

# THE FUNDAMENTALS OF POWER ULTRASOUND – A REVIEW

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The principal method behind applications of power ultrasound is that of acoustic cavitation. This paper aims to provide an overview of bubble behaviour during acoustic cavitation, including phenomena such as transient and stable cavitation, rectified diffusion, coalescence and sonoluminescence. Application of these effects to processes such as nanomaterial synthesis, emulsion formation and waste water treatment is then described.

## INTRODUCTION

Power ultrasound refers to the section of the sound spectrum from 20 kHz through to around 1MHz. The basis of many applications of ultrasound in this frequency range is acoustic cavitation, which is the formation, growth and collapse of microbubbles within an aqueous solution [1] resultant from pressure fluctuations that occur in the applied sound field. The event of a collapsing bubble is a microscopic implosion that generates high local turbulence and the release of heat energy. The consequence is a significant increase of temperature and pressure of up to several thousand degrees Kelvin and several hundred Bar. These physical phenomena are the same as those reported in hydrodynamic cavitation which results in damage of mechanical items such as pumps and propellers [2].

These effects can be exploited in a vast array of beneficial applications [3]. Elevated temperatures [4] in the vicinity of collapsing bubble “hot spots” can be utilised to enhance the chemical reaction rates of some processes, due to the increased heat and the formation of free radicals. Strong disturbances of pressure resultant from shockwave emissions lead to mechanical effects such as mixing and shearing which, for a chemical reaction, can serve to increase encounters between reactants, accelerate dissolution or aid the renewal at the surface of a solid reactant. These conditions, generated by the collapse of bubbles, are the basis for most aspects of sonoprocessing and sonochemistry. Examples of significant applications of acoustic cavitation developed for commercial use include wastewater treatment [5], food and beverages processing [6], and the formation of protein microbubbles which can be used for image contrast agents [7] or drug delivery vehicles [8].

The current review briefly covers the main concepts which are vital to the understanding of the cavitation phenomena followed by an overview of some of the current applications of ultrasound induced cavitation and some thoughts on what will be in store for the future. On the subject of acoustic cavitation, Neppiras [9] has written an excellent review that covers the important physics of cavitation in sound fields. Other invaluable sources of information can be found in the books by Young [1], Brennen [10] and Leighton [11] which detail the mathematical derivations of the basic theories of cavitation

and bubble dynamics along with experimental data for these theories. A more recent review by Lauterborn [12] is another excellent reference for those wishing to gain an insight to the fundamental behaviour of bubbles in an acoustic field.

## HISTORY

Cavitation was first reported in 1895 by Thornycroft and Barnaby [2] when they observed that the propeller of their submarine became pitted and eroded over a relatively short operation period. Their observation was the consequence of collapsing bubbles due to hydrodynamic cavitation that generated intense pressure and temperature gradients in the local vicinity. In 1917, Lord Rayleigh [13] published the first mathematical model describing a cavitation event in an incompressible fluid. It was not until 1927 when Loomis [14] reported the first chemical and biological effects of ultrasound, that workers recognised that cavitation could be a useful tool in chemical reaction processes. One of the first applications reported in the literature was the use of ultrasound induced cavitation to degrade a biological polymer [15]. Since then, applications of ultrasound induced cavitation have increased in popularity, particularly as novel alternatives to processes such as the production of polymer [16], for the enhancement of chemical reactions [17], emulsification of oils [18] and degradation of chemical or biological pollutants [19]. The advantage of using acoustic cavitation for these applications is that much more mild operating conditions are utilised in comparison to conventional techniques and many reactions which may require toxic reagents or solvents are not necessary.

## ACOUSTIC CAVITATION AND BUBBLE FORMATION

In acoustic cavitation, a sound wave imposes a sinusoidally varying pressure upon existing cavities in solution [1] (see Figure 1). During the negative pressure cycle, the liquid is pulled apart at sites containing such a gaseous impurity, which are known as “weak spots” in the fluid. The number of bubbles that are produced during this rarefaction cycle is proportional to the density of such weak spots present in the fluid [10].

