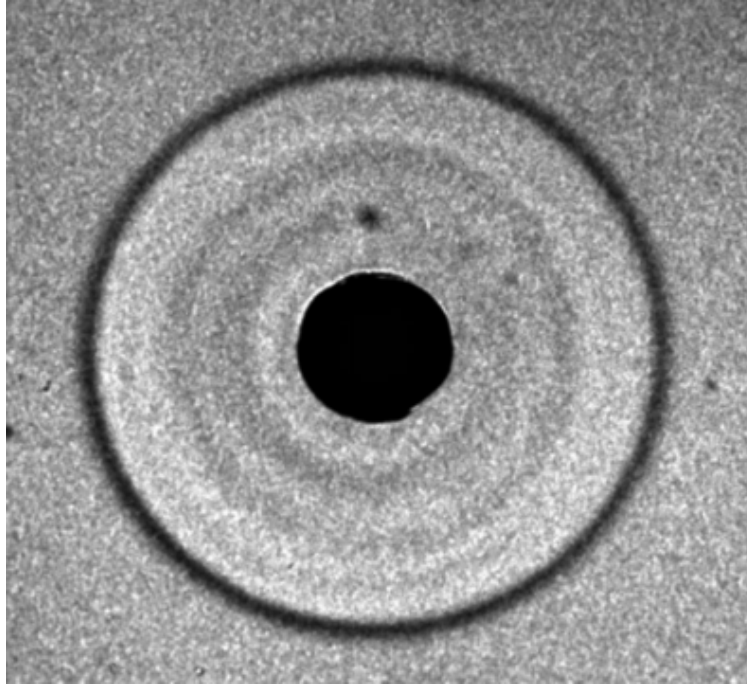




CHALMERS
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Development of 1D Numerical Framework for Laser Induced Cavitation

Master's thesis in Applied Mechanics

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DEPARTMENT OF MECHANICS AND MARITIME SCIENCES

CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover: Picture captured experimentally showing an expanding cavitation and a propagating shock wave. This picture was taken from "Cloud cavitation induced by shock-bubble interaction[9]"

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Abstract

In this thesis work, we numerically investigate the life cycle of a laser induced cavitation. An in-house numerical tool is used and further developed. Simulations are carried out to model the growth and collapse of a vapor bubble in a superheated solution. The purpose behind this study is to increase our understanding of the bubble dynamics and the extreme physical conditions within and surrounding the laser induced cavity. The application of this work is within the field of laser induced crystallization, where the cavity serves as the crystal nucleation site.

Proper modeling of all relevant physical phenomena is necessary to fully capture the right dynamics. The existing in-house code was developed for cavities induced by lower energy densities lasers. To extend the code to handle higher energy densities, often used in experimental studies, we identified the liquid compressibility and the formation of plasma to have significant effects. Different modeling techniques were implemented to account for a compressible liquid and simulations were performed to assess the effects of plasma formation.

The developed numerical framework is able to produce qualitatively and quantitatively promising results for both thermo- and laser induced cavitation. The results suggest compressibility effects are of major importance during the formation and collapse of the bubble. The presence of plasma is also shown to be significant, particularly during the early stages of the growth phase. Our results are in fair agreement with both experimental and analytical data from literature. The reasons behind observed differences are discussed, and suggestions for future work and improvements are proposed. This thesis work can help better understand the underlying physics of laser induced cavitation and help industry to design an adequate environment for a well controlled crystallization.

Keywords: Crystallization, Laser Induced Cavity, Bubble Dynamics, Vapor Bubble, Numerical Framework, Compressible Liquid, Plasma formation.

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And to you, the one and only... Where shall I begin, or how should I start! This is for you, This is all for you. To you I offer this thesis work, to you I offer my success, this and many more to come. There aren't enough words in the English language to describe how grateful I am, yet I will try. Thank you for being you, thank you for being mine, Thank you for everything you taught me, and thank you for everything you made me into. This thesis wouldn't have been without you, and neither I wouldn't have been if not for you. You are indeed the mother everyone should have, yet somehow no one deserves...Thank you for being my mother!

Gothenburg, November 2021

Khalil Jabberi

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1

Introduction

This chapter is intended to introduce the reader to the study performed in this thesis work. It gives an overview of the problematic including background, aim, purpose and limitations.

1.1 Background

Crystallization is the process by which solid matter with a highly organized molecular structure known as crystals is created, starting from a gaseous or liquid phase. It is a common purification and separation technique dedicated to the production of a set of crystals with desired and controlled properties. This process is of major importance in many industries e.g. chemical, pharmaceutical, food, and material industries...etc, making the study of such a phenomenon of high relevancy. Crystals can be produced by various techniques, cooling, evaporation, deposition, or furthermore, using a laser beam or ultrasounds to induce cavitation. The crystallization process itself will not be investigated but rather a mechanism leading to crystal formation, namely bubble nucleation by means of a laser pulse in a supersaturated solution. Laser-induced nucleation is the subject of this thesis and will be explained throughout this section. Additionally, the bubble dynamics resulting from the cavitation process will be the main focus, with the sole purpose of furthering our understanding of the extreme and often violent conditions within and surrounding the laser induced cavity in order to set an adequate environment for a well controlled crystallization.

