Chapter 2

Background

Acoustic Pressure and Intensity

Ultrasonic acoustic frequencies extend from the threshold of human hearing, about 20 kHz, to several hundred MHz. Sonochemical reactors are typically operated between 20 kHz and 2 MHz.¹ The local pressure, P_T , imparted to the medium by ultrasonic wavefronts is given by

$$P_{\rm T} = P_{\rm h} + P_{\rm a} \tag{1}$$

where P_h is the hydrostatic pressure of the solution and P_a is the applied acoustic pressure. Under sinusoidal acoustic waves, the local pressure can be represented by

$$P_{\rm T} = P_{\rm h} + P_{\rm a}(t) = P_{\rm h} + P_{\rm A}\sin(2\pi ft)$$
⁽²⁾

where f (s⁻¹) is the frequency of the wave, P_A is the amplitude of the acoustic pressure, and t is time. The magnitude of the acoustic pressure is related to the acoustic intensity, I, which is the average energy imparted to the solution per unit area, per unit time. For a plane progressive wave this relationship is expressed as

$$P_A = \sqrt{2I\rho c} \tag{3}$$

where ρ is the density of the solution and c is the speed of sound in the particular medium.

As the sound wave propagates through a solution, the intensity of the pressure pulse is strongest near the transducer surface and decreases as the distance from this acoustic source is increased. This decrease in pressure is due to reflection and scattering of the incident wave, as well as to the viscous dissipation of the kinetic energy of the fluid. The extent of this attenuation in intensity can be represented by

$$I = I_{a} e^{(-2\alpha d)} \tag{4}$$

where α is the absorption or attenuation coefficient and d is the distance from the acoustic source. Factors that influence the extent of sound propagation through a liquid include thermal conductivity and viscosity. For low intensity waves under isothermal conditions, α is inversely proportional to the square of the acoustic frequency due to frictional losses in the solution.² Therefore, in order to achieve similar pressures at a given depth, higher acoustic powers are required as the ultrasonic frequency is increased.

Because liquids are not perfectly elastic, these successive cycles of compression and rarefaction lead to non-uniform translational motion of individual molecules within the solution, which enhance the rates of transport processes. As the power is increased, more efficient mixing is typically observed. In addition, when applied above a critical intensity, ultrasonic irradiation can also induce oxidation and other chemical reactions. However, unlike UV or γ -irradiation where chemical reactions occur by the direct interaction between photons and the molecules, ultrasonically induced reactions result from an indirect process known as acoustic cavitation.

Acoustic Cavitation

First reported³ in 1895, cavitation is defined as the phenomenon of formation, growth, and eventual collapse of small bubbles within a liquid.^{4,5} It is believed that when the amplitude of the pressure wave becomes sufficiently large, the negative pressure achieved during the rarefaction phase of the acoustic cycle is able to overcome the intermolecular forces, increasing the molecular distance between individual solvent molecules and forming a cavity or void. Cavitation is routinely observed in water for laboratory reactors operating with acoustic pressures of several atmospheres. Because

these rarefaction pressures fall well below the experimental tensile strength of water⁶ (i.e., 500 - 1300 atmospheres), current theories suggest that small gas nuclei or trace impurities weaken the solution and serve as cavitation nucleation sites.⁵

During the remaining portion of the rarefaction phase of the acoustic cycle ($P_T \leq P_h$), the radius of a bubble initially at R_o will expand to a maximum radius, R_{max} , as additional gas and solvent diffuse into the cavity. In general, stronger acoustic forcing and lower acoustic frequencies generally increase R_{max} . This is due to an increase in both the time and magnitude of the pressure drop in the rarefaction cycle. The extent of this expansion is also dependent on the density of the liquid and the hydrostatic pressure. An estimate of the maximum radius is given by the following equation¹

$$R_{\max} = \frac{4}{3\omega} (P_A - P_h) \left(\frac{2}{\rho P_A}\right)^{1/2} \left[1 + \frac{2(P_A - P_h)}{3P_h}\right]^{1/3}$$
(5)