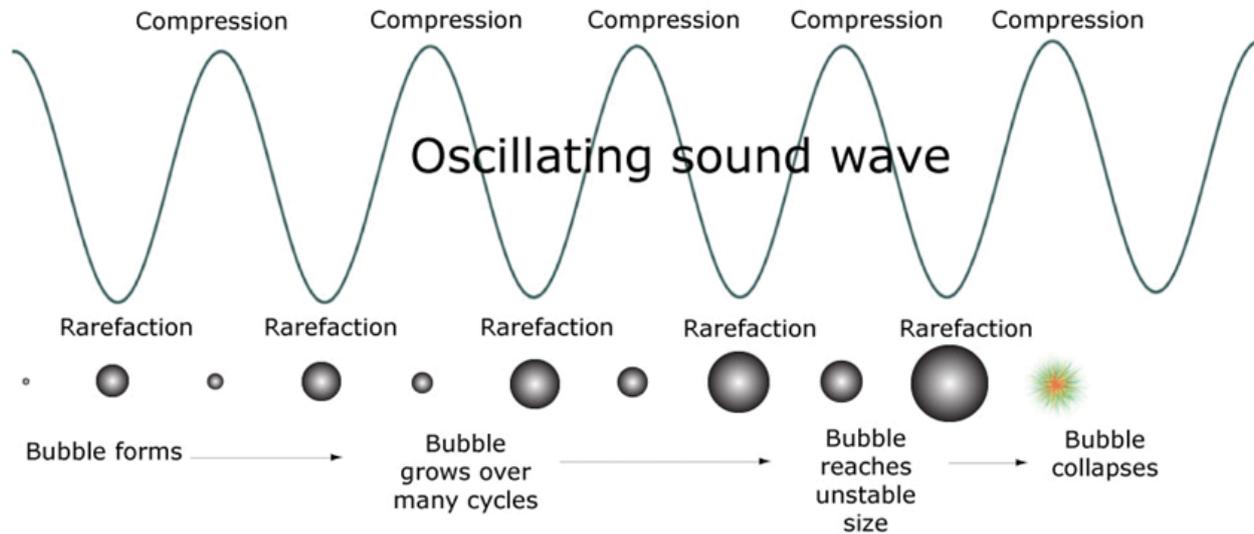


Figure 1: Graphical summary of the event of bubble formation, bubble growth and subsequent collapse over several acoustic cycles. A bubble oscillates in phase with the applied sound wave, contracting during compression and expanding during rarefactions.

There are two known mechanisms for cavity or bubble formation [1]. One mechanism involves pre-existing bubbles in the liquid which are stabilised against dissolution because the surface is coated with contaminants such as a skin of organic impurity. A second mechanism relies on the existence of solid particles (motes) in the liquid with gas trapped in these particles, where nucleation takes place. There can also be tiny crevices in the walls of the vessel or container where gas is trapped. The pressure inside a gas crevice is lower than the outside liquid pressure. Consequently, gas diffuses into the gas pocket, causing it to grow. A bubble is then created as the gas pocket departs from the crevice under the influence of a radiation force.

As can be seen in Figure 1, a bubble formed in one of these ways may then grow until it reaches a critical size known as its *resonance* size. The *resonance* size of a bubble depends on the applied frequency of the sound field. When bubbles reach their *resonance* size due to growth by processes called *rectified diffusion* or *coalescence*, two possible events may occur. The bubble may become unstable and collapse, often violently, within a single acoustic cycle or over a small number of cycles. This is termed *transient* cavitation. The other possibility is that the bubble oscillates for many cycles at, or near, the linear resonance size. This is termed *stable* cavitation. The terms *transient* and *stable* cavitation are also used to define whether or not the bubbles are active in light emission (sonoluminescence) or chemical reactions [20].

A simple relationship that can relate the resonance size of the bubble with the frequency is given by equation (1):

$$F \times R \approx 3 \quad (1)$$

where  $F$  is the frequency in Hz and  $R$  is the bubble radius in m. Note that this equation gives only a very approximate theoretical resonance size [1, 11].

A more accurate version of equation (1) is the linear resonance radius which can be calculated using the following equation [1]:

$$R_r = \sqrt{\frac{3\gamma p_\infty}{\rho\omega^2}} \quad (2)$$

where  $\gamma$  is the specific heat ratio of the gas inside the bubble,  $p_\infty$  is the ambient liquid pressure,  $\rho$  is the liquid density and  $\omega$  is the angular frequency of ultrasound (all in SI units). In practice, the size for an active bubble is usually smaller than this radius due to the nonlinear nature of the bubble pulsation [21].

At 20 kHz ultrasound frequency, the bubbles generated in the sound field are relatively large and their collapse results in strong shockwaves which can be useful for mechanical shearing applications such as emulsification [18]. Between 100 to 1000 kHz, the bubbles generated are much smaller. However, their collapse induces a higher increase in temperature which can be more useful for sonochemical purposes [22]. At above 1 MHz frequency, cavitation effects are much weaker. However, there are some industrial applications in this frequency range such as the gentle cleaning of electronic parts and the nebulisation of liquids to create fine sprays. This higher frequency range is also commonly used for medical and industrial imaging purposes.

## BUBBLE BEHAVIOUR IN AN ACOUSTIC FIELD

Gas bubbles in liquids under the influence of a sound field can do several things, as can be seen in Figure 2. A bubble can meet another bubble in solution, combining to form a larger bubble. This is termed *coalescence*. In a gas saturated solution such as water above a certain threshold pressure, individual bubbles can also grow with time over several acoustic cycles. This is termed *rectified diffusion*. If gas bubbles grow large enough, they can leave the system entirely due to buoyancy. This is termed *degassing*. Bubbles of a certain size can also become unstable and collapse, often violently. The range of bubble radii at which this occurs is very wide, and is usually much lower than the linear resonance radius [21]. Bubble collapse can sometimes be accompanied by fragmentation into smaller bubbles. Under suitable conditions, light emission can be observed, and this is