Since the early 20th century, the study of cavitations have increased in popularity. It first started with studying its presence near, and influence on ship propellers. Nowadays though, many are the applications that involve cavitations, from hydraulic turbomachines all the way to medical procedures that involve laser usage. In the past, many mathematical models had been introduced to predict the behavior of cavities, the most famous being introduced by Fujikawa and Akamatsu or Yasiu. These models however were replaced in 1917 and extended in 1949 by a Rayleigh-Plesset-type equation to particularly model the liquid surrounding the bubble which implicitly governs the motion of the the bubble boundary (interface). Laser induced cavitation by virtue of optical breakdown is also a cavitation-controlled-mechanism that has been heavily discussed lately, particularly, to produce crystals. The usage of a focused laser pulse into a supersaturated solution had been experimentally witnessed by *Soare et al.* to induce crystal nucleation with good control. The latter

process indeed introduces a wide range of flexibility and freedom in generating crystals with desired properties, it does however come with its own sets of restrictions and challenges.

For a bubble to form using a focused laser pulse, sufficient amount of energy is to be deposited to counteract the intermolecular forces (which "macroscopically" manifest as the surface tension). These forces hold the molecules together and prevent void initiation. With sufficient amount of deposited energy, these voids will finally enlarge or cluster to form a bubble. It is important to mention that the bubble growth/dynamics are governed by the type of nucleation mechanism, namely Cavitation or Boiling. Cavitation is a pressure governed process where the pressure is reduced beneath the saturation pressure, at almost constant temperature. Whilst, for boiling, the temperature is raised above the saturation temperature, and bubbles form when the critical superheating value is reached. Though quite similar, with similar outcomes, these two mechanisms take place at different time scales. In typical engineering applications pressure change within a liquid domain happens faster than a thermal change would. Consequently, the resultant dynamics from cavitation and boiling are completely different. Yet, there is a nucleation mechanism that combines both processes, namely laser induced thermo-cavitation. The bubble dynamics resulting from a laser induced thermo-cavitation are similar to that of cavitation, whilst the governing physical phenomena are more similar to those of boiling. The understanding of this mechanism, thermo-cavitation, is a fundamental tool in this thesis work. As mentioned earlier however, laser induced cavitation is the main topic of this thesis. The difference between this process and thermo-cavitation is a larger amount of energy and a higher energy density used for nucleation, to insure optical breakdown. This difference in energy densities will result in the generation of plasma by virtue of optical break down of water.

Once generated, the bubble will expand by means of pressure work due to evaporation that increases the bubble vapor pressure, whilst the pressure in the liquid region remains relatively low. As the pressure increases, so will the temperature by virtue of the ideal gas law. The bubble will continue to grow until it reaches static thermodynamic equilibrium i.e. both pressure and temperature reach the condensation limits. Eventually, the vapor inside the bubble will start to condensate and the bubble to collapse. It is important here to mention we have a non-equilibrium mass exchange at the interface of the bubble which leads the interface to either expand or contract. This exchange is dominated by the evaporation rate during the growth of the phase, and is dominated by the condensation rate during the collapse of the bubble.

Compressible liquid will be the main topic of investigation. Expanding pressure waves were experimentally observed by *Vogel et al.* during a laser induced cavitation scenario, at the beginning of the growth phase. Hence, compressibility effects are thought to be an important physical aspect in bubble dynamics, and need to be accounted for in both the liquid and the vapor phases. The hypothesis is that the energy deposited by the laser will partially be diffused by pressure waves decreasing

the available potential energy for the bubble to grow. *Vogel et al.* indeed quantified the amount of energy diffused by the pressure wave and it can reach up to 42% of the laser energy deposited. Pressure waves were also observed during the collapse period but are considered less relevant for this study since crystals are probably formed during the growth phase. Another physical aspect is the presence of plasma. This fourth state of matter was experimentally observed by *Sinibaldi et al.* during both formation and collapse of the bubble, and is thought to not only be important during the initial steps of the bubble growth but is also assumed to be correlated with liquid compressibility that alters the bubble dynamics, especially in scenarios where the bubble re-bounds before it collapses (which leads to plasma recombination if the re-bounce is violent enough).

