Hao Feng · Gustavo V. Barbosa-Cánovas · Jochen Weiss
Editors

Ultrasound Technologies for Food and Bioprocessing

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Preface

The use of acoustic energy in food or bioprocessing operations is a relatively new endeavor if compared with other sources of energy, such as mechanical or thermal, which have been utilized for centuries in various applications. There are two important factors that make the current ultrasound-assisted processes possible. One is related with the development in ultrasound generation technology and the other one is the better understanding of interactions between acoustic energy and liquid media, enabling the development of important guidelines for ultrasound-based processes.

In addition to existing applications, there is an increasing list of potential uses of ultrasound in a wide range of industries. For food and bioprocessing purposes, it includes, for example, homogenization, cutting, extraction, inactivation of microorganisms, inactivation/activation of enzymes, drying enhancement, surface cleaning, depolymerization, crystallization, sieving, bio-component separation, peeling, nanoparticle production, particle size reduction, improvement of interface heat and mass transfer, and so on. It is, therefore, the strong belief of the editors that a comprehensive compilation summarizing the fundamentals of ultrasound technology, current developments, new research findings, and more importantly examples of industrial applications is very much needed to further the uses of ultrasound technology.

This book was designed to be an aid to a broad range of scientists and engineers in several fields, including food processing, food safety, chemistry, physics, chemical engineering, material science, agriculture, and bioprocessing-related disciplines. The 25 chapters in the book are organized into three sections. Section I (Chapters 1 to 4) covers fundamental aspects of ultrasound as well as high-intensity ultrasound applications. The basic concepts in acoustics, the theory of acoustic cavitation, and the physical and chemical effects of cavitation on biomaterials are detailed in three chapters. There is also a chapter dealing with the thermodynamic and kinetic aspects of ultrasound. Section II (Chapters 5 to 8) focuses on recent developments in the power ultrasound domain, where the four chapters elucidate important topics, such as how to use variable frequency strategies to enhance an ultrasound treatment and how to avoid the pitting problem in probe-type sonoreactors. This section also
includes non-traditional approaches to generate cavitation, which are very promising. The 17 chapters in Section III (Chapters 9 to 25) are dedicated to current and potential applications of power ultrasound mainly in the food processing and bioprocessing industries. Topics covered in these chapters include ultrasound-assisted unit operations, such as cutting, cleaning, homogenization, extraction, freezing, crystallization, drying, and membrane separation. In addition, the inactivation of microorganisms and enzymes are covered in detail in three chapters. The use of acoustic energy to change the functionality of food components and ingredients is also extensively covered in the two following chapters, and later on, specific applications, such as the utilization of power ultrasound in the dairy industry, are included. At the end, there is a chapter dealing with the sonochemistry of power ultrasound as applied to the production of nanomaterials.

We hope this book will not only prove to be useful in research and development efforts but will also facilitate the industrial adoption of power ultrasound. Finally, we would like to thank all of the authors for their efforts to contribute very stimulating chapters. Many of these authors also participated in reviewing the manuscripts, for which we are grateful. It was indeed a great pleasure to work with such a fine group of professionals.

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Chapter 1  
The Physical and Chemical Effects of Ultrasound

Sandra Kentish and Muthupandian Ashokkumar

1 Introduction

When a violin string is vibrated by the bow, a pressure wave is generated which travels to the human ear and is perceived as music. All sound waves are similar to this; they are simply longitudinal pressure waves passing through a medium.

The type of sound wave is determined by its frequency (Fig. 1.1). “Infrasound” refers to sound waves of frequency below that detectable by the human ear. This is the zone used by whales and by submarine sonar devices. The range of human hearing is from around 20 Hz to ~20 kHz. The word “ultrasound” refers to sound waves that are at a frequency above this range. This ultrasonic spectrum can itself be divided into two zones. Power ultrasound will be the major focus of this book and refers to the frequency range from 20 kHz to around 1 MHz. Diagnostic ultrasound has a frequency in excess of 1 MHz and is used mainly for medical and industrial imaging purposes.

A major advantage of ultrasound to the food industry is that it is perceived as benign by the general public. Other processing techniques (microwaves, gamma radiation, pulsed electric field) can be considered cautiously by elements of the general population. However, sound waves are generally considered safe, non-toxic, and environmentally friendly – this gives the use of ultrasound a major advantage over other techniques.

