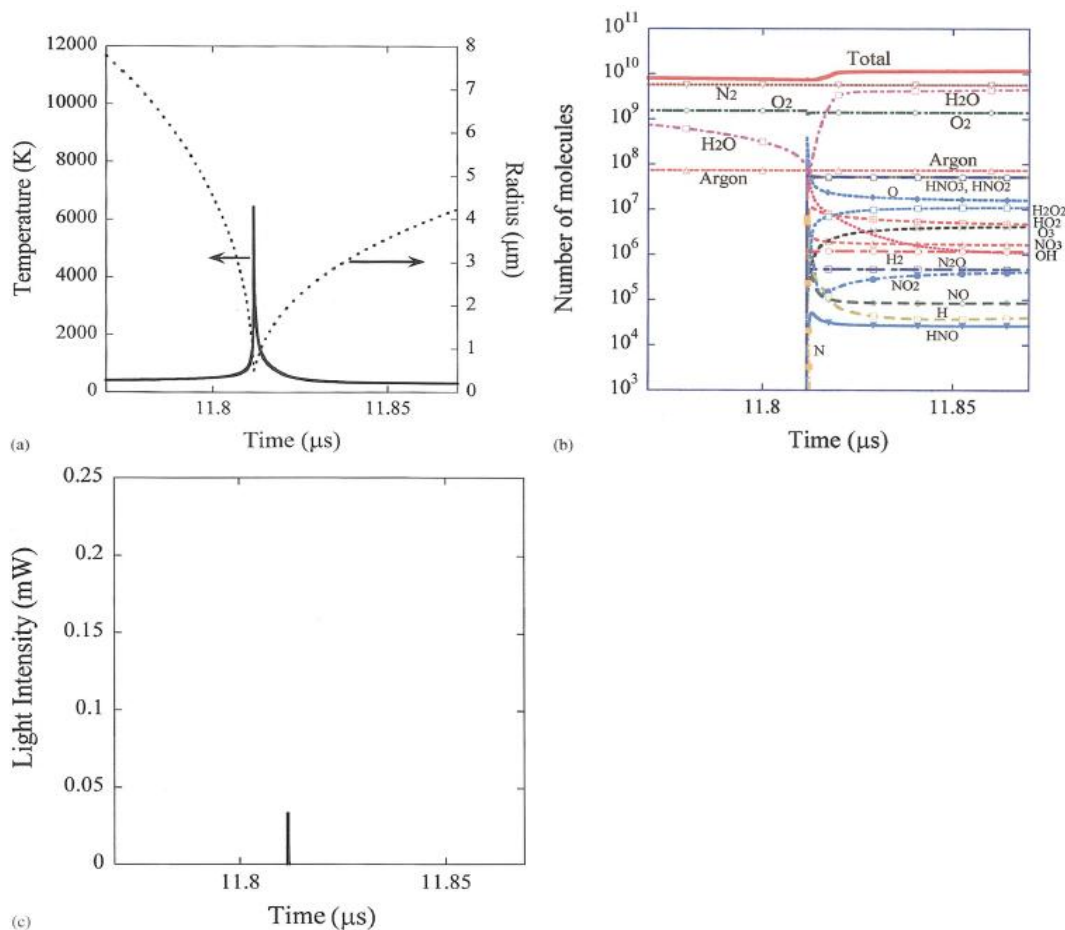


Figure 12: The calculated results for an initial air bubble at around the end of the bubble collapse only for 0.1 ms. (a) The bubble radius and the temperature inside a bubble. (b) The number of molecules inside a bubble. (c) The intensity of the light emitted from a bubble (Reprinted with permission from AIP Publishing LLC [89]; Copyright (2005)).

Didenko and Suslick have determined the amount of different chemical products experimentally. Table 1 shows the average amounts of chemical products per acoustic cycle. It can be seen from the data shown in Table 1 that the main chemical products are hydrogen molecule, oxygen atom, hydrogen peroxide, hydrogen atom, and nitrous acid. According to Didenko and Suslick [90], the amount of OH radicals that diffuses into the liquid after one acoustic cycle is  $8.2 \times 10^5$  (number of molecules,) which is consistent with the calculated result of  $6.6 \times 10^5$ . The generation of  $\text{NO}_2$  and further reaction of  $\text{NO}_2$  with  $\text{H}_2\text{O}$  leads to the formation of nitric acid [92]. It is for this reason that sonication of air-saturated water leads to a decrease in solution pH [1]. The amount of  $\text{NO}_2^-$  ions produced in one acoustic cycle was experimentally determined by Didenko and Suslick [90] was  $9.9 \times 10^6$  (number of molecules) (Table 1). A similar number was reported by Koda et al. [93], which was found to be larger than the numerically calculated value by Yasui et al. [89].