When the compression phase of the acoustic cycle is restored, this process is reversed and gasses diffuse out of the bubble as the radius of the bubble begins to shrink. Depending on the conditions within the system, two distinct types of cavitation can be identified within the liquid. They are known as 'stable' and 'transient' cavitation and are described as follows:

Stable Cavitation

For moderately forced systems, the internal gas pressure is able to balance the external pressure wave and the surface tension applied by the solution. This results in successive expansions and contractions of the bubble for multiple acoustic cycles. Above a critical acoustic pressure, the motion of the bubble

becomes uncoupled from the acoustic field resulting in non-linear oscillations which can lead to enhanced time-averaged mass diffusion into the bubble (i.e., bubble growth) through a process known as 'rectified diffusion.^{1,5} As mentioned previously, under an oscillatory pressure field, gas diffuses in and out of the bubble as the phases of the acoustic cycle transition between rarefaction and compression, respectively. Since the average surface area of the bubble is larger during expansion, there will be a net influx of gas into the bubble over several oscillations. The effect is further enhanced by differences in the concentration gradient of the fluid shell immediately surrounding the bubble. During expansion, this layer becomes thinner, increasing the concentration gradient across the fluid. Because the diffusion rate of gas into the bubble is proportional to the gradient times the bubble area, the net rate of inward diffusion is necessarily higher. Together, these separate phenomena promote bubble growth. Figure 1 shows the stable growth for a bubble of 2 mm initial size in the presence of a 20 kHz sound field. As these bubbles grow larger, they eventually become unstable and are either transformed into buoyant or transient bubbles.

Transient Cavitation

Transient cavitation is characterized by a significant growth of the cavitation bubble ($R_{max}/R_o \ge 2$) during the initial phase of the acoustic cycle followed by the complete and violent collapse of the cavity with the re-application of the compression phase.⁵ This instability and rapid implosion is attributed to the inability of the internal pressure to balance the large inertial force of the fluid flowing in to fill the void formerly occupied by the bubble. Figure 1 shows the transient collapse for a bubble of 5 μ m initial size in the presence of a 19 kHz sound field.⁷

It is during the compression phase of the acoustic cycle that significant chemical effects of cavitation occur. Electrical discharge mechanisms have been postulated⁸⁻¹¹ to explain the chemical transformations that result from the collapse of a cavitation bubble, but they have been abandoned in favor of an alternative mechanism known as the 'hotspot' theory.^{1,12} According to this mechanism first proposed by Noltingk and Neppiras^{13,14} and later by Griffing and co-workers,^{15,16} isobaric and isothermal conditions are maintained in the bubble for most of the acoustic cycle; however, during the final stages of the compression phase the velocity of the bubble wall exceeds the rates of heat and mass transfer across the gas-liquid interface, causing the system to become adiabatic. As the bubble continues to collapse, the trapped gasses are compressed and microenvironments are generated where the temperatures can approach thousands of degrees and the pressures can exceed hundreds of atmospheres. These high-energy events are thought to be responsible for a number of chemical effects in both the gas phase bubbles These processes are discussed in further detail in the and the bulk solution. 'Sonochemistry' section of this chapter.

Bubble Dynamics

Motion of the Bubble Wall

The first mathematical models developed specifically to describe the collapse mechanism of a cavitation bubble within a liquid were presented in 1917 by Lord Rayleigh.¹⁷ He considered the collapse of an empty, perfectly spherical bubble from an initial radius, R_o , to a new radius R at time t. By equating the work accomplished by the hydrostatic pressure to the kinetic energy of the fluid surrounding the bubble, he was to describe the motion of the bubble wall by the following relationship:

$$R\ddot{R} + \frac{3}{2}\dot{R}^{2} = \frac{P(R) - P_{\infty}}{\rho_{l}}$$
(6)