So why is ultrasound an effective processing aid for the food and bioprocessing industry? The impact of this phenomenon is generally classified into two categories: physical and chemical effects. These two categories are discussed in more detail in the sections below. The focus is on the use of ultrasound in liquid rather than gaseous media, as this will be the usual situation in such industrial applications.
2 Physical Effects of Ultrasound

As previously indicated ultrasound simply represents a high-frequency pressure wave. As this pressure wave passes through the medium, regions of high and low pressure are created. The size of these pressure variations, referred to as the amplitude of the pressure wave or the acoustic pressure, is directly proportional to the amount of energy applied to the system. As this wave passes through a viscous medium, be it air or water, it will dissipate this energy in the form of viscous flow. This is referred to as “steady streaming” (Riley, 2001). The flow pattern that results will depend upon the form of the original acoustic wave and whether the pressure wave is reflected from hard surfaces or otherwise interacts with the system boundaries. For example, Rayleigh streaming is the term used to refer to the specific flow patterns that arise from a standing wave pattern between two plane walls (Riley, 2001). Higher frequency ultrasound leads to higher energy absorption and in turn generates greater acoustic streaming flow rates than lower frequencies for the same power intensity (Suslick, 1988a).

In gases such as air, which are compressible fluids, the movement of fluid in streaming patterns is always sufficient to accommodate these pressure variations. However, most liquids are inelastic and incompressible and thus cannot respond as easily in this manner. If the changes in pressure are great enough, then the liquid can literally be “torn” apart under the influence of ultrasound. Microbubbles of gas and vapor form, which relieve the tensile stresses created by the pressure wave. Scientific theory would suggest that the acoustic pressure variation required for this to occur is very large, up to 3,000 MPa (Brennen, 1995). However, in practice, these microbubbles form at relatively mild acoustic pressures. It is generally believed that this is because any liquid already contains cavities of gas or nanobubbles, and that these nuclei assist in the formation of microbubbles. It is interesting that these nanobubbles, which have been the subject of speculation for many decades in the ultrasonic field, have only recently been proven to exist (Zhang et al., 2008) at least at the interface between water and a hydrophobic surface.

The bubble formation process is known as cavitatin. The lowest acoustic pressure at which it is observed is called the cavitation or the Blake threshold, $P_B$, and is a function of the solution vapor pressure, $P_v$, the surface tension ($\sigma$), the initial nanobubble radius ($R_0$), and the system pressure ($P_0$) (Leighton, 1994):
\[ P_B = P_0 - P_v + \frac{4}{5} \sigma \sqrt{\frac{2\sigma}{3 \left( P_0 + \frac{2 \sigma R_0}{R_0} - P_v \right) R_0^3}} \] (1.1)

It is much easier to generate an acoustic wave of high amplitude (high acoustic pressure) at lower frequencies. At higher frequencies (>1 MHz), acoustic pressures are lower and this amplitude is more readily dissipated within the fluid. For this reason, the Blake threshold is rarely exceeded at these frequencies in industrial applications and so cavitation is generally not observed.

It should be noted that while cavitation formally refers to the “creation” of a microbubble, most authors in the ultrasound field use this term to encompass the full range of bubble behavior once it has been formed. While the focus of this book is on acoustic cavitation, the hydrodynamic forces around pump impellers or in homogenizers can also create sufficient pressure changes so as to induce cavitation. Later chapters in this book discusses both acoustic cavitation and hydrodynamic cavitation in more detail.

Bubbles formed through cavitation will begin to expand and collapse under the influence of the acoustic field. The expansion/collapse cycle can be sinusoidal, mimicking that of the acoustic wave (Fig. 1.2a). Alternatively, for certain bubble sizes and acoustic pressures, the bubble expansion phase is extended and is followed by a violent collapse back to a smaller bubble size. This is referred to as inertial cavitation. This mode of bubble oscillation can persist for many hundreds of acoustic cycles, in which case it is referred to as stable, or repetitive transient cavitation. An example of this phenomenon is shown in Fig. 1.2b. In this example, a bubble initially of radius 0.5 μm expands to over 30 times this radius before collapsing back to the 0.5 μm size (Yasui, 2002). Alternatively, if the acoustic amplitude is higher, the bubbles grow and collapse spectacularly within a very few acoustic cycles and the collapsed bubble then disintegrates into a mass of smaller bubbles (Leighton, 1994; Yasui, 2002). These daughter bubbles are often small and themselves collapse rapidly so that complete annihilation of the original bubble occurs (Crum and Nordling, 1972; Strasberg, 1959). This is referred to as unstable or transient cavitation (Fig. 1.2c) and is generally observed at low frequencies (20–100 kHz). The size range at which transient cavitation occurs is often referred to as the resonance size. However, Yasui (2002) shows that the bubble size range for transient cavitation is often over an order of magnitude wide and does not necessarily coincide with the linear resonance radius.