The initial phase of the bubble growth is of special interest. Crystals were observed experimentally, ordered in a ring-shape with a radius of roughly $35\mu m$, however, the very first bubble interface photograph captured a bubble radius of roughly $200\mu m$ after $4\mu s$ of the laser pulse[18]. It is obvious in this case that the crystals had been nucleated well before $4\mu s$ i.e during the initial growth period. Further consideration of the presence of plasma as well as the pressure wave initiation at that time makes the study of this duration of fundamental importance. Numerical investigations are conducted to test this hypothesis. The reasons behind the crystal nucleation mechanism as well as the major driving phenomena are unfortunately not yet satisfactorily understood. A combination of theory, simulations, and experiments should allow us to shed some light on such dilemmas.

1.2 Purpose

The entire cavitation process is very short in duration namely of the order $10^{-6}s$, hence quite challenging to investigate experimentally. This short time lapse makes it almost impossible to fully capture the dynamical behavior of the bubble and the underlying physical aspects. Because of these constraints, we resort to simulation to shed some light on plausible mechanisms leading to crystallization. We do so to help understand, familiarize, and monitor the bubble dynamics and the conditions in the liquid surrounding the bubble. A more profound understanding of the underlying physics can help better control the crystal formation process and monitor the crystal quality, size, topography...etc. To achieve the desired results, we simulate the life cycle of a spherical bubble of a radius of the order of micrometers in an infinite liquid domain. The process is assumed to be spherical-symmetric and thus a 1D code is used and further developed from an already existing in-house one. A 1D reference frame would be computationally friendly, and will make it possible to investigate a wide set of problem parameters and predict favorable conditions for crystallization to occur.

1.3 Aim

The aim behind this study is to develop a numerical tool to simulate the life cycle of a nucleated bubble induced by a laser pulse, from growth to collapse. An in-house 1D code is used for such a purpose. Firstly we investigate the extend of the existing numerical tool. This code was designed for laser induced thermo-cavitation (low energy density). We investigate the applicability of the code to also study higher energy densities. This study indicates what phenomena need to be included in order to further develop our numerical framework to accurately capture laser induced cavitation (high energy density). To do so, we include compressibility effects in the liquid region by means of different modeling techniques, to account for the presence of shock waves. These waves induce drastic thermodynamic property alterations and constitute significant energy losses. These effects are important in both the liquid and the vapor phases and are thought to influence the evaporation as well as the condensation rates, hence influence the entire bubble life cycle. However, as mentioned earlier in section 1, plasma was also experimentally observed. The effects of plasma formation and recombination and their influence on the dynamical behavior of the bubble is also assessed.

1.4 Limitations

Two major limitations are present, temporal and complexity. Laser induced bubble dynamics is an extremely complex phenomenon. It would thus be challenging and abnormally computationally heavy to include all the dynamic and thermodynamic ambiguities surrounding the system. Furthermore, from a numerical point of view, compressible liquid can be lengthy and delicate to model. Thus, As mentioned numerous times before, the scope of this thesis is limited to studying the liquid compressibility only and exclude the modeling of plasma (optical breakdown). The effects of presence of plasma will be examined using theory and data from literature.

2

Theory

In this section, the main theoretical concepts used in this study will be discussed. A proper introduction of the governing physical aspects is necessary to understand how a vapor bubble behaves in supersaturated and in supercritical conditions, and how crystals form by the vicinity of the interface when the bubble is induced by a laser pulse.

First, the crystallization process, its importance, main applications, and how it occurs will be explained. Furthermore, the steps leading to crystals formation will be discussed and commonly used crystallization methods enumerated. The drawbacks of using these methods will be highlighted as well as the main challenges we face when manufacturing crystals.

Secondly, vapor bubble dynamics and thermodynamics will be discussed. The underlying physics will be outlined and the relevant governing physical phenomena will be emphasised.

Finally, laser induced cavitation mechanism will be explained and the theoretical foundation behind the numerical tool will be presented.

2.1 Crystallization

Crystallization is a common separation or purification technique dedicated to the production of a set of crystals with desired and controlled properties. The process of crystallization binds atoms or molecules into a well-defined, rigid crystal lattice in order to minimize their energetic state. During crystallization, atoms and molecules are arranged into well-defined angles to form a crystal with a characteristic shape with smooth surfaces and facets. The smallest entity of crystal lattice is called a unit cell, illustrated in figure (2.1), which can attract atoms or molecules by means of atomic or intermolecular forces to grow to a macroscopic crystal[34]. Crystallization occurs in two steps. These steps are driven by thermodynamics and chemical properties. The first is nucleation which is the appearance of a crystalline phase from either a supercooled liquid or a supersaturated solvent. The second is defined as crystal growth, which is the increase in the size of the particles (nucleus) to a crystal state, and various methods can lead to such result. Crystallization is also quite prominent in nature and is often unmanned. The majority of minerals and organic molecules crystallize easily, and the resulting crystals are generally of good

quality[36].