where \hat{R} is the velocity of the cavity wall of radius R, \hat{R} is the wall acceleration, P(R) is the pressure in the liquid at the bubble wall at radius R, P_{∞} is the pressure in the bulk liquid ($P_{\infty} = P_T$) and ρ_t is the density of the liquid. From this second-order non-linear equation Rayleigh was able to deduce the velocity of the bubble wall

$$\frac{dR}{dt} = \dot{R} = -\sqrt{\frac{2P_o}{3\rho} \left(\frac{R_o^3}{R^3} - 1\right)}$$
(7)

where R_o and P_o are the radius and the pressure, respectively, of the cavity at the onset of collapse. Rearrangement of equation 7 and integration from R_o to 0 provides an estimate of the collapse time of this bubble

$$\tau \approx 0.915 R_o \left(\frac{\rho}{P_o}\right)^{1/2} \tag{8}$$

The formulation of the equations 6, 7 and 8 neglects the effect of surface tension and vapor pressure and it assumes constant acoustic pressure during the collapse.

Nonetheless, equation 8 can still provide a reasonable estimation of the collapse time for bubbles forced at low to moderate ultrasound frequencies and pressures in low temperature solutions. For example, the bubble in Figure 2 has a radius of 40 μ m at the onset of the compression cycle (P_a = 0, P_h = 1 atm = 1.01 × 10⁵ Pa). According to equation 8, a collapse time of 3.6 μ s is calculated, in satisfactory agreement with experimental values.

In an effort to extend the range over which cavitation physics could be modeled, Rayleigh's equations were later modified to incorporate the internal gas and vapor pressure and the effects of surface tension, viscosity and an oscillatory acoustic field.^{13,14,18,19} The culmination of this work produced Equation 9 which is commonly referred to as the Rayleigh-Plesset equation (RPE)^{1,5,20}

$$R\ddot{R} + \frac{3}{2}\dot{R}^{2} = \frac{1}{\rho} \left[\left(P_{h} + \frac{2\sigma}{R_{e}} - P_{\nu} \right) \left(\frac{R_{e}}{R} \right)^{3\kappa} - 4\eta \frac{\dot{R}}{R} - \frac{2\sigma}{R} - P_{h} + P_{a}(t) \right]$$
(9)

where R is the velocity of the cavity wall of radius R, R is the wall acceleration, K is the polytropic index of the gas ($1 \le K \le \gamma = C_p/C_v$, the specific heat ratio), and η and σ are the fluid viscosity and surface tension, respectively. The important assumptions of the RPE are:

- (1) There exists a single bubble in an infinite liquid
- (2) The bubble is always spherical
- (3) The temperatures and pressures inside the bubble are uniform
- (4) The bubble's radius is smaller than the acoustic wavelength
- (5) Gravity and other body forces are neglected
- (6) The density of the liquid is large and it is minimally compressible
- (7) The gas content of the bubble is constant
- (8) Evaporation and condensation of the solvent occur freely (i.e., the vapor pressure is constant during the acoustic cycle)

Despite the fact that these conditions may not necessarily be valid at the time of the collapse,²¹ numerical simulations derived from variations of the RPE do provide reasonable agreement between calculated and experimentally measured time-resolved radius profiles¹². An example of such a fit is shown by the thick gray line in Figure 2.⁷