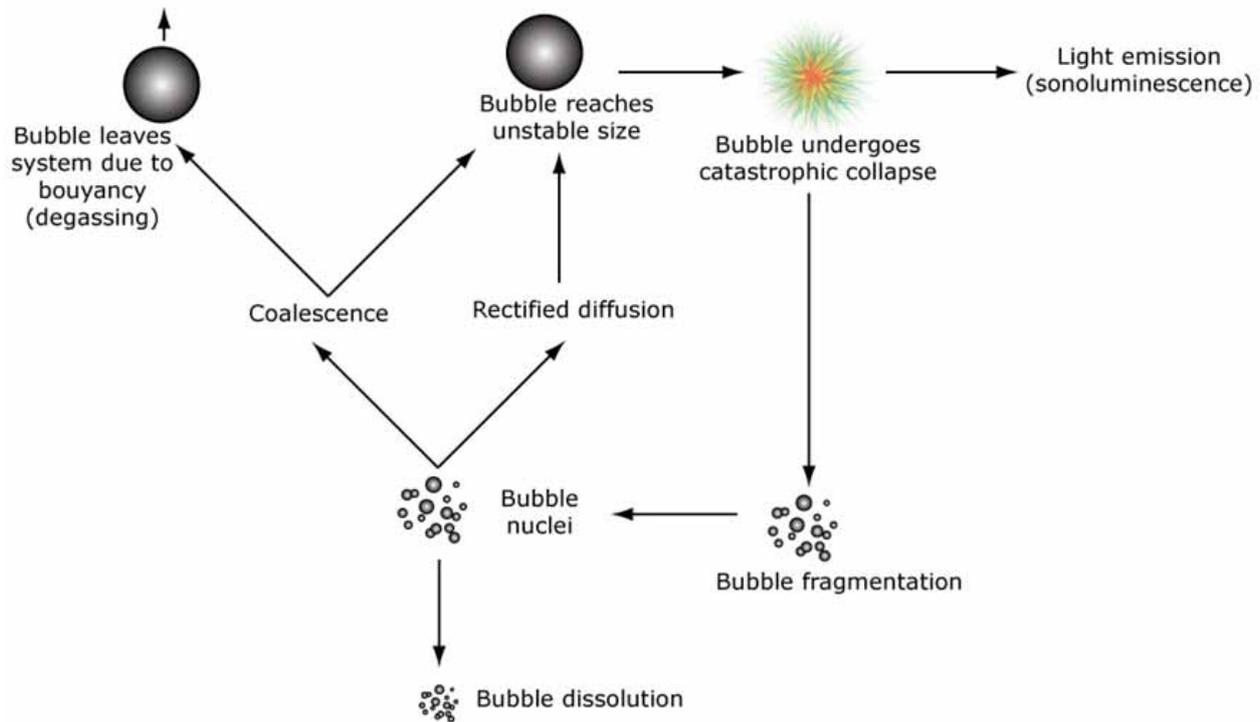


Figure 2: Bubble nuclei under the influence of an acoustic sound field can grow via either coalescence or rectified diffusion. Upon reaching an unstable size, the bubble will collapse, possibly fragmenting to form smaller bubbles accompanied by an emission of light if conditions are suitable. Bubbles that become bigger than the resonance size will leave the system by buoyancy.

termed *sonoluminescence*. Bubbles below the threshold pressure for rectified diffusion can dissolve into solution.

It is possible to predict the behaviour of a single gas bubble provided knowledge is known about the radius, the driving frequency, the driving pressure and the dissolved gas concentration. Each of these phenomena is described in more detail in the following sections.

### The onset of stable and transient cavitation

Apfel [23, 24] has used equations for bubble growth thresholds developed by Safar [25] to produce a series of cavitation prediction charts. An example of these charts, for a 10 kHz frequency system is shown in Figure 3 and illustrates the areas of different cavitation activity:

Region A – The bubbles are under inertial control and bubble growth only occurs via rectified diffusion. Upon reaching resonance ( $R/R_r = 1$ ) the bubbles undergo more violent behaviour and collapse.

Region B – Growth by rectified diffusion and/or by mechanical means may occur although the bubble is not initially transient. Upon fragmentation, the microbubbles formed may exist in region C.

Region C – This region is the transient region for cavitation and the border with region B indicates the transient threshold, also known as the *Blake threshold* [26].

Safar's equation enables the prediction of the rectified diffusion pressure threshold  $P_D$  for a bubble of radius  $R_D$  (Equation (3)) and indicates the threshold between Regions A and B:

$$\frac{P_D}{P_0} = \frac{[3\eta(1+2\sigma/P_0R_D) - 2\sigma/P_0R_D][1 - \omega^2/(\omega^2r)] [1+2\sigma/P_0R_D - C_l/C_0]^{1/2}}{[6(1+2\sigma/P_0R_D)]^{1/2}} \quad (3)$$

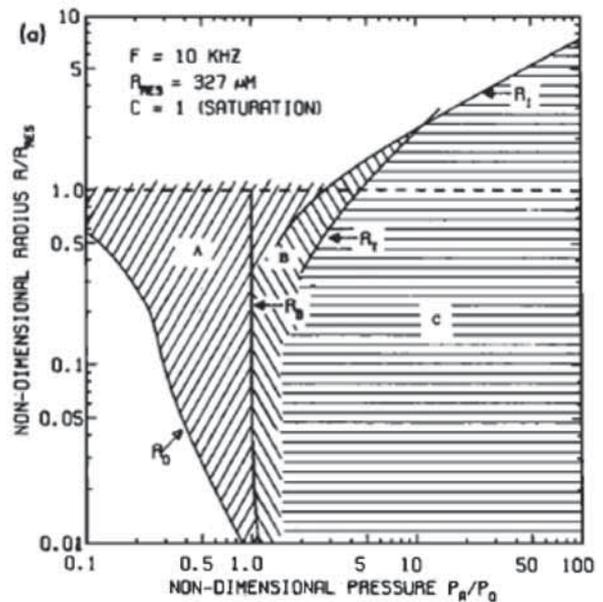


Figure 3: Cavitation prediction chart for a 10 kHz system in a 100% gas saturated system taken from Apfel [24]. Region A is for a bubble under inertial control, B the region for growth by rectified diffusion and C the region for transient cavitation.