Conditions	22°C	3°C
$R_{\max}$ ( $\mu\text{m}$ )	28.9	30.5
Number of OH Radicals per cycle	$6.6 \times 10^5$	$8.2 \times 10^5$
Number of photons per cycle	$8.1 \times 10^3$	$7.5 \times 10^4$
Number of $\text{NO}_2^-$ ions per cycle	$3.7 \times 10^6$	$9.9 \times 10^6$
Potential energy at $R_{\max}$ (eV)	$6.4 \times 10^{10}$	$7.5 \times 10^{10}$
Energy to form OH radicals (eV per cycle)	$3.4 \times 10^6$	$4.3 \times 10^6$
Energy to form $\text{NO}_2^-$ ions (eV per cycle)	$1.6 \times 10^6$	$4.2 \times 10^6$

In Table 2, the average amount of chemical products diffusing into a liquid per acoustic cycle for the case of *an air bubble* is shown. A single bubble trapped at the pressure antinode of a standing ultrasonic wave initially consists mainly of air, and its main content gradually changes to argon. Yasui et al. [89] have shown that the average amount of  $\text{HNO}_2$  ( $4.0 \times 10^7$ ) dissolving in the liquid per oscillation from an initial air bubble is an order of magnitude larger than that from a SBSL bubble in steady state (an argon bubble) and it is even larger than the experimentally reported value of  $9.9 \times 10^6$ . This suggests that the experimentally reported production rate of  $\text{NO}_2^-$  ions maybe the time averaged value during the course of the gradual change of the bubble content from air to argon. The amount of OH radicals  $9.9 \times 10^5$  dissolving into liquid from an initial air bubble is not so different from that  $6.6 \times 10^5$  from a SBSL bubble in a steady state and is consistent with the experimentally reported value  $8.2 \times 10^5$ .

The main oxidants dissolved in the liquid are oxygen and hydrogen peroxide besides the OH radicals. It has been found that in a multibubble system, where a standing wave is established, many bubbles behave as single spherical SBSL bubbles [87, 89, 94-97]. The reason behind this is Bjerkness force. The radiation force, which acts on the bubbles leads to the gathering of bubbles at the regions where the acoustic amplitude is comparable cavitation threshold. It has been concluded that even in a multibubble system oxidant produced is not only OH radicals but also oxygen atom and hydrogen peroxide irrespective of the effect of neighbouring bubbles on the bubble dynamics, shielding of acoustic field, etc. [89, 98]. According to Yasui et al. [89], O atom may have been created by the dissociation of oxygen molecules and water vapour molecules inside the collapsing bubble as given in Reactions 16-19 (radicals are represented in bold letters; M is an inert third body).



**Table 2: the average amount of chemical products that dissolve into the liquid from the interior of an initial air bubble in one acoustic cycle (Reprinted with permission from AIP Publishing LLC [89]; Copyright (2005))**

Chemical species	Number of molecules per acoustic cycle
HNO <sub>2</sub>	4.0 x 10 <sup>7</sup>
HNO <sub>3</sub>	3.7 x 10 <sup>7</sup>
O	1.6 x 10 <sup>7</sup>
H <sub>2</sub> O <sub>2</sub>	5.1 x 10 <sup>6</sup>
O <sub>3</sub>	2.7 x 10 <sup>6</sup>
HO <sub>2</sub>	2.3 x 10 <sup>6</sup>
NO <sub>3</sub>	1.1 x 10 <sup>6</sup>
H <sub>2</sub>	1.0 x 10 <sup>6</sup>
OH	9.9 x 10 <sup>5</sup>
NO <sub>2</sub>	3.9 x 10 <sup>5</sup>
N <sub>2</sub> O	3.0 x 10 <sup>5</sup>
NO	1.3 x 10 <sup>5</sup>
H	1.1 x 10 <sup>5</sup>
HNO	2.8 x 10 <sup>4</sup>
N	2.7 x 10 <sup>3</sup>
N <sub>2</sub> O <sub>5</sub>	6.8 x 10 <sup>2</sup>