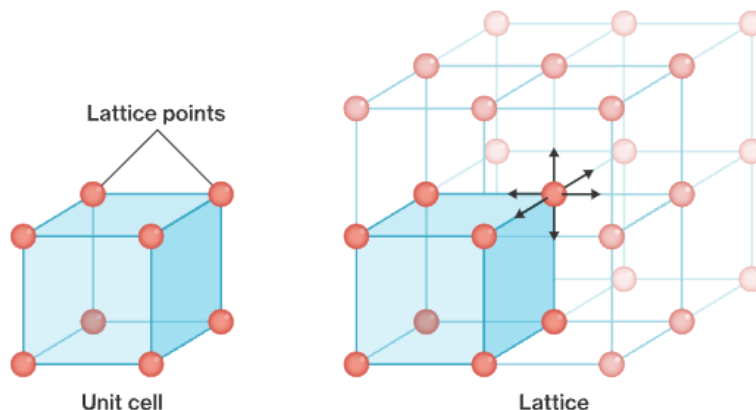


Figure 2.1: A Unit Cell and an example of Crystal Lattice Structure[37]

2.1.1 The Importance of Crystallization and its Applications

Examples of organic crystal molecules are Hydrocarbons such as n-Octane and Naphthalene. These molecules are primary components of fuels we use to generate power. On the other hand, crystallization has a broad spectrum of industrial applications that touches every aspect of our daily lives, that includes the foods we eat and the medicines we take as well as chemical products used in agriculture. The majority of agrochemical and pharmaceutical products go through many crystallization steps during their development and manufacture[34]. Also, key food ingredients such as lactose and lysine are manufactured using crystallization. Biochemical crystals like protein, in contrast to organic crystals, are difficult to manufacture and often introduce many challenges. Crystallization processes are also sometimes unwanted. This is the case for crystallization of gas hydrates in deep sea pipelines which is a major safety concern for the petrochemical industry[34].

2.2 Crystallization Methods

Crystallization can occur using several means. The main analogy however is to reduce the solubility of a solution (solution = solvent + solute, example of solvent could be pure water and the solute NaCl i.e. Salt). The reduction in solubility will introduce the proper thermodynamic conditions for the particles (crystals at the nucleation stage) to start to cluster and grow in size. Dissolving the solute beyond its maximum equilibrium concentration point will introduce high levels of supersaturation which is the major driving force for crystallization. The supersaturation level influences all properties of the crystals namely, the size, morphology, purity etc[39]...

To reach this high supersaturation one can resort to cooling or evaporation in order to induce crystallization. The physical phenomena behind each of these processes is

however similar. With cooling, the solute is dissolved at usually relatively high temperatures into the solution. Crystals will then simply start to form as the solution is cooled off. Cooling effects will result in higher supersaturation levels, and a good control of the cooling rates is critical to ensure the desired crystals quality. This method has proven to be more efficient when the solution's solubility is temperature dependent. In contrast, when the solubility is less temperature dependent, evaporation is more common. Evaporation is simpler and more straightforward since the heating rates do not need to be rigorously monitored. It consists in increasing the concentration levels by evaporating the solute. This evaporation will result in an increase in the solution concentration above its solubility threshold, and will lead to precipitation of crystals. Evaporative and cooling Crystallization both rely on primary nucleation. Seeding however, also a common crystallization technique, rely on secondary nucleation. Small crystal particles are produced externally and then seeded into a supersaturated solution to further grow into larger crystals. Despite the popularity of these techniques (evaporation, cooling, and seeding) other methods are available, particularly for specific industries, and the selection of the method is dictated by the application of interest, the desired crystals quality as well as the amount of samples. Common non popular technique are Anti-solvent Addition, Solvent/Non-Solvent Diffusion, Precipitation Through Chemical Reaction, Vapour Diffusion and Sublimation and many variations on these themes[35].

It is not necessary in this thesis to separately define and understand the functioning of these common industrial techniques. A general understanding of the underlying physics and driving mechanisms is assumed sufficient in order to understand the nature of the problem in question and the challenges that come along.

2.2.1 Crystallization Challenges

Crystallization is quite prominent in many industries and is used as the primary purification and separation technique. It is indeed an advanced process that involves many disciplines, hydrodynamic, heat and mass transfer, chemistry and so forth. Advances are continuously being made within the field of crystal engineering that further our understanding and helping design novel crystallization methods in order to optimize the product quality[35]. However, many challenges still remain, primarily related to the understanding of some physical phenomena such as the nucleation mechanism and polymorphic transformation and how to consequently monitor it. Further down the road, many handicaps are also introduced due to the lack of good control of the crystallization process itself. The presence of impurities, additives, and solvent seem to include unwanted chemical reaction that alter the properties of the product. Additionally, other undesired phenomena such as liquid-liquid phase separation, jelly-like phase formation and gelation phenomena occur when cooling or evaporation of the solution.