Here,  $\eta$  is the solution viscosity,  $\sigma$  is the surface tension,  $\omega$  and  $\omega_r$  the driving and resonance frequency respectively,  $P_0$  the ambient pressure, and  $C_i$  and  $C_0$  are the concentrations of dissolved gas in the liquid far from the bubble and at saturation, respectively. The *Blake threshold pressure*  $P_B$  is defined as:

$$P_B = P_0 + \frac{8\sigma}{9} \left\{ \frac{3\sigma}{2[P_0 + (2\sigma/R_B)] R_B^3} \right\}^{1/2} \quad (4)$$

Neppiras [27] developed similar predictions for the transient thresholds based on Apfel's criterion for a bubble at the radius of the transient threshold and Blake's threshold pressure. He used another expression from Safar [25] which included a multiplying factor that extended the formula so that it applied for bubbles through to resonance, not just  $R_0 < R_r$ . More recently, computer simulations performed by Yasui [28] for various acoustic frequencies have been used to show different regions of bubble behaviour, namely *dissolving* bubbles, *stable* and *unstable* bubbles which may emit SL under the correct conditions, and *degas* bubbles, which oscillate radially at a low amplitude and do not emit SL.

In a multibubble system, the behaviour of bubbles is more complex due to the multiple pathways in which a bubble can enter or leave the system and also different pathways in which it can grow or collapse. It is both difficult to predict theoretically and monitor experimentally the precise bubble behaviour in such systems. In order to understand bubble behaviour in an acoustic field, it is prudent to begin from the simplest case of a single bubble that is oscillating in an acoustic field.

### Dynamics of a single bubble

The *Rayleigh-Plesset* equation is commonly used to model the fundamental motion of a bubble in an acoustic field. Those looking for an in depth derivation of the equation can find it in the book by Young [1].

For motion of the bubble wall we have the result derived by Besant [29]:

$$\frac{P_L - P_\infty}{\rho} = R\ddot{R} + \frac{3}{2}\dot{R}^2 \quad (5)$$

where  $R$  is the radius of the bubble wall at any time,  $\dot{R}$  is the wall velocity,  $P_\infty$  is the pressure in the liquid at infinity,  $P_L$  is the pressure in the liquid at the bubble wall and  $\rho$  the liquid density.

Noltingk and Neppiras [30, 31] extended this fundamental equation to include the effects of surface tension due to the Laplace pressure of the bubble (Equation (6)). To take this into account, at  $R = R_0$  the gas pressure in the bubble is  $P_0 + 2\sigma/R_0$  where  $P_0$  is the ambient pressure in the liquid and  $\sigma$  is the surface tension. Adiabatic heat transfer is assumed with  $\gamma$  being the ratio of specific heats of the gas.

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho} \left[ \left( P_0 + \frac{2\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^{3\gamma} - \frac{2\sigma}{R} - P_\infty \right] \quad (6)$$

A viscosity term for the liquid was later added by Poritsky [32] and he showed that this term arises only in the boundary conditions rather than through the Navier-Stokes equation. The equation then becomes

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho} \left[ \left( P_0 + \frac{2\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^{3\gamma} - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} + P_\infty \right] \quad (7)$$

where  $\eta$  is the viscosity of the liquid. Equations (5), (6) and (7) are often referred to as the *Rayleigh-Plesset* equation and are fundamental in the analysis of bubble behaviour.

We usually subject the bubble to a sound field such that the pressure  $P$  varies as

$$P = P_0 - P_A \sin\omega t \quad (8)$$

where  $P_0$  is the steady state pressure (usually atmospheric pressure),  $\omega$  is the angular frequency and  $P_A$  is the amplitude of the driving pressure. When we add this pressure term into Equation (6), we obtain

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho} \left[ \left( P_0 + \frac{2\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^{3\gamma} - \frac{2\sigma}{R} - (P_0 - P_A \sin\omega t) \right] \quad (9)$$

which is the fundamental equation of a single gas bubble under the influence of an oscillating sound wave.

### Rectified diffusion – growth of a single bubble

The fundamental equations from the previous section have been applied to model the process of bubble growth or dissolution known as rectified diffusion. This phenomenon relates to an unequal transfer of mass across the bubble interface during the rarefaction and compression of the sound wave cycle. Above the threshold pressure for rectified diffusion, this unequal mass transfer causes the bubbles to slowly grow. Below this pressure, the bubble dissolves due to the greater influence of the Laplace pressure exerted on the bubble wall by surface tension. Those looking for an elegant review of the history of the developments of the theory behind rectified diffusion should refer to the work by Crum [33].

Eller and Flynn [34] developed a theory to account for this uneven mass transfer by two main effects. These are known as the *area* and *shell* effects. The *area* effect refers to the fact that diffusion of gas into the bubble occurs when the bubble is larger during the expansion phase, whilst diffusion out of a bubble occurs when the bubble is smaller during the compression phase. As the rate of diffusion across an interface is proportional to the surface area available for mass transfer, more gas diffuses into the bubble than out. Over a number of acoustic cycles, a net inflow of gas into the bubble results, leading to bubble growth.

The *shell* effect refers to the mass transfer boundary layer through which mass transfer occurs. As the bubble shrinks in the compression phase, this shell thickness increases. In contrast, as the bubble expands, the shell thins as depicted in Figure 4. The concentration gradient is thus lower when the bubble is in compression, thereby resulting in a lower driving force for mass transfer.

