



Effects of ultrasound frequency and acoustic amplitude on the size of sonochemically active bubbles – Theoretical study

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ABSTRACT

Numerical simulation of chemical reactions inside an isolated spherical bubble of oxygen has been performed for various ambient bubble radii at different frequencies and acoustic amplitudes to study the effects of these two parameters on the range of ambient radius for an active bubble in sonochemical reactions. The employed model combines the dynamic of bubble collapse with the chemical kinetics of single cavitation bubble. Results from this model were compared with some experimental results presented in the literature and good apparent trends between them were observed. The numerical calculations of this study showed that there always exists an optimal ambient bubble radius at which the production of oxidizing species at the end of the bubble collapse attained their upper limit. It was shown that the range of ambient radius for an active bubble increased with increasing acoustic amplitude and decreased with increasing ultrasound frequency. The optimal ambient radius decreased with increasing frequency. Analysis of curves showing optimal ambient radius versus acoustic amplitude for different ultrasonic frequencies indicated that for 200 and 300 kHz, the optimal ambient radius increased linearly with increasing acoustic amplitude up to 3 atm. However, slight minima of optimal radius were observed for the curves obtained at 500 and 1000 kHz.

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1. Introduction

One of the most fundamental parameters which characterize the sonochemical reaction field is the size of bubbles that can undergo inertial collapse to produce sonochemical effects. The measurement of this parameter is difficult due to the complex nature of acoustic cavitation. There have been several studies [1–3] investigating the cavitation bubble size using different techniques, with the majority conducted at 20 kHz. Recently, Brotchie et al. [4] investigated the effects of ultrasound frequency and acoustic power on the bubble-size distribution in water using a new pulsed ultrasound method. They found that the mean bubble size increased with increasing acoustic power and decreased with increasing ultrasound frequency.

Theoretically there have been several models investigating the rates of chemical reactions inside a collapsing bubble [5–9]. However, to the best of our knowledge, there are only a few studies that investigate the size (in term of ambient bubble radius) of bubbles which can produce sonochemistry. The most extensive of these studies was that conducted by Yasui et al. [10]. Using a comprehensive model, they have estimated the range of ambient radius for the production of oxidants in an oscillating air bubble. Despite the detail of this model, a limited amount of information about the

effect of ultrasound frequency and acoustic amplitude on the range of ambient radius for an active bubble was given.

The purpose of this paper is to investigate the effects of ultrasound frequency and acoustic amplitude on the range of ambient radius for an active bubble in sonochemical reactions using a model that combines the dynamic of bubble collapse with the chemical kinetics of single cavitation bubble. Numerical simulations of chemical reactions inside an oxygen bubble were performed for various ambient bubble radii at different frequencies (200, 300, 500 and 1000 kHz) and acoustic amplitudes (up to 3 atm).

2. Model

In the adopted model, the oscillated bubble is assumed to be spherically symmetric and is initially composed of mixture of oxygen and water vapor. The temperature and pressure in the bubble are assumed to be spatially uniform and the gas content of the bubble behaves as an ideal gas [11]. The radial dynamics of the bubble is described by the Keller equation that includes first order terms in the Mach number $M = \dot{R}/c$ [12,13]:

$$\left(1 - \frac{\dot{R}}{c}\right) R \ddot{R} + \frac{3}{2} \left(1 - \frac{\dot{R}}{3c}\right) \dot{R}^2 = \frac{1}{\rho_L} \left(1 + \frac{\dot{R}}{c} + \frac{R}{c} \frac{d}{dt}\right) \left[p - p_\infty - \frac{2\sigma}{R} - 4\mu \frac{\dot{R}}{R} + P_A \sin(2\pi ft)\right] \quad (1)$$

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in this equation dots denote time derivatives (d/dt), R is the radius of the bubble, c is the speed of sound in the liquid, ρ_L is the density of the liquid, σ is the surface tension, μ is the liquid viscosity, p is the pressure inside the bubble, p_∞ is the ambient static pressure, P_A is the acoustic amplitude and f is the sound frequency. The acoustic amplitude P_A is correlated with the acoustic intensity I_a , or power per unit area, as $P_A = (2I_a \rho_L c)^{1/2}$ [14].