A number of other processes may also be occurring within the bubble population, even below the cavitation threshold. If the bubbles are small, they will simply dissolve away (Fig. 1.2a). However, the mass transfer boundary layer is thinner and the interfacial area is greater during bubble expansion than during bubble collapse. This means that more air transfers into the bubble during the expansion phase than leaks out during collapse. This causes larger bubbles to grow over a very large number of acoustic cycles in a process referred to as rectified diffusion (Crum, 1980; Lee et al., 2005a). Larger bubbles may also form through coalescence of smaller bubbles.
Fig. 1.2  Simulated radius time curves at 140 kHz for (a) a dissolving bubble (initial radius 0.1 μm and acoustic pressure 500 kPa), (b) a bubble in repetitive transient cavitation (initial radius 0.5 μm and acoustic pressure 250 kPa), and (c) a bubble in transient cavitation (initial radius 5 μm and acoustic pressure 500 kPa). This last bubble disintegrates into a mass of smaller bubbles just after the third collapse (t∼22 μs) (reproduced from Yasui (2002) with permission)

(Ashokkumar et al., 2007; Lee et al., 2005b). These coalesced bubbles may eventually be of a size where they simply float away from the sonication zone through the influence of gravity. Further, the oscillating bubble will generate fluctuations in velocity and pressure in the surrounding fluid (see Fig. 1.3). This is referred to as “cavitation microstreaming” (Elder, 1959) and generates turbulence within the fluid on a microscale.

More significantly, the collapse of a bubble during transient or repetitive transient cavitation is a cataclysmic event – extremely high pressures can be generated (70–100 MPa) (Laborde et al., 1998; Suslick, 1988b) that result in outward propagating shockwaves. This propagation causes severe turbulence within the immediate surroundings. These dramatic “micro” events can easily cause polymer chains to break (Price, 1990) or the cell walls of plant and animals to be destroyed (Cioffi and Wolfersberger, 1983; Lin and Thomas James, 2004; Simon, 1974). Hacias et al. (1997) comment that the energy released from a single transient collapse is
The Physical and Chemical Effects of Ultrasound

Fig. 1.3 Cavitation microstreaming patterns around a 272 μm radius bubble excited at acoustic frequencies 9 and 11 kHz (reproduced from Tho et al. (2007) with permission)

extremely small, but millions of bubbles collapse every second and the cumulative effect is large.

Of particular relevance to many food applications is the occurrence of transient cavitation within the proximity of a solid surface. In this case, the bubble collapses asymmetrically. In doing so, a microjet of fluid or bubbles (Lee et al., 2007) can be emitted from the bubble (Fig. 1.4). This microjet is directed toward the solid surface and this can lead to pitting and erosion. The surface action can also dislodge particles attached to the surface and break down large aggregates into smaller particles (Hagenson and Doraiswamy, 1997; Suslick, 1988a).

Acoustic standing waves can result from the reflection of sound from a solid surface or an air–liquid interface back into the solution at the same time that a wave is generated at the transducer (Fig. 1.5). At the pressure antinode of such a standing wave pattern, the pressure fluctuates from a maximum to minimum amplitude with time. Conversely, at the pressure node the acoustic pressure is invariant and close to zero. A phenomenon referred to as Bjerknes forces causes smaller bubbles to accumulate at the antinode, while larger bubbles accumulate at the node (Crum and Eller, 1970; Yasui, 2002). In moving to the antinodes, the cavitation bubbles travel in ribbon-like structures (referred to as “streamers”) coalescing as they collide. In doing so, a filamentary structure, referred to as an acoustic “Lichtenberg” figure

Fig. 1.4 Selected images of the release of a fountain of microbubbles from a parent bubble in water within a confined microspace. Acoustic frequency 59.67 kHz and intensity 0.5–0.7 W/cm² (reproduced from Lee et al. (2007) with permission)
Fig. 1.5 Effects of a standing wave pattern. Bubbles smaller than the resonance size accumulate at the pressure antinodes, larger bubbles accumulate at the nodes.

Fig. 1.6 The movement of bubbles toward a solid surface acting as a pressure antinode within an acoustic standing wave pattern.

is created (Fig. 1.6) (Mettin et al., 1999). At 20 kHz these bubbles are typically <10 μm in size, about a millimeter apart and traveling at less than 1 μm/s (Luther et al., 2001). This bubble translation is known to dislodge particles from fouled surfaces, in cases where the surface itself acts as the pressure antinode (Lamminen et al., 2004).

Of particular interest to many of the applications discussed in this book is that these physical effects are strongest near to fluid/solid and fluid/liquid boundaries. Specifically, the microjetting that occurs with asymmetric bubble collapse and the acoustic streaming patterns around solid objects are strongest within a few millimeters of the surface. Similarly, the movement of bubbles toward a solid surface acting as a pressure antinode within an acoustic standing wave pattern results in increased turbulence within this same zone. These boundary layer effects are important, because it is usually such boundary layers that offer the greatest resistance to both heat and mass transfer. By concentrating the acoustic energy dissipation in these areas, ultrasound is extremely effective in improving heat and mass transfer kinetics, often proving to be more effective than other less site-specific options such as high-shear mixers or microfluidic devices. Surface effects are also important in emulsification, where interfacial turbulence is associated with droplet formation (Li and Fogler, 1978) and in nebulization, where acoustic streaming effects cause a
“fountain structure” to form at the air/water interface from which microdroplets are ejected (Lang, 1962).