Estimating Conditions within a Cavitation Bubble

Despite the general agreement between experimental observations and theoretical simulations of bubble dynamics using the Rayleigh-Plesset Equation¹², the use of this equation to estimate the conditions within the cavitation bubble during the final moments of the collapse are fraught with more difficulties. Based on approximate solutions to the RPE, Noltingk and Neppiras^{13,14} and Flynn²² developed simple equations for estimating the theoretical pressure (P_{max}) and temperature (T_{max}) inside a bubble at the moment of total collapse as follows:

$$P_{\max} = P \left\{ \frac{(P_m(K-1))}{P} \right\}^{\left(\frac{K}{K-1}\right)}$$
(10)

$$T_{\max} = T_o \left\{ \frac{(P_m)(\mathrm{K} - 1)}{P} \right\}$$
(11)

where P is the pressure of the bubble at its maximum size, T_o is temperature bulk solution, and P_m is the total solution pressure at the onset of adiabatic collapse. In these cases, P_m is typically assumed to be the pressure at the beginning of the compression cycle (~ $P_h + P_a$) and P is the vapor pressure of the liquid. The derivation of Equations 10 and 11 is provided in the appendix of this chapter. These approximations are found to be adequate for small to moderate acoustic forcing, providing satisfactory agreement with experimental measurements which have estimated collapse temperatures between 3000 and 6000 K.²³⁻²⁶ However, for larger amplitudes, estimates using the RPE predict temperatures in excess of 10^5 K,²⁷⁻³⁰ and even approaching 10^8 K.³¹

In an attempt to correct these discrepancies between computer simulations and experimental observations, a number of new models for bubble dynamics models for use in sonochemistry have recently been developed.^{21,27,32-40} Unlike the models developed directly from the RPE, these modified models incorporated other processes, such as heat and mass transfer, diffusion of the solvent vapor within the vapor, chemical reactions within the bubble, and non-uniform bubble collapse dynamics.

The consensus of the current models^{21,27,32-34,38-40} is that the parameter which most significantly affects the collapse temperature of the bubble is the limited mass diffusion of solvent vapor out of the bubble during collapse. The maximum average temperatures predicted by these models range between 4500 and 8000 K. As shown in bubble simulations of Storey and Szeri²⁷ in Figure 3, the gas inside an expanded bubble is primarily water vapor. As the bubble shrinks during the compression phase, these water molecules move towards the bubble interface and condense into the bulk solution. Initially the timescale for diffusion and condensation is shorter than the timescale of the collapse, so the concentration of vapor within the bubble remains uniform. However, approximately 50 ns before the minimum radius is reached, the rate of collapse of the bubble becomes faster than either the rate of diffusion of the vapor or the rate of condensation. At this point, up to 20% of the water vapor initially present in the bubble at the onset of collapse is trapped inside the cavity. The presence of this additional vapor in the bubble physically slows the motion of the bubble wall vapor, cushioning the collapse. The affects of this additional vapor on the average bubble temperature are

shown in Figure 4. When endothermic chemical reactions involving the homolytic splitting of the water vapor (see 'Sonochemistry' section) are also included in their model, the average bubble temperatures are even further suppressed to $T_{max} \leq 7000$ K.

Sonochemistry

Sonochemistry is generally defined as the use of ultrasonic irradiation to promote or initiate chemical reactions. While most chemical effects originate from the extreme conditions produced during the collapse of unstable cavitation bubbles, reactions are not limited to the bubble, but also occur in the liquid sheath immediately surrounding the bubble and in the bulk solution. These three separate regions are illustrated in Figure 5. The dominant chemical reactions that occurs in each region are described as follows:

Bubble Interior

Upon collapse this region experiences transient temperatures of several thousand Kelvin and pressures of several hundred atmospheres. O_2 , N_2 , volatile solutes, and solvent vapor exposed to these extreme conditions within the bubble will rapidly undergo homolytic bond cleavage producing reactive free-radicals. These intermediate species will either self-react or attack additional molecules present in the bubble. In aqueous systems, a substantial amount of the energy used to induce cavitation is ultimately used to decompose water. Appreciable dissociation of water vapor (rxn 9) occurs if temperatures above 3500 K are maintained for a few $\mu s.^{12}$ The following reaction scheme shows the principle reactions of the free-

radical chain that is initiated by the ultrasonic irradiation of a neat aqueous solution:

$$H_2O \xrightarrow{)))\Delta} \cdot OH + H \cdot$$
 (9)