The solution to the rectified diffusion problem is an interesting one, as it is complicated by a moving boundary layer as the bubble oscillates. This problem has been solved in two different ways by both Eller and Flynn [34] and Hsieh and Plesset [35,36], and details of their approach can be obtained in their papers.



Figure 4: A depiction of the change in mass transfer boundary layer (shell) thickness of a bubble during the expansion and compression cycles of an acoustic wave. The concentration gradient is thus enhanced during bubble expansion.

In the case of Eller and Flynn, they showed that the change in the number of moles  $n$  of a gas in a bubble is given by

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

where  $H$  is defined by

$$H = \frac{C_i}{C_0} - \left\langle \left( \frac{R}{R_0} \right)^4 \left( \frac{P_g}{P_0} \right) \right\rangle / \left\langle \left( \frac{R}{R_0} \right)^4 \right\rangle \quad (11)$$

The pointed brackets in this case imply time average, where  $t$  is the time.  $C_i$  is the concentration of dissolved gas in the liquid far from the bubble,  $C_0$  is the saturation concentration of gas in the liquid and  $D$  is the diffusivity of the gas.

Crum [33] later used Eller's derivation and extended it by taking into account the thermodynamics of the process. The end result for the change in bubble radius for a spherical bubble as a function of time is

$$\frac{dR_0}{dt} = \frac{Dd}{R_0} \left[ \left\langle \frac{R}{R_0} \right\rangle \left( 1 + \frac{4\sigma}{3P_0 R_0} \right)^{-1} \left( \frac{C_i}{C_0} - \langle (R/R_0)^4 (P_g/P_0) \rangle / \langle (R/R_0)^4 \rangle \right) \right] \quad (12)$$

where  $d = R_g T C_0 / P_0$ . Here  $R_g$  is the universal gas constant and  $T$  is the temperature.

An alternative mathematical analysis was presented by Fyrrillas and Szeri [37-39] in a series of papers to analyse the phenomena of rectified diffusion. Their derivation utilised Lagrangian coordinates rather than spherical coordinates in order to account for the moving boundary condition. The Henry's Law boundary condition describing the gas concentration at the surface of the bubble wall was also split into a smooth and oscillatory solution to the problem.

### Bubble coalescence

In a single bubble system, the only growth pathway possible is via rectified diffusion. To investigate the behaviour of a multibubble system, we must also consider the process of bubble coalescence. The bubble coalescence process can be described in three steps [40,41]:

1. The bubbles come into contact to form a film of thickness between 1 to 10  $\mu\text{m}$
2. This film reduces in thickness
3. When the film becomes sufficiently thin, rupture occurs and the bubbles coalesce.

Studies of coalescence behaviour in the absence of ultrasound have been performed by various workers [40-43]. The review by Chaudhari and Hofmann [44] provides a comprehensive overview of the coalescence behaviour of gas bubbles in liquids.

Studies by Lee [45] and Sunartio [46] have found that coalescence behaviour is similar to that reported in the absence of ultrasound. An improved understanding of coalescence behaviour in ultrasound systems will ultimately improve the efficiency of a range of sonoprocessing applications where bubble population and sizes are important.

### Sonoluminescence

The violence of a transient collapse can sometimes be characterised by the emission of light, termed sonoluminescence. Sonoluminescence was first observed in the 1930s by two different groups of workers; Marinesco and Trillat [47] in 1933 and Frenzel and Schultes [48] in 1934. Paounoff [49] validated these observations in 1947 by showing that the exposure of photographic plates occurred at locations of pressure maxima (antinodes) of the standing wave. It became clear to workers in the field that the gas bubbles generated during acoustic cavitation were responsible for the emission of light.

The high temperatures and pressures generated with the onset of inertial cavitation also serves to induce a range of chemical reactions within and surrounding the bubble [50]. The extreme conditions enable the transduction of acoustic energy into light energy that has a very short emission lifetime.

Sonoluminescence can be produced in the case of a single bubble (see Figure 5) undergoing extremely nonlinear pulsations, termed single-bubble sonoluminescence (SBSL) and also in the case of a field of bubbles undergoing cavitation, termed multibubble sonoluminescence (MBSL). In the former case, a single intensely bright dot suspended in a standing wave can be observed [22]. The intensity of the emitted light is dependent on various factors that include the amount and type of dissolved gases in the liquid [51], the frequency of the applied ultrasound [52], the applied sound pressure amplitude, hydrostatic pressure and addition of particular solutes [53-56]. Multibubble sonoluminescence can often be used as a probe for cavitation activity in a solution.

There are a number of theories as to the mechanism for sonoluminescence. These are discussed by Finch [57] and Jarman [58]. During the compression phase of the oscillating bubble, the contents of the bubble are heated [1]. This causes excitation of the gas in the bubble, promoting the formation and recombination of excited species. Recent numerical simulations by Yasui et al. [21] showed that the main mechanism of the light emission in sonoluminescence is actually electron-atom bremsstrahlung that occurs in the weakly ionised plasma formed inside the heated bubble. Bremsstrahlung radiation is light that results from an electron being accelerated by the collision with an ion or a neutral atom.