Increasing the external pressure increases the cavitation threshold within an ultrasonic field and thus fewer bubbles form. However, increasing the external pressure also increases the collapse pressure during transient cavitation (Bondy and Sollner, 1935; Suslick, 1988b; Young, 1989). This means that the collapse of the bubbles when cavitation occurs becomes stronger and more violent. This use of “over-pressure” is a common feature of many commercial sonoprocessing applications. Conversely, increasing the external temperature increases the water vapor pressure inside the cavitating bubbles. This water vapor “cushions” the bubble collapse and the collapse event is subdued. Hence, ultrasound is less effective at temperatures significantly above ambient levels.

Finally, regardless of the mechanism for dissipation of acoustic energy, be it steady streaming, microstreaming, transient cavitation, or microjetting, the energy is ultimately converted to heat. This means that all applications of ultrasound will result in an increase in temperature unless cooling is simultaneously applied. In most circumstances, the temperature increase is relatively mild, of the order of a few degrees Celsius, but it is dangerous to ignore this effect in system design. Experimentally, the change in temperature can be used to determine the fraction of the electrical energy originally applied to the transducer that is converted to acoustic energy and ultimately to heat. This is referred to as the calorimetric determination of acoustic energy and it is simply determined from an energy balance (Kimura et al., 1996; Ratoarinoro et al., 1995) as

$$Q = mc_p \Delta T$$  \hspace{1cm} (1.2)

where $Q$ is the energy input in Watts, $m$ is the sample mass, $C_p$ is the heat capacity of the sample, and $\Delta T$ is the change in temperature.

3 Chemical Effects

The violent collapse events that occur during transient and repetitive transient cavitation can also generate enormous temperatures at a localized level (>5,000 K) (Ashokkumar and Mason, 2007). These high temperatures and the violent pressure changes occurring simultaneously can cause a number of chemical changes to occur within both the vapor phase inside the cavitation bubble and in the immediate fluid surrounding it. There are a number of review articles (Luche, 1998; Ashokkumar et al., 2007; Mason and Lorimer, 2002) that provide detailed information on these chemical effects, commonly referred to as sonochemistry. This section summarizes key aspects of this extensive field of research.

Primary radicals are formed as a direct result of the high temperatures inside a collapsing bubble. If water vapor is present, H and OH primary radicals are generated and these can recombine to form molecular products as shown in Reactions (1.3)–(1.6).
When a single bubble is considered, the number of radicals generated is high when the temperature inside the collapsing bubble is at a maximum. This temperature can be increased by increasing the sonication power, increasing the external pressure, or decreasing the external (solution) temperature as described above. Changing from an air-saturated medium to one saturated with an inert gas such as argon is also effective. The heavier inert gases have a lower thermal conductivity and hence are less efficient at transferring heat away from the bubble to the surrounding fluid (Ashokkumar et al., 2007; Leighton, 1994).

The amount of heat generated also depends upon the size of the cavitation bubble. A 20 kHz bubble grows to the largest size (60–100 μm) and hence generates a relatively large amount of heat. Thus the amount of primary radicals generated per bubble is higher at 20 kHz compared to that generated at higher frequencies.

In a multibubble field, the total number of primary radicals generated is controlled not only by the bubble temperature, but also by the number of active bubbles generated. In fact, it has been shown that the number of bubbles generated is the dominant factor in controlling the radical yield (Ashokkumar et al., 2007). Thus, for a given liquid volume and acoustic power, a greater number of radicals are generated at higher frequencies and this can dominate over the radical production per bubble (see Fig. 1.7). For this reason, sonochemical effects are generally most dominant at intermediate frequencies (200–500 kHz).

A number of analytical methods have been developed to quantify the number of primary radicals generated during acoustic cavitation (Ashokkumar et al., 2007).

\[ \text{H}_2\text{O} \rightarrow \text{H}^\bullet + \text{OH}^\bullet \quad (1.3) \]
\[ \text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2 \quad (1.4) \]
\[ \text{OH}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O}_2 \quad (1.5) \]
\[ \text{H}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O} \quad (1.6) \]
These include electron spin resonance trapping and terephthalic acid, luminol, and iodide methods. Among these methods, the iodide method is a simple and common method that can be used to estimate the amount of OH radicals generated. This method is based on the amount of hydrogen peroxide formed due to Reaction (1.5). The actual number of OH• radicals generated may be higher than estimated using this method since some of the OH• radicals recombine with H atoms and form water.