$$\cdot OH + H \cdot \to H_2 O \tag{10}$$

$$\mathbf{H} \cdot + \mathbf{H} \cdot \to \mathbf{H}_2 \tag{11}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{12}$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^ pK_a = 11.9$$
 (13)

$$\cdot OH + H_2O_2 \rightarrow HO_2 \cdot + H_2O \tag{14}$$

$$HO_2 \rightarrow H^+ + O_2 \rightarrow pK_a = 4.8$$
 (15)

$$\cdot OH + \cdot O_2^- \to OH^- + O_2 \tag{16}$$

$$HO_{2} + HO_{2} \rightarrow H_{2}O_{2} + O_{2}$$
(17)

$$HO_2 \cdot + \cdot O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^-$$
(18)

Interfacial Region

Immediately surrounding the bubble is a thin, superheated liquid shell. Estimates of the temperatures within this region are as high as 1900 K.⁴¹ Pyrolytic decomposition of solutes, even those with particularly low vapor pressure (e.g., polymers) are thought to occur in this region.⁴² The existence of a transient supercritical water phase (T > 647 K, P > 221 bar) has also been proposed to account for the enhanced reactivity at the bubble/water interface.⁴³ In addition to thermal reactions, any species present in this region will be subject to attack by

radicals exiting the bubble.⁴⁴. The concentration of \cdot OH in this interfacial region has been estimated to be as high as 4 mM.⁴⁵

Bulk Solution

Free radicals not consumed in the previous regions are dispersed into the bulk solution as the bubble breaks apart during the final stage of collapse.³³ These species can either react with solutes present in the solution or recombine to form more stable oxidants such as hydrogen peroxide.

These various regions of chemical reactivity make ultrasonic irradiation a practical method for degrading a wide array of organic pollutants in an aqueous solution. The physical properties of a solute are important in determining its fate in a sonochemical system.^{1,42,46} Solutes with higher vapor pressures and/or hydrophobicity are particularly well suited to sonochemical degradation since they are subject to both pyrolysis within or near the cavitation bubble as well as attack by free-radicals. Some examples of the classes of compounds that has been successfully remediated using sonolysis include: carbon tetrachloride^{47,48} and other chlorinated hydrocarbons,^{46,49-54} aromatic compounds,^{44,50,51,55-66} pesticides,⁶⁷ methyl tert-butyl ether (MTBE),^{68,69} surfactants,^{70,71} and azo dyes.⁷²⁻⁷⁴

Combined Sonochemical Techniques

The examples mentioned in the previous section indicate that sonochemical methods could be used for a variety of water treatment applications. Although the

sonochemical degradation rates of many solutes are relatively fast, there is still much work needed in order to improve the performance of this technique. In particular, recent research in sonochemistry has focused on enhancing free-radical production within the bulk solution with the concurrent application of an additional Advanced Oxidation Processes (AOP). Some examples of AOPs used in combination with ultrasound include ultraviolet irradiation,⁷⁴⁻⁷⁷ metal oxide photocatalysts,^{78,79} elemental iron,^{80,81} and Fenton's reagent (Fe^{2+}/H_2O_2).^{80,82}

One AOP in particular that has been shown to have quite promising results when combined with ultrasonic irradiation is ozonolysis. Ozone is a powerful oxidant commonly used in water purification and disinfection. While possessing a relatively large reduction potential (2.07 V), it is highly selective, predominantly reacting with saturated hydrocarbons or other molecular sites possessing a relatively high electron density.⁸³ When used simultaneously with ultrasound, this treatment protocol has been shown to successfully enhance the degradation rates of wide variety of chemical species, oftentimes with net transformation rates greater than would be predicted by the linear addition of the rates from the independent systems.^{1,55,65,68,69,84-87} Remarkably, this synergistic effect appears to be most dramatic for solutes which are inert towards direct reactions with molecular ozone.^{86,87} For many systems, the thermal decomposition of O₃ (g) within the cavitation bubble appears to be the main mechanism for the enhanced destruction of chemical contaminants to produce atomic oxygen.⁸⁸

$$O_3 \xrightarrow{)))\Delta} O_2 + O(^3P)$$
(19)