Product design, quality, and control are the motivations for scientists and industrialists to indulge and invest in lab-scale processes in order to sort out the issues with the modern crystallization methods. Newly emerging techniques are being discussed

and investigated for such purposes. Many and diverse are such techniques, but we will only mention the ones that are relevant for this study, namely, Ultrasound, NPLIC, and eventually LIC. Scaling up though, from lab-scale to industry-scale can lead to changes in nucleation, growth, breakage, and agglomeration, and will affect crystals qualities and quantities[33]. These experimental techniques are however dawning. It is necessary to understand and idealize the design process itself first before we start looking at large scale manufacturing, which also is a challenge.

2.2.2 Experimental Techniques

2.2.2.1 Ultrasound

Crystallization by Ultrasound or Ultrasonics consists in generating a cavity by acoustic means which will respectively result in crystal formation. Short duration, high amplitude, focused acoustic pulses can generate a large enough pressure difference, or in some cases, near-vacuum conditions, for micro-bubbles to form and consequently lead to crystallization[7]. Inducing ultrasonic pressure waves in an initially crystal-free solution with lower supersaturation levels than usually required can indeed result in crystal nucleation. Eventually, the generated cavitation will collapse inducing a local region of extreme excitation, with temperatures and pressures as high as $11300K$ and $23GPa$ [18], respectively, as well as concurrent shock waves. It is indeed after the collapse that nucleation and consecutive crystallization have been observed. However, the reasons as to why and how these events correlate is not yet fully understood[38].

2.2.2.2 LIC - Laser Induced Cavitation

LIC has been observed to produce crystal nucleation in a supersaturated solution[4, 12]. A laser pulse can be used to superheat a solution and consequently induce a single micro-cavity. The laser beam is focused (using magnifying lenses) within a supersaturated solution. Its set-up and parameters are very important to generate enough radiant energy and assure optical breakdown. In simple terms, optical breakdown is the irradiance of electrons from their atomic valence shell by virtue of extremely high and dense optical radiations as well as a particular range of wavelength ($\lambda = 532 - 1064nm$ [6]). Optical breakdown will be neatly discussed in a later section, but for now, it is sufficient to know that optical breakdown leads to plasma formation, a magnetized gas with extremely high temperatures, of the order 10^5K , and extremely high pressure, 10^8Pa [6]. Accordingly, the formation of plasma and the extremely high temperature it withholds are responsible for superheating the solution. The presence of plasma however is very brief, usually shorter in duration than the laser pulse itself, yet impacts the bubble dynamics drastically[11]. After the pulse, which is usually of the order of nano- or pico- seconds, a bubble will start to form at the location of the focal point. The superheated liquid will rapidly evaporate into the bubble exponentially increasing the temperature and pressure within the vapor bubble. These conditions will drive the bubble to expand until it reaches thermodynamic equilibrium and then start to condense and finally collapse. The bubble

life cycle for LIC is roughly of the order of milli- or micro- seconds[2, 5, 7, 8, 12].

Crystals were experimentally witnessed by *Soare et al.* gathered in a ring-like shape shortly after the bubble collapses[12]. However, during the initial growth phase of the cavity, optical disturbances were observed at the vicinity of the interface at the same location where crystals latter appear. *Soare et al.*[12] as well as *Hidman et al.*[4] hypothesize that crystals are 'immediately' nucleated on the interface as the bubble starts to form and are further shifted outward by the expanding bubble.

The suggested mechanisms behind crystal nucleation using LIC is that the solvent is evaporated into the vapor bubble but not the solute. The solvent evaporation at the interface causes a local increase in concentration within a thin layer surrounding the bubble. During further evaporation and simultaneous cooling, this thin liquid layer zone reaches high levels of supersaturation causing primary nucleation to take place. The solute will cluster into crystal nucleus thus reducing the concentration levels as the crystals grow in size. This is a reasonable assumption to why the concentration levels do not further increase or why no more crystals are further produced other than the ones at the beginning of the bubble life cycle[12].

The crystals produced experimentally were ordered in a ring-shape with a radius of roughly $35\mu m$, however, the very first bubble interface photograph captured a radius of roughly $200\mu m$ after $4\mu s$ of the laser pulse[18]. It is obvious in this case that the crystals had been nucleated well before $4\mu s$. This initial growth period is therefore of special interest and should be investigated numerically in order to test this hypothesis. Further consideration of the presence of plasma as well as the pressure wave initiation at that time makes the study of this duration of critical importance.

2.2.2.3 NPLIN

Non-Photochemical Laser Induced Nucleation (NPLIN) is a techniques similar to LIC that excludes the presence of a vapor bubble. Instead, the nucleation is consequence of polarized electromagnetic waves rather than evaporation mechanism. Better known as Kerr effect, the electromagnetic vectors, originating from a laser beam with a particular setup align the molecules in an orderly manner with the aim of creating a stable nuclei[12]. Another hypothesis argue NPLIN is due to the heating of nano-particles present in the solution. These particles evaporate the liquid around them and the assumption is that the crystal nucleation process is similar to the LIC case[13].