In air-saturated solutions, other reactions involving oxygen and nitrogen occur. In particular, this results in the formation of NO₂, which forms nitric acid in solution. It is for this reason that sonication of air-saturated solutions often leads to a decrease in the pH (Superno and Kruus, 2000). Some secondary radicals may also be produced by the reaction between the primary radicals and other solute molecules. For example, alcohols and surfactants readily adsorb at the bubble/solution interface and generate highly reactive secondary reducing radicals. A variety of chemical reactions have been studied that use the primary and secondary radicals generated during acoustic cavitation (Ashokkumar et al., 2007).

The high temperatures within the bubble can also result in a range of pyrolysis reactions if organic solutes are present. Further, the primary and secondary radicals generated during the bubble collapse can be consumed in a range of secondary reactions that may occur within the bulk fluid and some distance from the bubble itself. For example, the OH• radicals generated within the bubbles have been used to oxidize organic pollutants (Inazu et al., 1993; Kotronarou et al., 1992), and the H• atoms and other secondary reducing radicals have been used to reduce metal ions to generate metal nanoparticles (Hyeon et al., 1996; Suslick et al., 1996). Of particular importance in food applications, Suslick and Grinstaff (1990) proposed that the superoxide species (HO₂•) formed from primary radicals may induce disulfide cross-linkage between proteins. These effects have been used to generate both gas- and liquid-filled protein microspheres that have applications for drug delivery (Dibbern et al., 2006; Toublan et al., 2006) and medical imaging (Webb et al., 1996). Similarly, Ashokkumar et al. (2008) propose that hydroxyl radicals generated during sonication can be used to enhance the degree of hydroxylation in food materials and hence increase the antioxidant activity of foods.

It should be noted that the generation of OH• radicals may affect the quality of some foods by reducing the antioxidant capacity (Ashokkumar et al., 2008). Intense sonication is also known to generate off-flavors. Riener et al. (2009) showed that extended sonication of milk generated a range of volatile organic compounds that might be responsible for a “rubbery” aroma. They related these compounds to both pyrolysis reactions inside the cavitating bubbles and to free radical-induced lipid oxidation resulting from the decomposition of unsaturated fatty acid hydroperoxides. In these applications, it may be important to minimize sonochemical reactions by either utilizing a low frequency, where free radical formation is very low (20 kHz), or by the addition of a free radical scavenger such as ascorbic acid (Ashokkumar et al., 2008).

Finally, the bubble collapse is also accompanied by light emission known as sonoluminescence (Fig. 1.8). The high-temperature conditions generated on bubble collapse are responsible for the light emission (Ashokkumar and Grieser, 2004). In
Fig. 1.8 Multibubble sonoluminescence observed at 440 kHz and 30 W in a rectangular Pyrex cell containing 1,000 mL water with a piezoelectric transducer attached at the bottom of the cell. The photograph is taken with a total exposure time of 30 s. The light emitting cavitation bubbles are located at several antinodes in a standing wave pattern.

Fig. 1.8, the sonoluminescence observed in a multibubble standing wave field is shown. Since the topic of this book is concerned with physical effects and chemical reactions of ultrasound, further discussion on sonoluminescence is not provided; however, interested readers may refer to the literature (Young, 2005).

4 Conclusions

Most of the applications to be considered in the remainder of this book will focus on the physical effects of ultrasound which dominate at lower frequencies of around 20 kHz. The physical effects of ultrasound can be generally summarized as increased turbulence throughout the medium but with the strongest effects in the vicinity of system boundaries and interfaces. At lower frequencies (20–100 kHz), this increased turbulence results primarily from transient cavitation, that is, the catastrophic collapse of microbubbles throughout the fluid.

At intermediate frequencies, say between 200 and 500 kHz, chemical effects are more dominant as the number of active bubbles generated is higher. Transient cavitation events are less frequent and hence the strong physical effects experienced at 20 kHz are weaker here, although they are still present.

At higher frequencies (>1 MHz), cavitation and the associated chemical effects are less likely and acoustic streaming effects are more dominant. Thus for example, ultrasound in the MHz range is used in the electronics industry to clean sensitive components such as silicon wafers and disk drive parts without risking the erosive damage that might occur in the cavitation frequency range.
References


Chapter 2
Acoustic Cavitation

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1 Introduction

The benefit of acoustic cavitation owes to its ability to concentrate acoustic energy in small volumes. This results in temperatures of thousands of kelvin, pressures of GPa, local accelerations 12 orders of magnitude higher than gravity, shock-waves, and photon emission. In a few words, it converts acoustics into extreme physics.

The counterpart is that it constitutes a complex multidisciplinary problem, involving a wide range of temporal and spatial scales, and is therefore difficult to measure. Furthermore, it is a diphasic problem in essence, with the peculiarity that the cavitation bubbles rise up “from nowhere” and self-arrange in a fascinating variety of structures. For all these reasons it is difficult to control, to predict, and to scale up. Several features of cavitation fields remain unexplained, although the progress in optic recording systems recently shed light on previously unreachable characteristics.