At high temperatures, atomic oxygen reacts with water to produce two hydroxyl radicals⁸⁹

$$O(^{3}P) + H_{2}O \rightarrow 2 \cdot OH$$
⁽²⁰⁾

Research by Kang *et al.*^{68,69} has also proposed that free-radical production in the O_3/US system is enhanced by reactions between O_3 and the sonically generated H_2O_2 which accumulates in the bulk solution. While H_2O_2 does not react directly with O_3 , HO_2^- is known to degrade aqueous ozone.^{90,91}. Staehelin and Hoigne⁹¹ have proposed that the reaction between HO_2^- and O_3 initiates a free radical chain which ultimately produces $\cdot OH$.

$$O_3 + HO_2^- \to HO_3 + O_2^- \tag{21}$$

$$O_3 + O_2 \rightarrow O_3 + O_2 \tag{22}$$

$$HO_3 \leftrightarrow O_3 + H^+$$
 (23)

$$HO_3 \rightarrow OH + O_2$$
 (24)

Each of these mechanisms would provide new sources for ·OH radical formation during sonolysis, thereby enhancing solute degradation rates.

Chapter 1 - Appendix

The classical equations for the maximum temperature and pressure encountered within a cavitation bubble are derived in the following manner^{1,5}:

Considering a perfectly spherical bubble irradiated with a time-varying pressure field, $P_a(t)$ the equation for the motion of the bubble wall is given by the Rayleigh-Plesset equation

$$R\ddot{R} + \frac{3}{2}\dot{R}^{2} = \frac{1}{\rho} \left[\left(P_{h} + \frac{2\sigma}{R_{e}} - P_{\nu} \right) \left(\frac{R_{e}}{R} \right)^{3\kappa} - 4\eta \frac{\dot{R}}{R} - \frac{2\sigma}{R} - P_{h} + P_{a}(t) \right]$$
(A.1)

where R is the velocity of the cavity wall of radius R, R is the wall acceleration, R_e is the initial radius of the bubble, at the ρ is the density of the solution, P_h and P_v are the hydrostatic and vapor pressure, respectively, K is the polytropic index of the gas $(1 \le K \le \gamma = C_p/C_v)$, the specific heat ratio), and η and σ are the fluid viscosity and surface tension, respectively. The historical review of the development of this equation is given in references 20 and 5. For moderately forced systems, the time for the collapse of a bubble (τ given in eqn. 8) can be assumed to be significantly shorter than the total time of the compression phase of the acoustic cycle. Therefore the pressure at the onset of adiabatic collapse, P_o, can be assumed to be constant during this process, replacing the term (-P_h + P_a(t)) in eqn. A.1. Also neglecting the surface tension and viscosity, eqn. A.1 can be expressed as

$$R \overset{\bullet}{R} + \frac{3}{2} \overset{\bullet}{R}^{2} = \frac{1}{\rho} \left[P_{g} \left(\frac{R_{o}}{R} \right)^{3\gamma} - P_{o} \right]$$
(A.2)

where P_g is the pressure of the trapped gas within the bubble.

As shown in Figure 2, a bubble doesn't completely shrink to R = 0 during the compression phase, but rather is reduced to a minimum size after which expands again in a phase known as the afterbounce.^{5,12} In this state it oscillates between R_{min} and R_m ($R_m \sim R_e$). To determine these two extreme radii eqn. A.2 can be integrated with respect to R to give

$$\frac{\rho R^2}{2} = P_o(Z-1) - \frac{P_s(Z-Z^{\gamma})}{1-\gamma}$$
(A.3)