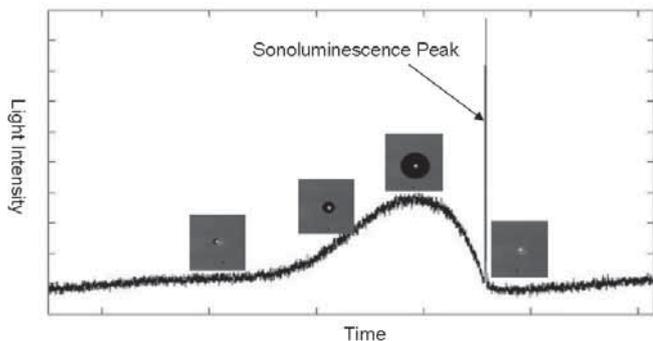


Figure 5: Sonoluminescence response of a single bubble in degassed water. The curve corresponds to the scattered laser light intensity of a levitated bubble undergoing non-linear oscillation in a standing wave. Still images show the corresponding bubble expanding from approximately 5  $\mu\text{m}$  radius to 60  $\mu\text{m}$  radius during one acoustic cycle at a frequency of 20 kHz. The sharp peak corresponding to the point of bubble collapse, with a lifetime of several picoseconds, is the sonoluminescence emitted by the bubble and is visible by the naked eye as a bright glow.

The relative intensities of the sonoluminescence from many different gases dissolved in water have been studied [51]. The general trend found was that as the thermal conductivity of the gas increases, the sonoluminescence was found to decrease and this correlated (for the series of noble gases) with the size of the atom. If sonoluminescence is due to an adiabatic compression during rapid collapse of the cavitation bubble, then energy loss due to thermal conduction will indeed lower the final temperature. Other factors that influence the bubble temperature include the amount of bubble vapour that becomes trapped inside the bubble [59] and the concentration of gas as the sonoluminescence intensity is related to the number of bubbles [60].

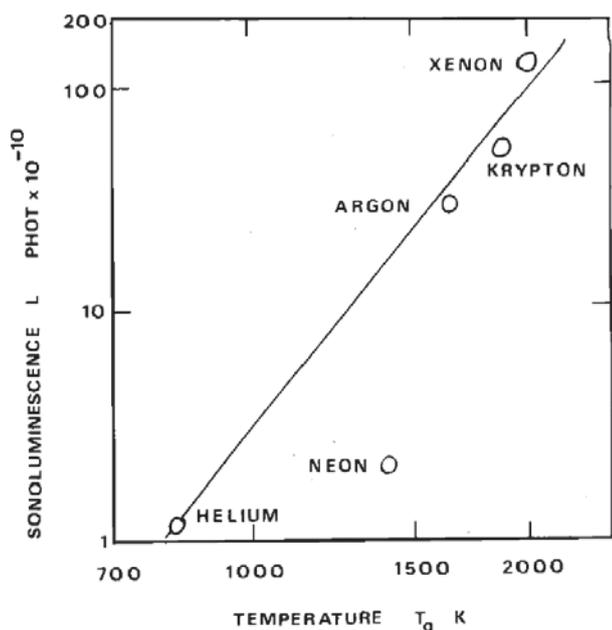


Figure 6: Experimental data taken from Young [51] showing the fit of experimental sonoluminescence intensity data with that of the theoretically determined cavitation temperature for the noble gases.

Hickling [61] explained that if bubbles are sufficiently small, loss of heat from the bubble into the liquid can significantly reduce the temperature of the collapse, resulting in lower sonoluminescence intensity. He demonstrated his theory analytically by means of solution of the equation of motion of gas in the collapsing bubble and good agreement between theory and experimental measurements were confirmed.

Figure 6 (taken from Young [51]) compares the experimental data points for the noble gases of the SL intensity as a function of the theoretical temperature of the gas. This correlation between the predicted temperatures and the SL intensity supports the hot-spot theory for SL.

The intensity of the emitted light can be approximated by the following equation from Yasui et al. [21]:

$$P_{Br,atom} = 4.6 \times 10^{-44} n_e n T / V \quad (13)$$

where  $n_e$  is the number of free electrons inside the bubble,  $n$  is the total number of neutral atoms inside a bubble,  $T$  is the temperature inside the bubble, and  $V$  is the bubble volume.

It is possible to determine the temperature of the gases inside the bubble during cavitation, by correlation with the sonoluminescence emission spectra. This is quite readily achieved in multibubble systems, where the emission spectra consist of detailed line structures. Temperatures of approximately 5000 K were determined by Flint and Suslick [4]. However, in the case of a single bubble, free from disturbances of other bubbles, the emission spectra normally obtained are featureless, as shown from the comparison by Matula et al. [62]. Work by Suslick [63, 64] has recently overcome this hurdle, by using xenon and argon filled bubbles in sulfuric acid. They were able to obtain good spectral details, from which a temperature of 15,000 K was deduced – a temperature as high as that found on the surface of bright stars [65].

## SONOCHEMISTRY

Ultrasound induced cavitation is an extremely useful and versatile tool to carry out chemical reactions. Sonochemistry refers to the area of chemistry where chemical reactions are induced by sound. The range of ultrasound frequency commonly used in sonochemistry range from 20 kHz to ~ 1 MHz. A recent review for sonochemistry has been written by Ashokkumar and Mason and forms the basis of the following section [66].

### Radical formation

The extreme temperature conditions generated by a collapsing bubble can also lead to the formation of radical chemical species. Ultrasonic waves in water have been shown to form radicals by the following reaction due to homolytic cleavage:



The hydroxy and hydroxyl radical formed in this reaction are highly reactive and rapidly interact with other radical or chemical species in solution.  $\text{H}^\bullet$  atoms are highly reducing in nature and  $\text{OH}^\bullet$  radicals are highly oxidizing. A common product of this reaction in water is hydrogen peroxide.