Different methods to estimate the amount of oxygen atoms have been reported in the literature [99-101]. In 1985, Hart and Henglein [102] suggested that O atoms created inside a bubble may oxidize I<sup>-</sup> ion in an aqueous KI solution containing a mixture of argon and O<sub>2</sub>. In their experimental results (Figure 13), the amount of I<sub>2</sub> production in aqueous KI solution was considerably larger than that of H<sub>2</sub>O<sub>2</sub> generated in pure water (in the absence of O<sub>2</sub>). Based on this observation, they concluded that there should be some oxidant such as O in addition to OH radicals and H<sub>2</sub>O<sub>2</sub>. Hart and Henglein [102] as well as Yasui [89] suggested that considerable amount of O atoms can be produced in an air filled collapsing bubble. Therefore sonochemistry can serve as important tool to study the chemical reactions of oxygen atom in liquids [103].

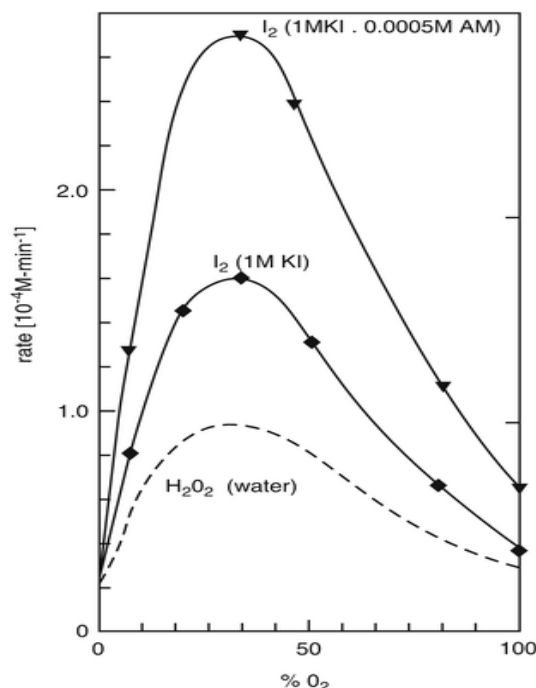


Figure 13: Experimental results of the rate of production of  $\text{H}_2\text{O}_2$  in pure water and  $\text{I}_2$  in 1 M KI solution or 1 M KI + 0.0005 M ammonium molybdate solution under different mixtures of argon and oxygen dissolved in the solution (Reprinted with permission from American Chemical Society [102]; Copyright (1985)).

## 1.6. Effect of ultrasound frequency on sonochemistry

The extent of sonochemical reactions (for example, yield of primary and secondary radicals) and sonoluminescence intensity produced by acoustic cavitation depends on the frequency, power, etc. Various methods have been used to estimate the cavitation yield such as the amount chemical products obtained,  $T_{\max}$ , SL intensity etc. as a function of acoustic frequency. Yasui et al. [48] have estimated the average temperature and rate of production of main oxidant OH at different frequencies (20, 100, 300 and 1 MHz) as a function acoustic amplitude (Figure 14). At lower frequencies (20 kHz and 100 kHz), maximum temperature was reached at relatively lower acoustic amplitudes. This is due to bubble expansion to a relatively larger volume caused by the longer acoustic period, resulting in an increase in the amount of water vapour inside a bubble [104]. For a vaporous bubble, which is defined as a bubble with higher molar fraction of vapour than 0.5 at the end of the bubble collapse, the main oxidant created is OH radicals [48].

The amount of  $\text{H}_2\text{O}_2$  produced at 100 kHz is higher compared to that produced at 20 kHz because a high temperature is maintained at 20 kHz for longer time as compared to higher frequencies, which can dissociate  $\text{H}_2\text{O}_2$  into OH radicals. It has been shown that  $T_{\max}$  is proportional to  $R_{\max}$  for the frequencies greater than 16 kHz [105]. It has been observed for a gaseous bubble that when the molar fraction of vapour is less than 0.5, the collapse temperature ranges from 4000 K to 6500 K and the main oxidant is  $\text{H}_2\text{O}_2$ . However, when the bubble temperature is greater than 6500 K in gaseous bubbles, the main oxidant is O atom. The consumption of oxidants took place inside an air bubble by an oxidizing nitrogen when the bubble temperature is higher than 7000 K and the main chemical products are  $\text{HNO}_2$ , NO, and  $\text{HNO}_3$  [48, 106].