where $Z = (R_m/R)^3$ is the volume compression ratio, and $K = \gamma$ due to the adiabatic conditions within the bubble. Because the motion of the bubble wall is halted at R_m , $\dot{R} = 0$. Substituting this value into eqn. A.3 and rearranging the terms yields

$$P_m(1-\gamma) = \frac{P_g\left(Z-Z^{\gamma}\right)}{(Z-1)} \tag{A.4}$$

This equation can be further simplified assuming $Z-1 \approx Z$. Making this substitution eqn. A.4 can be written as

$$P_m(1-\gamma) \approx -P_g Z^{\gamma-1} \tag{A.5}$$

which rearranges to give

$$Z = \left(\frac{R_m}{R}\right)^3 = \left(\frac{P_m(\gamma - 1)}{P_g}\right)^{\frac{1}{\gamma - 1}}$$
(A.6)

Recalling that the volume of a sphere is given by $(4/3)\pi R^3$, eqn. A.6 also gives the volume ratio of the bubbles at R_m and R. Because the collapse of the bubble and its rapid afterbounces are assumed to be adiabatic

$$\mathbf{P}_1 \mathbf{V}_1^{\gamma} = \mathbf{P}_2 \mathbf{V}_2^{\gamma} \tag{A.7}$$

At R_{min} (V_{min}) the pressure within the bubble will be its greatest, P_{max} , whereas at R_m (V_m) it is assumed to be at the initial pressure within the bubble, P_g . Subsituting these values into eqn. A.7 and rearranging the terms yields

$$\frac{P_{\max}}{P_g} = \left(\frac{V_m}{V_{\min}}\right)^{\gamma} = Z^{\gamma}$$
(A.8)

Replacement of Z from eqn. A.6 and rearrangement of the terms finally produces the desired relationship

$$P_{\max} = P_g \left(\frac{P_m(\gamma - 1)}{P_g}\right)^{\frac{\gamma}{\gamma - 1}}$$
(A.9)

At this increased pressure, the temperature within the bubble will also reach a corresponding maximum, denoted as T_{max} . To determine this temperature, we can apply the following relationship between temperature and volume for an adiabatic ideal gas

$$T_{max}V_{min}^{\gamma-1} = T_m V_m^{\gamma-1}$$
 (A.10)

Rearrangement of eqn. A.10 yields

$$\left(\frac{V_{\rm m}}{V_{\rm min}}\right) = \left(\frac{T_{\rm max}}{T_{\rm m}}\right)^{\frac{1}{\gamma-1}}$$
(A.11)

Substituting eqns. A.6 and A.11 into eqn. A.8 gives

$$T_{\max} = T_{\max} \left(\frac{P_m (\gamma - 1)}{P_g} \right)$$
(A.12)

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Figure 1. The radius/time plot of an air bubble in water ($R_o = 2 \text{ mm}$) under the influence of an applied acoustic field (20 kHz, $P_A = 2.7 \text{ atm}$).



Figure 2. Mie-scattering (dots) collected from a pulsating bubble (Ro = 5 μ m) under the influence of an applied acoustic field (black line) (19 kHz, P_A = 1 atm). The thicker continuous grey line is the calculated fit to a modified Rayleigh-Plesset equation. From Ref. 7.



Figure 3. Calculated spatial molar fraction of water present within a collapsing cavitation bubble. Numbers above each profile indicate the time prior to complete collapse at t = 0 ns. From Ref. 27.



Figure 4. Calculated maximum average collapse temperature within a transient cavitation bubbles of increasing expansion ratios (R_{max}/R_{min}) during the rarefaction phase of the acoustic cycle. o: water vapor freely condenses and evaporates during the acoustic cycle; •: the diffusion and condensation rates of water are included in the model; +: the diffusion and condensation rates of water, as well as chemical reactions within the bubble are included in the model. From Ref. 27.



Pressure: $P_T \le 100$'s of bar

Figure 5: Schematic representation of the reactive regions of a collapsing cavitation bubble.