The generation of H<sup>•</sup> and OH<sup>•</sup> radicals, commonly referred to as primary radicals, has been confirmed and quantified by a number of experimental techniques. Common methods include the use of ESR spin traps and dosimeters [67] or the reaction with chemicals such as terephthalic acid [68] that will lead to the formation of hydroxyterephthalate which can be assayed with spectroscopy. One of the more simple methods to quantify the amount of OH<sup>•</sup> radicals formed is by use of the “Weissler” method, which involves the oxidation of iodide ions [69]. In this technique, iodine is added to water which has been sonicated which reacts with the hydrogen peroxide formed. The reaction scheme for this method is:



The quantity of I<sub>3</sub><sup>-</sup> can be measured by ultraviolet spectrophotometry at 353 nm.

Suslick [70] has suggested that sonochemical reactions can occur at two sites of a bubble. The first is the bubble's interior gas phase, and is suggested as the dominant site for sonochemical reaction due to the intense temperatures attained during collapse (~5000 K). The second is the liquid shell surrounding the bubble, which can reach temperatures of up to 1900 K. In addition to these two primary reaction sites on the bubble, solutes in bulk solution beyond the bubble itself can react with the radicals formed inside or on the surface of the collapsing bubble.

### Nanomaterial synthesis

Due to the reducing and oxidizing potential of the primary radicals generated during acoustic cavitation, sonochemistry has been used extensively in materials synthesis. The radicals are useful in initiating certain chemical reactions in organic and organometallic chemistry, as well as initiating polymerization [71]. They can also be used as a means to cross link proteins and this is an important mechanism for the synthesis of protein microspheres. A comprehensive review by Suslick and Price [72] gives examples of many applications of material synthesis using ultrasound.

A simple example of metal synthesis in an aqueous medium is that of the reduction of gold from Au(III) nanoparticles to Au(0) [73]. Under an inert atmosphere, the only reducing species in water are H<sup>•</sup> atoms and these act to reduce the Au(III) ions to produce Au(0) by the following reaction:



Ultrasound processing has generally been found to provide selectivity in the reaction product. For example, under ultrasonic irradiation, switching from an ionic pathway to a radical pathway is often observed. An example is the reaction of styrene with lead tetra-acetate in acetic acid [74].

In recent years, ultrasound generated radicals have been widely used as a novel technique for polymer synthesis [71]. The advantage of ultrasound induced polymerization has several advantages, namely that no chemical initiators or

costabilisers are required, reaction temperatures are lower, polymerization rates are faster, conversions of reactant are greater and larger molecular weights can be produced. Teo et al. [75] for example, has used ultrasound to initiate emulsion polymerization of methacrylate monomers. Their results show that the mechanism involved is very similar to that of conventional polymerization processes.

### Shear and mechanical mixing

Ultrasound-driven growth and collapse of bubbles is accompanied by the generation of shock waves, microstreamers, and microjets which lead to increased turbulence and shear forces which can facilitate mass transport. These physical phenomena can be used for a range of shearing and mixing applications. Cavitation can be used to induce emulsification of two immiscible liquids such as oil in water. The jetting behaviour from transient collapse can be used to disperse fine drops of one liquid into the other when cavitation occurs at the interface between the two liquids. Leong et al. [18] showed that oil emulsions with mean particle sizes as low as 40 nm could be generated using a 20 kHz ultrasound frequency and an appropriate surfactant/co-surfactant system. These results were comparable to those generated from homogenization with a Microfluidizer™ [76], with the advantage that the ultrasonic horn would be easier to clean and more efficient due to lower equipment wear rates.

Mason [77] provides an example of the use of ultrasound as an alternative to phase transfer catalysts, which are compounds that enable the transfer of a water-soluble reagent into an organic phase. The use of ultrasound produces fine emulsions that can be used to disperse the aqueous phase into the organic phase. An example is the formation of dichlorocarbene which has been reported to achieve a much higher conversion in the presence of ultrasound in comparison with the case where the reagents were simply stirred.

### Medical applications

More recent advances of sonochemistry are in the field of microbubble synthesis. Grinstaff and Suslick [78] developed an ultrasonic technique whereby cavitation induced radical formation and emulsification were used to synthesise air or liquid filled proteinaceous microspheres. In this procedure, proteins dissolved in a liquid are irradiated with ultrasound to form a stable foam-emulsion. The stability of this foam is caused by cavitation induced radicals that cause the protein molecules to cross-link, generating a spherical protein shell. The principal cross-linking agent is the superoxide ion created by the extremely high temperatures produced during acoustic cavitation. The mechanism proposed by Suslick suggests that disulfide cross-linkages form, although other workers [79] suggest that the presence of SH groups is not necessary for successful microsphere formation.

Air-filled microbubbles are in clinical use as echo-contrast agents for sonographic applications. Many articles and review articles are available in the literature for those interested in the medical applications available [7, 8]. Commercial microbubbles such as Definity™ and Optison™ are marketed for *in vivo* use where these spheres are injected into the bloodstream of a patient. The application of ultrasound to

the affected area causes bubbles to vibrate in response to the pressure changes of the sound wave. Bubbles of an appropriate size range will vibrate very strongly at resonance, making them several thousand times more reflective than normal body tissues. The result is improved image resolution of tissues and organs. In some cases, a liquid can be encapsulated inside these protein spheres. This ability to encapsulate liquids can be used for targeted or time released drug delivery [80]. Figure 7 taken from Zhou et al. [81] shows lysozyme protein microbubbles filled with various types of organic oils. Care must be taken however when generating sonicated protein products intended for *in vivo* use or as food ingredients. Stathopoulos et al. [82] have recently reported that the sonication of proteins can lead to the formation of amyloid aggregates. It is possible that such aggregates can give rise to immunogenicity, toxicity or even disease responses in the subject.