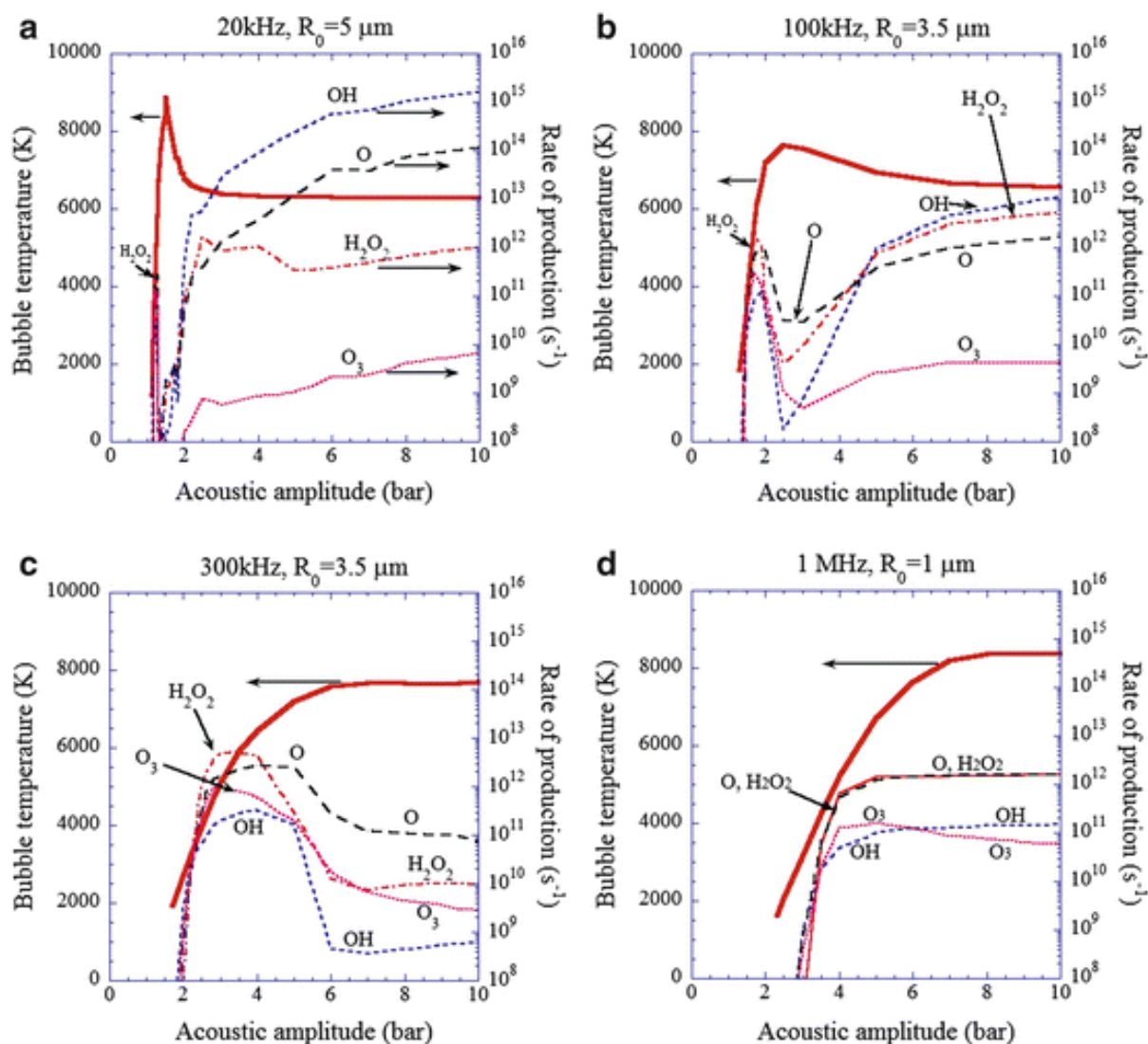


Figure 14: The numerical simulations on the rate of production of each oxidant inside an isolated air bubble per second estimated by the first bubble collapse as a function of acoustic amplitude with the temperature inside a bubble at the end of the bubble collapse ( *the thick line*): (a) 20 kHz and  $R_0 = 5 \mu\text{m}$ . (b) 100 kHz and  $R_0 = 3.5 \mu\text{m}$ . (c) 300 kHz and  $R_0 = 3.5 \mu\text{m}$ . (d) 1 MHz and  $R_0 = 1 \mu\text{m}$  (Reprinted with permission from AIP Publishing LLC [48]; Copyright (2007)).