2.3 Nucleation

Nucleation is the process of formation of a new thermodynamic phase. It is a stochastic process, and can occur homogeneously where it is governed by the thermal motion of the molecules only, or heterogeneously where it is heavily influenced

by weaknesses within the flow domain i.e. by the vicinity of solid walls or suspended particles (as well as impurities and contaminants). Needless to mention that heterogeneous nucleation governs most practical engineering applications.

It would be wise at this stage to emphasize the difference between bubble nucleation and crystal nucleation. Bubble nucleation is when a micro- or nano- vapor bubble forms in a liquid by virtue of locally increasing temperature or decreasing pressure, respectively above and below the saturation points. Crystal nucleation on the other hand, is the first step leading to crystallization, where crystals start to form. The next step, crystal growth, is the crystal increase in size due to clustering.

2.4 Bubble dynamics

The dynamical behavior of a bubble can be divided into two phases, namely bubble formation and bubble evolution. Bubble formation is a different name for nucleation, where the bubble forms on a microscopic scale. Nucleation is a stochastic process and it can occur differently depending on the inducing mechanism as explain in an earlier section. The stochastic nature of this process as well as the extremely small length scale makes it hard to investigate. The nucleation event and the underlying molecular physics are still not fully understood. Small scale bubbles (micro- and nano-) are commonly present within liquids. Therefore, it is reasonable to only study the evolution of a bubble and disregard the process behind its nucleation. The second phase, bubble evolution, which includes both growth and collapse, is also governed by the inducing mechanisms namely cavitation or boiling. The difference in inducing mechanisms will result in considerably different dynamics.

Cavitation takes place when the pressure in the liquid surrounding the bubble drops beneath the saturation point. This difference in pressure causes the interface to move. In other words, the evolution of the bubble boundary for a cavitating scenario is governed by the inertial effects of the surrounding liquid. In general, the change in pressure occurs rapidly and uniformly which results in fast dynamics (fast growth and fast collapse). In contrast, for boiling, the evaporation rate governs the bubble evolution by virtue of phase change as well as the temperature distribution in the interfacial liquid. As the temperature rises the saturation level is reached and the liquid will evaporate into the bubble. The evaporation leads to a rise in the vapor pressure which in turn will move the interface. This difference will lead to slower dynamics compared with a typical cavitation event. Nevertheless, there are processes that generate a fast and sometimes uniform change in both pressure and temperature. For such processes the difference in dynamics between boiling and cavitation are no longer obvious, and are thought to demonstrate a behavior that is a combination of both. As mentioned earlier, one such process is laser induced cavitation where the system undergoes a fast change in pressure and in temperature, and results in fast growth and a violent collapse. Consequently, a good understanding of the dependence between pressure and temperature, phase change, as well as saturation conditions is necessary.

By increasing the temperature you will eventually superheat a liquid and consequently increase the so-called vapor pressure. At this stage, the vapor pressure will be larger than the pressure within the surrounding liquid. Such conditions are thermodynamically favorable for bulk vaporization to take place (vaporization within the bulk liquid). The vapor pressure is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phase, at a given temperature, in a closed system[35]. In equilibrium state the condensation and evaporation rates of molecules are equal. This is because the kinetic energies of the liquid and vapor molecules are equal at the interface. However, if the temperature of the system is increased, so will the kinetic energy, which in turn will increase the molecules transition rate into vapor. Such an increase in evaporation rate will consequently increase the vapor pressure until it reaches equilibrium once again. Inversely, if the temperature of the system is reduced, the evaporation rate will decrease leading the vapor pressure to decrease as well. The vapor pressure is thereby a direct function of the temperature, $p_v(T)$, and, at a given temperature, the pressure in the vapor will always tend to thermodynamic equilibrium.

Figure 2.2 illustrates a typical water-vapor phase change diagram. It describes the behavior of water and shows the dependence between pressure and temperature as well as phase change mechanisms in between its different phases. The green line separates the solid phase and liquid phase where water exists at atmospheric conditions (1 bar, 20°C). In this phase, the bulk of water is stable and in thermodynamic equilibrium. By raising the temperature at a constant pressure, water will reach its boiling point which is located along the blue line, also known as the coexistence curve. On this curve, water and vapor coexist by virtue of equivalent amount of internal energies. At boiling conditions however, phase change to vapor may occur within the bulk of the liquid in contrast to interface evaporation which occurs at a 'solid' surface. Just upon reaching boiling conditions, the liquid is in saturation conditions i.e. it contains as much thermal energy as it can before it boils. Following the same analogy, a saturated vapor contains as little thermal energy as it can before it starts to condense. Pressure and temperature values along the blue line are therefore respectively called saturation pressure and saturation temperature[35].