In the model, the expansion of the bubble is assumed as isothermal and its total compression is considered as adiabatic [7]. This assumption is very accepted as for higher frequencies the lifetime of the bubble is very short and the implosion event occurs very rapidly. A further assumption used is that in one acoustic cycle, the mass and heat transfer at the bubble wall are neglected. However, it should be recognized that the inclusion of these effects will not affect strongly the bubble dynamics and thus the qualitative trend of the bubble temperature and pressure with variation in the operating parameters will not be also affected [7,14,15]. Thus, the current model takes, as input, initial bubble vapor content and neglects mass and heat transfer during bubble expansion and collapse.

On the basis of the above assumptions, the pressure and temperature inside the bubble at any instant during adiabatic phase can be calculated from the bubble size as

$$p = \left[P_v + P_{g0} \left(\frac{R_0}{R_{\max}} \right)^3 \right] \left(\frac{R_{\max}}{R} \right)^{3\gamma} \quad (2)$$

$$T = T_\infty \left(\frac{R_{\max}}{R} \right)^{3(\gamma-1)} \quad (3)$$

where P_v is the vapor pressure, $P_{g0} = p_\infty + (2\sigma/R_0) - P_v$ is the gas pressure in the bubble at its ambient state ($R = R_0$), R_0 is the ambient bubble radius, T_∞ is the bulk liquid temperature, R_{\max} is the maximum radius of the bubble and γ is the ratio of specific heats (c_p/c_v) of the mixture.

For a bubble initially containing oxygen and water vapor, a kinetic mechanism consisting in nineteen elementary chemical reactions is taken into account involving O_2 , H_2O , $\cdot OH$, $H\cdot$, O , $HO_2\cdot$, H_2 and H_2O_2 chemical species. Detailed informations of the kinetics mechanism used in the present numerical simulations were available in the literature [5,16].

The chemical kinetics model consists of the reaction mechanism and determines the production of each species during the bubble collapse. The detail of the chemical model used for the simulation of the reactions system has been well described by Choi et al. [17].

The simulation of the reactions system starts at the beginning of the adiabatic phase. The input parameters of the reactions system are the composition of the bubble on water vapor and oxygen at this point, and the temperature and pressure profiles in the bubble during adiabatic phase. These parameters are obtained by solving the dynamics equation (Eq. (1)). As the bubble temperature increases during the adiabatic phase, the reaction system evolves and radicals start to form by thermal dissociation of H_2O and O_2 molecules in the bubble. Thus, the composition of the bubble on all species expected to be present (O_2 , H_2O , $\cdot OH$, $H\cdot$, O , $HO_2\cdot$, H_2 and H_2O_2) was determined at any temperature during the collapse phase. The numerical simulation performed for all conditions of this study indicated that the amount of each chemical species created inside a bubble attained their upper limit at the end of the collapse as the bubble temperature and pressure reached their upper values at this point. Thus, in the following, the amount of each species created in the bubble is defined as that of the end of the bubble collapse. Also, in the following, the sonochemical activity of a bubble is represented by the amount of the oxidants, which is defined as the sum of the number of moles of all the oxidants ($\cdot OH$, $HO_2\cdot$, $H\cdot$, O , H_2O_2) formed in the bubble per collapse.

3. Results and discussion

Because most of the important researches on sonochemistry are performed at ultrasound frequencies in the range of 200–1000 kHz, the present theoretical study has been performed at these sonication conditions.

3.1. Effect of ambient bubble radius on the production of the oxidants

Numerical calculations for an ultrasonic frequency of 500 kHz and acoustic amplitude of 2.5 atm have been performed for various ambient bubbles radii. The obtained results are plotted in Fig. 1. From this figure, it seems that among all the oxidants, only $\cdot OH$ radicals and oxygen atoms are formed in the bubbles at appreciable amounts. The lower bound of the ambient radius for the production of the oxidants is nearly the same for all the oxidants ($0.3 \mu m$ if the threshold of the production is assumed as 10^{-22} mol [10]), whereas the upper bound varies from $6.8 \mu m$ for $H\cdot$ and O atoms to $7 \mu m$ for $\cdot OH$ and $HO_2\cdot$ radicals (the threshold of the production is also assumed as 10^{-22} mol). For each oxidant, there exists an optimal ambient bubble radius at which the amount of this oxidant is highest. The existence of an optimal radius for the production of the oxidants has been previously obtained by Sochard et al. [6] at 20 kHz and Yasui et al. [10] at 300 kHz.