From a theoretical point of view, the physics of the single-bubble model has progressed considerably, thanks to single-bubble sonoluminescence experiments. Many features specific to multibubble fields, however, remain obscure and constitute an active research field. From an engineering point of view, the main unknown remains the bubble size distribution and spatial repartition, which in general constitute the main barrier to extrapolate the more or less known action of one bubble on a specific process, to macroscopically observed effects.

By this contribution, we would like to help the reader to assess the main physics involved when he switches on his sonotrode. This chapter is organized as follows. We first present general results for bubbles in a quiet liquid (Section 2). Then, in Section 3, the purely radial forced oscillations of a single bubble in an infinite liquid will be addressed, focusing on thermal effects, solvent evaporation in inertial
bubbles, and their relevance to sonochemistry. Bubbles’ loss of sphericity and the resulting effects will be presented in Section 4. The last section addresses cavitation bubble fields and their interaction with the sound field, from both experimental and theoretical points of view.

2 The Quiet Bubble

Before entering in the complex field of acoustic cavitation, it is instructive to examine the behavior of a free spherical gas bubble in a quiet liquid, which can be intuitively apprehended from everyday life.

2.1 A Key Phenomenon: Surface Tension

Increasing the interface between two media requires energy in order to bring molecules from the bulk to the interface. Without a compensating force, an interface therefore has a natural tendency to decrease. In the case of the bubble, the compensating force is an overpressure in the bubble, known as Laplace tension:

\[ p_b = p_0 + \frac{2\sigma}{R} \]

where \( p_0 \) is the liquid pressure, \( R \) is the bubble radius, and \( \sigma \) is the surface tension. This overpressure is unimportant for large bubbles but increases when \( R \) approaches the value \( \frac{2\sigma}{p_0} \) from above. For example, for an air bubble in water at atmospheric pressure (\( \sigma = 0.072 \) N\(^{-1}\), \( p_0 = 101 \) kPa), \( 2\sigma/p_0 = 1.45 \) \( \mu \)m so that the effect of surface tension becomes important in this range of radii. This is precisely the order of magnitude of the bubbles involved in cavitation, so that one can suspect that surface tension will play an important role.

2.2 Bubble Ambient Radius

We consider a bubble containing a given mass \( m_g \) of incondensable gas in a liquid at ambient pressure \( p_0 \), temperature \( T_0 \). The bubble also contains vapor of the liquid, in equilibrium with the latter at \( T_0 \), so that the partial pressure of vapor is the equilibrium saturation pressure \( p_{v, eq}(T_0) \). We seek the radius \( R_0 \) of such a bubble in mechanical equilibrium. Owing to surface tension, the pressure inside the bubble \( p_b \) is \( p_0 + 2\sigma/R_0 \). Using the law of perfect gases yields

\[ p_{v, eq}(T_0) + \frac{m_g}{M_g} \frac{RT_0}{\frac{4}{3}\pi R_0^3} - \frac{2\sigma}{R_0} = p_0 \]

(2.2)
This cubic equation yields the bubble ambient radius $R_0$. The vapor pressure $p_{v,\text{eq}}(T_0)$ can be neglected for temperature well below the boiling point. For further use, we define the dimensionless Laplace tension for the bubble in ambient conditions

$$\alpha_S = \frac{2\sigma}{p_0 R_0} \quad (2.3)$$

### 2.3 Radial Mechanical Stability: The Blake Threshold

Equation (2.2) gives the radius of a bubble in mechanical equilibrium for a given liquid ambient pressure $p_0$. One might look for the evolution of the bubble radius from $R_0$ to $R$ when the liquid pressure $p_0$ is decreased to $p = p_0 - p_a$. Assuming that this variation is slow enough to allow isothermal transformations of the gas, the evolution of $R$ can be obtained implicitly by

$$p_{v,\text{eq}}(T_0) + \left( p_0 - p_{v,\text{eq}}(T_0) + \frac{2\sigma}{R_0} \left( \frac{R_0}{R} \right)^3 - \frac{2\sigma}{R} \right) = p_0 - p_a \quad (2.4)$$

Rather than seeking explicitly $R$ from Equation (2.4), it is more instructive to look for a graphical solution. Figure 2.1 is obtained by using Equation (2.4), and it shows the variation of the equilibrium radius $R$ as a function of the liquid pressure $p_0 - p_a$. It is seen that if the external pressure is lowered to a value smaller than $p_0 - p_a^\text{crit}$, there is no possible equilibrium radius $R$. Physically, at this point, the liquid starts to flow outward and the bubble undergoes an explosive expansion. This analysis is the key point of inertial cavitation.