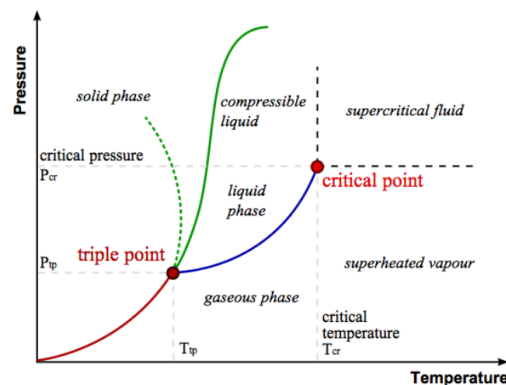


Figure 2.2: Water-Vapor phase change diagram[35]

In our case, interface evaporation will take place across the vapor-liquid boundary

and it governs the evolution of a vapor bubble in a superheated liquid. After its formation the small bubble will rapidly increase in size due to the fast evaporation rate. Phase transition from liquid to vapor requires a certain amount of energy. This energy is better known as latent heat, which is a function of the temperature at which the phase changes takes place. In principal, when heat is provided, temperature will increase within the liquid, vapor, and the interface itself. Nevertheless, the evaporation of the liquid across the interface will requires energy and therefore cool off the liquid and the vapor at the interface. The molecular density in the interface (since the interface is a relative coexistence domain of vapor and liquid, roughly of the order of $10^{-6}m[5]$) is lower than the molecular density in liquid. Hence heat is diffused quicklier within the interface. The difference in temperature between the interface and surrounding liquid causes a diffusion heat flux towards the interface. Furthermore, the molecular density is even lower in vapor. This gives birth to another temperature difference and another heat flux is induced from the interface towards the vapor. Once the superheated liquid is evaporated, the bubble will reach thermal and dynamic equilibrium, and the direction of the heat flux (or the sign of the temperature gradient) will change and molecules will instead travel from the vapor across the interface towards the liquid. At this stage, the vapor will condense and the bubble will shrink and eventually collapse.

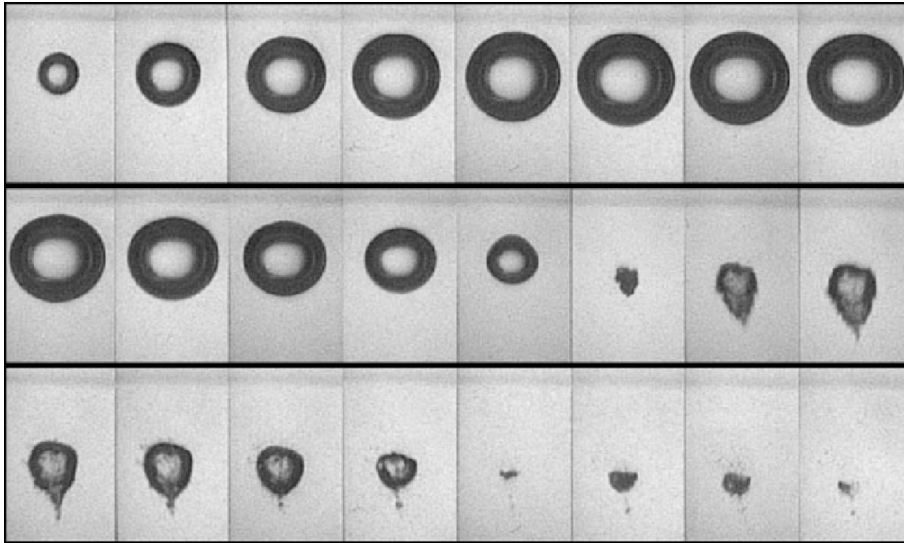


Figure 2.3: An entire bubble life cycle including growth (1st line), collapse (2nd line), and rebound (3rd line)[8]

2.4.1 Rayleigh-Plesset Equation

After its formation (nucleation), the bubble can remain as it is, expand, shrink (or dissolve since it exists on a macroscopic scale), or collapse. However, at equilibrium, the pressure inside the bubble, the pressure in the surrounding liquid and the surface tension are balanced over the bubble interface following the Young-Laplace equation such that :

$$p_B(t) = p_v(T_B) = p_\infty(t) + 2\sigma/R \quad (2.1)$$

The pressure inside the bubble p_B is the vapor pressure corresponding to the saturation temperature $T_B = T_{sat}$, the pressure acting against the bubble to compress it p_∞ is the pressure within the surrounding liquid, and $2\sigma/R$ is the pressure force created by the surface tension.