From Fig. 1, it was noticed that the range of ambient bubble radius for sonochemically active bubble is from 0.3 to $7 \mu m$ and the optimal ambient bubble radius is $3 \mu m$. According to some experimental data, the range of ambient bubble radius for an active bubble is rather narrow: from 2.8 to $3.7 \mu m$ at 515 kHz for sonoluminescing bubbles [18] and from 2.6 to $4.2 \mu m$ at 575 kHz for sonochemiluminescing bubbles [4].

3.2. Effect of ultrasound frequency and acoustic amplitude on the size of sonochemically active bubbles

Numerical simulations of chemical reactions were performed for various ambient bubble radii at different frequencies (200, 300, 500 and 1000 kHz) and acoustic amplitudes (up to 3 atm). Normalized values of the production of the oxidants are shown in Fig. 2 as function of ambient bubble radius for the four selected

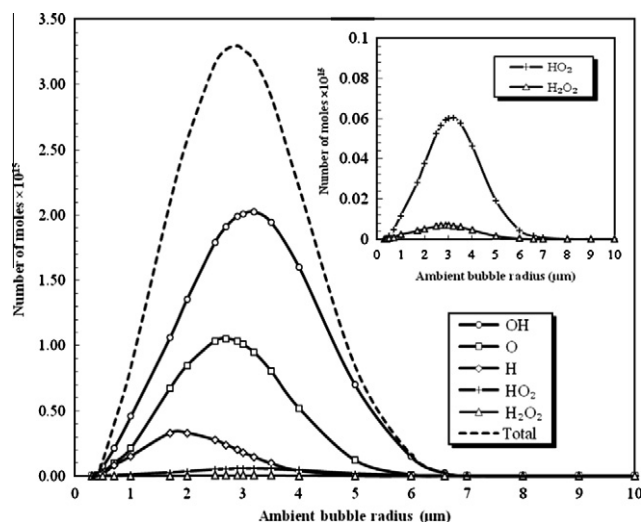


Fig. 1. Production per collapse of each chemical oxidant as function of ambient bubble radius. The lateral figure is a zoomed view for HO_2 and H_2O_2 (conditions: frequency: 500 kHz; acoustic amplitude: 2.5 atm; temperature: 20 °C; static pressure: 1 atm).

frequencies. The values are normalized with respect to the maximum value obtained at each acoustic amplitude for each frequency.

From Fig. 2, it is quite clear that as the ultrasound frequency increases, the range of ambient radius for an active bubble becomes less wideness and the optimal ambient radius becomes smallest. This behavior was observed for all employed acoustic amplitudes. Experimentally, in addition to the size distribution decreasing with increasing acoustic frequency, Brotchie et al. [4] have also observed that the mean bubble size decreases as the frequency of ultrasound increases, which is qualitatively what we observe in the present numerical investigation. We would like to mention here that Brotchie's experimental data were obtained from a bulk solution (multibubble system), whereas our results were obtained from a single bubble system. Therefore, a direct comparison between this model and experimental results is not possible but, despite all these considerations, a similar general trend between results provided by the model and the experimental data has been observed.

In Table 1, the range of the ambient radius and the optimal bubble radius determined in this study for 1.5 and 2.5 atm, the linear resonance radius (R_r), and other theoretical and experimental results collected from the literature are presented together as function of ultrasonic frequency. First of all, it is important to notice that the most experimental results presented in Table 1 were

determined at low acoustic amplitudes; whereas Yasui's results have been obtained at relatively high acoustic amplitudes. This is the reason why we select the two representative acoustic amplitudes (1.5 and 2.5 atm) in this section.

The most important observation that can be made from Table 1 is that the optimal ambient bubble radius for the production of the oxidants is always smaller than the linear resonance radius. Similar behavior has been observed by Burdin et al. [1], Yasui et al. [10] and Brotchie et al. [4]. Another feature in Table 1 is that the range of ambient radius for sonochemically active bubbles determined experimentally is rather narrow than that obtained in our study. Yasui's numerical calculations at 300 and 1000 kHz for an air bubble yield values were more consistent with our numerical calculations. The observed difference in the range of ambient radius for an active bubble between the theoretical and experimental results might be also due to different saturating gases: oxygen for our study and air for Yasui's investigations and Brotchie's experimental data. Indeed, according to some studies in sonochemistry [23,24], oxygen produces more sonochemical yield than air. This possible effect of the saturating gas has been experimentally examined by Brotchie et al. [22].