This critical value $p_a^\text{crit}$, which depends on $R_0$ and thus on the quantity of gas $m_g$ contained in the bubble, is called the “Blake threshold” (Akhatov et al., 1997a; Blake, 1949; Hilgenfeldt et al., 1998; Louisnard and Gomez, 2003) and can be calculated explicitly by seeking the minimal value of $R$ from Equation (2.4). This yields

$$p_a^\text{crit} = p_0 - p_{v,\text{eq}} + p_0 \left( \frac{\alpha^3}{27 \left( 1 + \alpha_S \right)} \right)^{1/2} \quad (2.5)$$

The values of $p_a^\text{crit}$ are represented in Fig. 2.2 for an air bubble in water in ambient conditions ($\sigma = 0.0725 \text{ N} \cdot \text{m}^{-1}, p_{v,\text{eq}} = 2,000 \text{ Pa}, p_0 = 100 \text{ kPa}$).

An important point to note from Equation (2.5) and Fig. 2.1 is that the corresponding external pressure $p_0 - p_a^\text{crit}$ can be lower than the vapor pressure of the liquid, and even negative for small values of $R_0$. It should be recalled that a liquid, owing to internal cohesion force, can effectively support negative pressures or “tensions” (see Section 5.2).
Fig. 2.1 Evolution of the bubble equilibrium radius $R$ when the liquid pressure $p_0 - p_a$ is decreased, for a 1-μm bubble in ambient conditions.

Fig. 2.2 Blake threshold for an air bubble in water in ambient conditions ($p_0 = 101325$ Pa, $\sigma = 0.0725$ N·m$^{-1}$).

### 2.4 Perturbations of Radial Equilibrium: Free Frequency

The gas filling the bubble provides elasticity to the bubble/water mechanical system; the bubble will oppose a resistance to any compression or expansion imposed by the liquid motion. This force may in turn put the liquid into motion, so that the bubble/liquid constitutes a mass–spring system. Perturbing the bubble slightly from its equilibrium radius therefore results in free radial oscillations, whose frequency can be calculated from energy conservation consideration or from a bubble dynamics equation (see Section 3.2.3). If the oscillations are assumed isothermal, the angular frequency of the free oscillations reads...
\[ \omega_0 = \frac{1}{R_0} \left\{ \frac{p_0}{\rho_l} \left[ 3(1 + \alpha_S) - \alpha_S \right] \right\}^{1/2} \]  

(2.6)

where \( \rho_1 \) is the liquid density.

Bubble-free oscillations are responsible for the noise emitted by running water. In the context of acoustic cavitation, one would expect that a bubble excited at its free frequency would undergo strong oscillations and would be the main factor for cavitation effects. Active bubbles in strong sound fields are in fact excited well below their resonant frequency, as will be discussed throughout further in the chapter.

### 2.5 Gas Exchange with the Liquid

In saturation condition, that is, if the liquid is saturated with gas at ambient pressure \( p_0 \), a gas bubble dissolves because of surface tension. This can be readily understood from Fick’s law, as shown below.

Let us denote \( C_\infty \) as the concentration of dissolved gas in the solution, and let us consider a bubble of ambient radius \( R_0 \) in mechanical equilibrium in the liquid. Far from the bubble, the concentration is \( C_\infty \). At the bubble wall, the dissolved gas is in equilibrium with the gas inside the bubble, at pressure \( p_{g0} = p_0 + 2\sigma/R_0 \) (let us neglect vapor to simplify the reasoning). Therefore, by virtue of Henry’s law, the dissolved gas concentration at the bubble wall is \( C_R = p_{g0}/k_g \), where \( k_g \) is the Henry constant. We therefore express the difference in concentration between the bubble wall and at infinity as

\[ C_R - C_\infty = C_0 \left[ \frac{p_{g0}}{p_0} - \frac{C_\infty}{C_0} \right] = C_0 \left[ 1 + \alpha_S - \frac{C_\infty}{C_0} \right] \]  

(2.7)

where \( C_0 = p_0/k_g \) is the saturation concentration, that is the concentration of dissolved gas in the liquid in equilibrium with the gas at \( p_0 \). Thus if \( C_\infty/C_0 < 1 \) the liquid is under-saturated, if \( C_\infty/C_0 > 1 \) the liquid is supersaturated (as is the case in bubbly beverages that are saturated in CO\(_2\) at a few bars)

For a saturated liquid, we have \( C_\infty/C_0 = 1 \), so that from Equation (2.7), \( C_R - C_\infty > 0 \). Fick’s law thus predicts an outward gas diffusion flux, so that the bubble dissolves increasingly faster as its size decreases. The analytical solution of the problem has been given by Epstein and Plesset (1950). A practical implication of this phenomenon is that no stable gas bubble should exist in a quiet saturated liquid.

If the liquid is supersaturated in gas, that is \( C_\infty/C_0 > 1 \), Equation (2.7) shows that there exists a critical value of \( R_0 \) above which the bubble grows by gaining gas from the liquid, and below which it dissolves. The bubble growth can be easily observed in a glass of champagne, for example.