While Yasui's calculations on frequency effect are based on a single bubble system, the overall chemical activity in a multibubble system should be looked at with a different approach. While single bubble dynamics calculations provide an avenue to theoretically calculate bubble temperatures, chemical yield, sonoluminescence intensity, etc., such calculations may not provide insight into multibubble systems. Single bubble calculations tend to provide overestimates of bubble temperatures and chemical yields in when multibubble systems are considered. This is due to various factors that include bubble clustering, bubble coalescence, asymmetric collapse of bubbles, inhomogeneous nature of acoustic field, etc.

It is well known that with an increase in frequency, the number of antinodes and hence the number of cavitation bubbles generated increase. Figure 15 shows the schematic and

photographic images of the standing waves observed at 37 and 440 kHz, which clearly illustrates the increase in the number of standing waves as well as the bubble population. It has been noted that the radical yield increases with an increase in frequency, reaches a maximum value and decreases with further increase in the frequency. The highest sonochemical yield is obtained between 200-800 kHz and demonstrated in various studies [61, 86, 107-109].

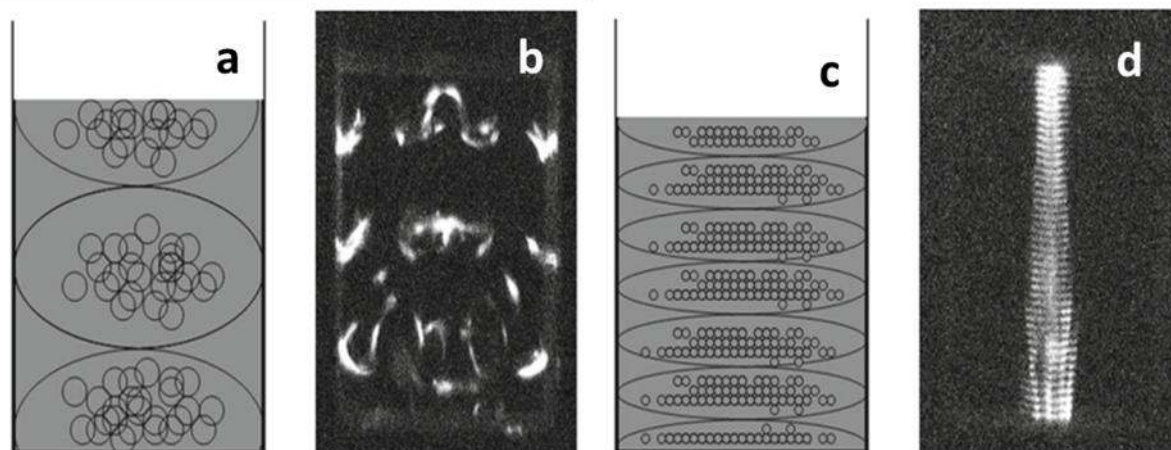


Figure 10: (a) and (c) schematic representation of the standing wave leading to increase in the number of bubbles with increasing frequency, (b) and (c) Images of Sonoluminescence profile at 37 and 440 kHz respectively (Reprinted with permission from Springer [19]; Copyright (2016)).

Figure 16 represents the OH radical yield as a function of sonication time obtained by sonicating water for different frequencies (20 kHz, 358 kHz and 1062 kHz) at power of 0.90 W/cm<sup>2</sup> [110]. The amount of OH radicals produced was highest at 358 kHz whereas decrease was observed when the frequency was increased to 1062 kHz.