Now, let discussing the effects of acoustic amplitude on the size (the range and the optimal bubble radius) of sonochemically active bubble. From Fig. 3, it is seen that, for a given ultrasound frequency,

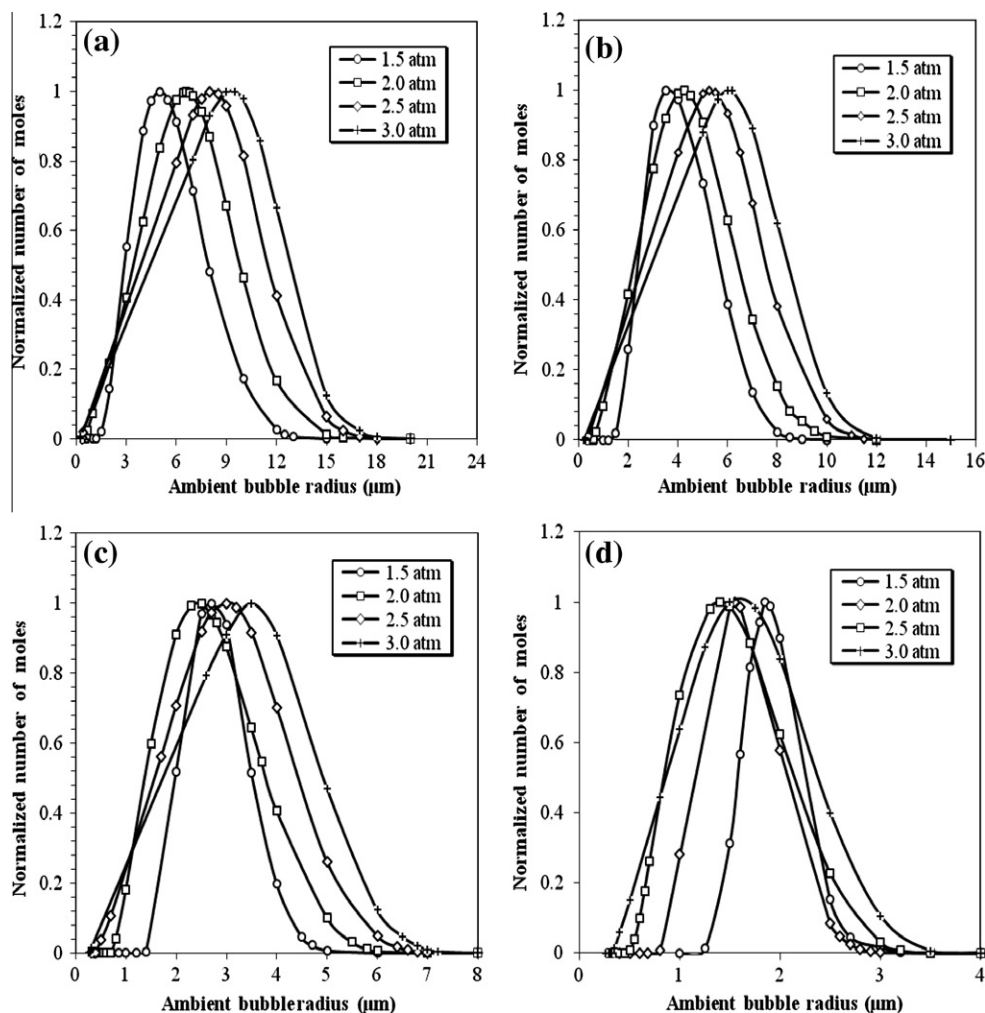


Fig. 2. Normalized values of the number of moles of the oxidants formed per collapse as function of ambient bubble radius for various acoustic amplitudes and frequencies (a) 200 kHz, (b) 300 kHz, (c) 500 kHz, (d) 1000 kHz (conditions: temperature: 20 °C; static pressure: 1 atm). The values are normalized with respect to the maximum value at each amplitude.

Table 1
Comparison between theoretically and experimentally determined cavitation bubble radii at different acoustic frequencies.