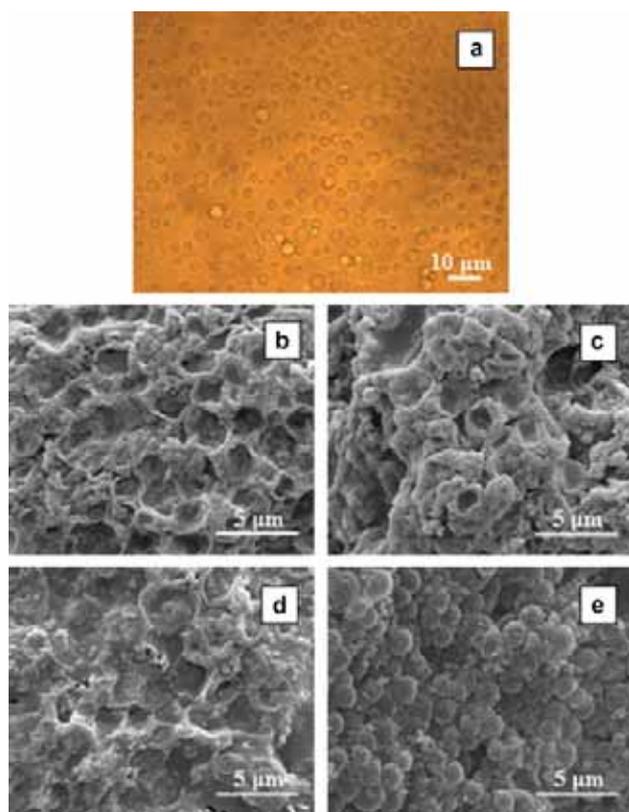


Figure 7: (a) Optical microscopic image and SEM images of (b) tetradecane, (c) dodecane, (d) sunflower oil and (e) perfluorohexane-filled lysozyme microspheres taken from Zhou et al. [81].

### Sonochemical degradation of pollutants

Another useful application of sonochemistry is in the field of wastewater treatment. Articles by Colarusso and Serpone [83] and Adewuyi [84] provide a comprehensive overview of sonochemistry for use in environmental applications such as the degradation of pollutants. The hydroxyl radicals generated during cavitation can be used for the oxidative degradation of organic pollutants in an aqueous system. The heat produced in the cavitation process can also be used to remove volatile pollutants by pyrolytic decomposition. Singla et al. [19]

recently reported that sonochemical degradation of various organic pollutants could be achieved by both oxidative and pyrolytic mechanisms.

Destruction of microorganisms by power ultrasound is also possible [85]. However, ultrasound has been shown to have no direct impact on spores or gram positive organisms and so is often used in conjunction with more conventional techniques such as chlorination or treatment with heat and pressure, such that increased effectiveness is achieved with lower requirements for chemical or energy usage.

## CONCLUSIONS, FUTURE DEVELOPMENTS AND EXPECTED ADVANCEMENTS

Ultrasound induced cavitation is an effective tool to induce mechanical shear and to perform a variety of chemical reactions. This approach has been available for some decades but deployment is now rapidly increasing due to the recent availability of industrial scale ultrasonic horns and ultrasonic reactors.

Ultrasound can be energy intensive and hence emerging applications are likely to be where high value can be added. There exists a diverse range of applications that are well established or have exciting future potential that meet this criterion. The development of effective drugs for treatments of disease by ultrasound is one of the areas which could have widespread health benefits. Another emerging area is the use of ultrasound to provide novel food ingredients and our work is focused in particular on the production of novel dairy products. The need for more sustainable processing of consumer goods will be satisfied in part by such continuing developments in ultrasound processing and sonochemistry.

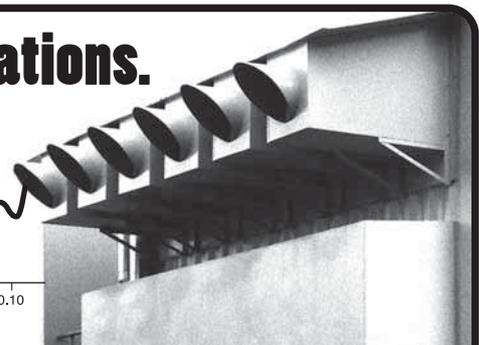
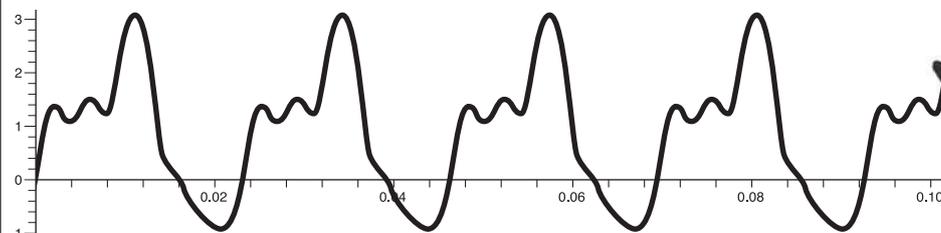
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