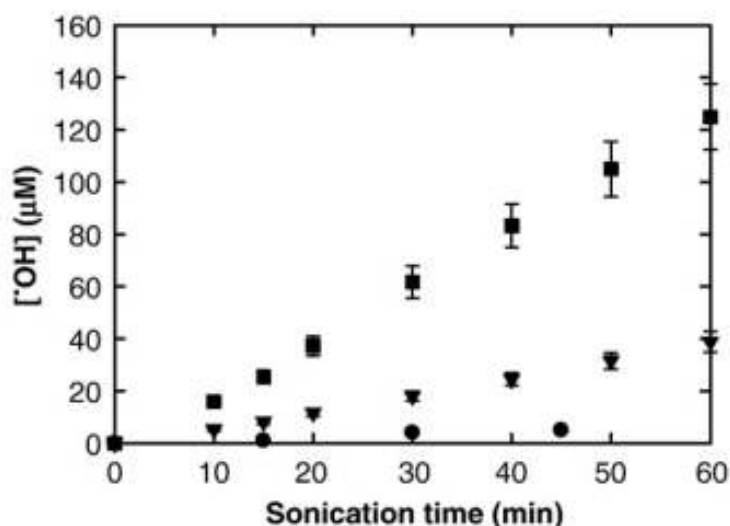


Figure 11: OH radicals yield as a function of sonication time for different ultrasonic frequencies (■ 358 kHz, ▼ 1062 kHz, ● 20 kHz) at 0.90 W cm<sup>-2</sup> (Reprinted with permission from Elsevier [110]; Copyright (2008)).

This is due to a relatively lower bubble temperature generated at higher frequency and a lower amount of water vapour that could evaporate into a bubble during the expansion phase [110], as shown in Figure 17 by theoretical calculations.

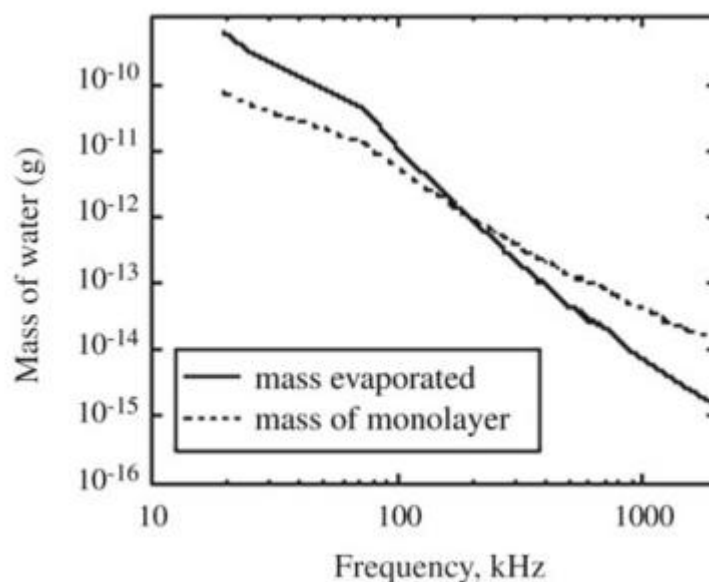


Figure 17: Mass of water evaporated from bubble surface during a single expansion phase at various frequencies (Reprinted with permission from Springer [19]; Copyright (2016)).

Using the resonance radius of the bubbles at each frequency, the amount of water molecules in a monolayer on the surface of bubbles could be calculated [110]. As for the evaporation process, a finite time is required. From the time required for evaporation and expansion cycle and the number of molecules at the interface, it can be seen that the mass that evaporates exceeds the amount present in a monolayer on the bubble surface at lower frequencies. At higher frequencies, the amount that could evaporate is less than a monolayer, which is due to very short expansion time available during bubble oscillations. Though a surge in bubble population occurs at higher frequency, the size of bubble reduces leading to a decrease in the bubble temperature hence the radical yield. Thus, a combination of lower bubble temperature and lower amount of water vapour present inside a collapsing bubble is responsible for a decrease in sonochemical efficiency at very high frequencies.

## 1.7. Summary

This chapter has provided an overview of the basics and fundamentals of sonochemistry including the dynamics of bubble motion, growth and collapse as well as different physical and chemical effects generated after the bubble collapse. The primary and secondary radicals and physical effects such as microjetting, microstreaming, shear forces and the shock waves



generated during acoustic cavitation have been used in material synthesis, sonochemical degradation of pollutants, mass transfer enhancement, electrochemistry, food technology, phase separation, alteration of enzyme activity and removal of deposits and biofilms [108-113], which will be discussed in various chapters of this book.

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