In a sound field, an oscillating bubble can grow even in a saturated or under saturated liquid. The phenomenon is termed “rectified diffusion” and will be discussed in Section 3.4.
2.6 Translational Motion

Common observation tells us that a bubble rises. This is because the buoyancy force \( F_A = -\frac{4}{3} \pi R_0^3 \rho_l g \) is greater in magnitude than the weight of the bubble \( F_G = \frac{4}{3} \pi R_0^3 \rho_b g \), where \( \rho_b \) is the bubble density. After some time, the bubble will reach a steady velocity, which can be obtained by balancing the buoyancy force \( F_A \) with the viscous drag force \( F_V = -\frac{4}{3} \pi R_0 \mu_l v \) (the weight being negligible since \( \rho_b \ll \rho_l \)):

\[
v = -\frac{1}{3} \frac{R_0^2 \rho_l}{\mu_l} g
\]

where \( \mu_l \) is the dynamic viscosity of the liquid.

In a sound field a bubble undergoes generalized buoyancy forces, termed Bjerknes forces, and can be either attracted or repelled by zones of high acoustic pressures. They also undergo mutual attraction or repulsion as they experience the field radiated by a neighboring bubble. This issue will be presented in Section 5.3.

2.7 Departure from Spherical Shape

Above some critical size, quiet bubbles depart from their spherical shape as they rise in the liquid, generally flattening their rear part. Radially oscillating bubbles exhibit various shape instabilities, leading to their destruction, and have a peculiar behavior near solid boundaries (Section 4).

3 The Forced Spherical Single Bubble

3.1 Introduction

This section recalls the main features of a radially oscillating spherical bubble in an infinite liquid. This ideal picture may sound unrealistic, and anyone having looked at a cavitation experiment may have doubts on its practical use. However, it leads to important fundamental results, whose usefulness in cavitation prediction has been proved. Moreover, levitation experiments of single bubbles, designed much earlier than their initial use by Gaitan et al. (1992) for single-bubble sonoluminescence (SBSL), produced numerous experimental confirmations of theory in a configuration relevant to the above hypothesis.

This section will refer frequently to recent theoretical and experimental work developed in the context of SBSL. This is because the latter issue has raised numerous papers presenting either new issues or theoretical and experimental refinements of known results. Most of these results are also relevant to multibubble fields.

In this section, after presenting the equations governing the forced oscillations of a spherical bubble and their reduction in the linear case, we will focus on the
case of inertial oscillations, which is responsible for most of the practical effects of acoustic cavitation. The thermal behavior of the bubble interior, along with vapor and gas transport at the interface will next be discussed. The chemistry in the bubble will only be briefly mentioned, and we refer the reader to the chapter of K.S. Suslick in this book. Finally, the rectified diffusion phenomenon, possibly leading to accumulation of gas in the bubble, will be presented.

3.2 Radial Oscillations

3.2.1 Rayleigh–Plesset Equations

Rayleigh (1917) studied the collapse of a spherical empty cavity, whatever its origin, in order to assess its possible responsibility for the erosion damage on ship propellers. He derived a differential equation, which is basically the principle of mechanical energy conservation in the absence of dissipative forces.

We assume a spherical bubble filled with incondensable gas and vapor, in a liquid of infinite extent, and we first neglect gas transport between the liquid and the bubble. A correct representation of the problem would require the resolution of conservation equations in both phases, but several levels of approximations have allowed us to obtain the equation of motion in the form of a second-order ordinary differential equation.

The most common assumption is the uniformity of the pressure inside the bubble, which, along with the liquid incompressibility hypothesis, yields the Rayleigh–Plesset family of equations (Noltingk and Neppiras, 1950; Plesset, 1949). The first assumption is questionable in view of the order of magnitude of the bubble wall velocities, which may attain several times the sound velocity in the gas. The validity of this assumption has been addressed recently by Lin et al. (2002a), and the Rayleigh–Plesset equation, almost one century after its first derivation, was finally found to be valid in a very wide range of parameters. In its most basic form, it reads

\[ R\ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho_l} \left[ p_b(t) - \frac{2\sigma}{R} - 4\mu_l \frac{\dot{R}}{R} - p(t) \right] \]  

(\text{2.8})

where over-dots denote time derivatives. \( p(t) \) is the driving pressure, which can be understood as either the pressure infinitely far from the bubble, or the pressure that would be measured in the liquid at the bubble center, if the latter would be absent. For sinusoidal driving, \( p(t) \) can be written as

\[ p(t) = p_0 - p_a \sin(\omega t) \]  

(\text{2.9})

where \( p_a \) is the driving pressure amplitude, and \( \omega \) is the angular frequency of the driving. In what follows, we note \( f = \omega/2\pi \) the frequency, and \( T = 1/f \) the period of the driving. It should be noted that a value of \( p_a \) greater than \( p_0 \) means that the liquid pressure becomes negative during some part of the expansion phase.