Frequency (kHz)	Linear resonance radius (μm) ^a	Theoretical range of bubble radius (μm) ^b		Yasui's theoretical results (μm) ^c	Optimal bubble radius (μm) ^b		Mean measured bubble radius (μm)
		1.5 atm	2.5 atm		1.5 atm	2.5 atm	
200	16.31	1.2–13.5	0.33–18.5	–	5.0	8.0	3.9 (213 kHz) [4] 8.0 (230 kHz) [20]
300	10.87	1.5–8.5	0.35–12.5	0.28–8.0	3.5	5.2	3.2 (355 kHz) [4] 5–7 (350 kHz) [21]
500	6.52	2.0–5.0	0.38–7.0	–	2.7	3.0	2.8–3.7 (515 kHz) [18] 4.3 (515 kHz) [22]
1000	3.26	1.25–3.2	0.45–3.2	0.1–3.0	1.85	1.5	2.0 (1056 kHz) [4] 0.9–1.38 (1 MHz) [2]

^a Calculated using Minnaert's equation [14]: $R_r = \sqrt{3\gamma p_\infty / \rho_l \omega^2}$ where $\omega = 2\pi f$.

^b Calculated results in this study.

^c Yasui's calculated results [10,19].

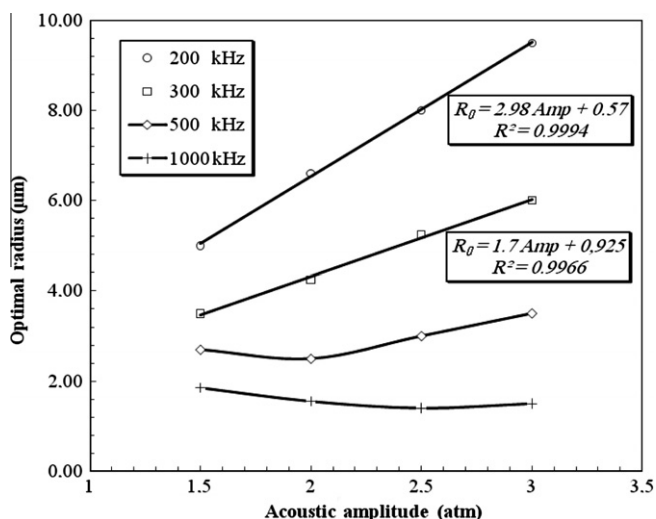


Fig. 3. Optimal bubble radius as function of acoustic amplitude for various ultrasound frequencies (conditions: temperature: 20 °C; static pressure: 1 atm).

an increase in the acoustic amplitude leads to an increase in the range of ambient radius for an active bubble. This result agrees well with the experimental results of Labouret and Frohly [21] that observed at 350 kHz and 1.1 MHz an increase in the range of ambient radius with the acoustic pressure. On the other hand, increasing acoustic amplitude presents different behaviors on the optimum ambient radius. Nevertheless, the general trend is an increase in the optimal radius with an increase in the acoustic amplitude. The relationship between the optimal bubble radius and the acoustic amplitude is examined in Fig. 3 for various ultrasonic frequencies. The first observation that can be made from this figure is that the slope of the curves decreases with increasing ultrasonic frequency. For 200 and 300 kHz, strong linear correlations were observed between the optimal ambient radius and the acoustic amplitude. However, for 500 and 1000 kHz, the optimal ambient radius as function of acoustic power shows a slight minimum at 1.5 and 2.5 atm, respectively. A similar trend has been experimentally observed by Huang et al. [25] at 25 kHz. At 1000 kHz, it seems that the range of acoustic amplitude used in this study has no great effect on the optimal bubble radius for the production of the oxidants.

Finally, although experimental determination of the bubble size is based on mass balance and is not related directly to the calculations, the general trends of increasing size with increasing acoustic amplitude obtained in this numerical simulation are consistent with several experimental studies of single-bubble and multibubble systems [4,26–28].

4. Conclusions

In the present paper, a model that combines a dynamic of single cavitation bubble with the chemical kinetics inside an oxygen bubble has been used to investigate the effects of ultrasound frequency and acoustic amplitude on the size of sonochemically active bubble. The numerical calculation results have shown that, in all conditions of frequency and amplitude, an optimal ambient bubble radius exists for the production of the oxidants. It was shown that the range of ambient radius for an active bubble increased with increasing acoustic amplitude and decreased with increasing ultrasound frequency. The optimal ambient radius decreased with increasing frequency. For 200 and 300 kHz, linear relationships between the optimal radius and the acoustic amplitude were observed, whereas slight minima of optimal radius were observed at 500 and 1000 kHz.

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