At non-equilibrium conditions on the other hand, the pressures will not be balanced and the interface will grow or shrink depending on the magnitude and sign of the pressure difference following the generalized Rayleigh-Plesset equation such that[1]:

$$\frac{p_B(t) - p_\infty(t)}{\rho_L} = R \frac{d^2 R}{dt^2} + \frac{2}{3} \left(\frac{dR}{dt} \right)^2 + \frac{4\nu_L}{R} \frac{dR}{dt} + \frac{2\sigma}{\rho_L R} \quad (2.2)$$

The equation above (2.2) was first derived by Rayleigh in 1917 and further developed by Plesset in 1949 to govern the motion of the interface of a bubble. The generalized R-P equation takes into consideration thermal, inertial, and the viscous effects but disregards mass transfer. However, rearranging (2.1) and substituting into (2.2) yields a version of the R-P equation that takes phase change into account as follows[1]:

$$\underbrace{\frac{p_v(T_\infty) - p_\infty(t)}{\rho_L}}_{(1)} + \underbrace{\frac{p_v(T_B) - p_v(T_\infty)}{\rho_L}}_{(2)} = \underbrace{R \frac{d^2 R}{dt^2}}_{(3)} + \underbrace{\frac{2}{3} \left(\frac{dR}{dt} \right)^2}_{(4)} + \underbrace{\frac{4\nu_L}{R} \frac{dR}{dt}}_{(5)} + \underbrace{\frac{2\sigma}{\rho_L R}}_{(6)} \quad (2.3)$$

The first term (1) represents the instantaneous tension or driving force determined by conditions far from the bubble. The second term (2) is the thermal term since it is governed by the temperature difference between the liquid far from the bubble and the vapor inside and is characteristic of the conditions inside and outside of the bubble. Terms (3) and (4) describe the inertial effects of the liquid, term (5) represents viscous forces, and term (6) are the forces induced by surface tension[1].

The R-P equation is a major tool in this study. A proper introduction to this equation, derivation process, main assumptions, and limitations can help better understand the nature of our problem and how our numerical tool is constructed.

We first consider a spherical bubble with radius $R(t)$ in an infinite liquid domain. The conditions in the liquid far from the bubble are T_∞ and $p_\infty(t)$ where the temperature pressure are constants.

It is argued that compressibility effects are important during the initial growth phase[2][5][6][10] as well as the end of the collapse period[1][2][6][7][8][11]. Nevertheless, when first deriving the generalized form of the R-P equation, liquid was assumed incompressible hence the density constant. This is often a fair assumption. *Akhatov et al.* studied the validity of this hypothesis and investigated different compressibility levels within the liquid. He concluded that compressibility effects are a necessity, particularly during the collapse period. Furthermore, the dynamic viscosity is also assumed constant and uniformly distributed. Also, the content of the bubble is assumed homogeneous and the temperature and pressure distributions uniform.

We first start by stating the law of conservation of mass in radial coordinates which yields:

$$u(r, t) = F(t)/r^2 \quad (2.4)$$

$R(t)$, the radius at time t , is the primary results of the resolution of equation (2.3), and is related to $F(t)$ through a kinematic boundary condition at the bubble boundary. At the interface $r = R$, and in the absence of mass transfer, the rate of evolution of the bubble interface is $u(R, t) = dR/dt$. Combining the latter stated expression with equation (2.4) yields:

$$F(t) = R^2 \frac{dR}{dt} \quad (2.5)$$

The expression above (2.5) is actually an approximation. It relates the rate of production of vapor to the rate of increase in size of the bubble. Nevertheless, and even in the presence of evaporation or condensation, the approximation still prevails since $\rho_{liq} \gg \rho_{vap}$.

Moreover, assuming a Newtonian fluid, the Navier-Stokes equation in the radial coordinates yields:

$$-\frac{1}{\rho_L} \frac{\partial p}{\partial r} = \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} - \nu \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) - \frac{2u}{r^2} \right] \quad (2.6)$$

substituting (2.4) into (2.6) one gets:

$$-\frac{1}{\rho_L} \frac{\partial p}{\partial r} = \frac{1}{r^2} \frac{dF}{dt} - \frac{2F^2}{r^5} \quad (2.7)$$

Note that the viscous term vanished from equation (2.7), indeed the only inclusion of viscous effects in the R-P equation is through a dynamic boundary condition at the interface. To construct this boundary condition, consider a small control volume that is extremely thin and located on the interface. The net force on this control volume in the radially outward direction is[1]:

$$(\sigma_{rr})_{r=R} = -p_B + 2\mu_L \frac{\partial u}{\partial r} \quad (2.8)$$

Thus the force per unit area is:

$$p_B - (p)_{r=R} = \frac{4\mu_L}{R} \frac{dR}{dt} - \frac{2S}{R} \quad (2.9)$$

Note that in the absence of mass transfer this force must equal to zero.

Now if we integrate equation (2.7) such that, when $r \rightarrow \infty$, $p \rightarrow p_\infty$, then substitute (2.5) and (2.9) into the integrated (2.7), and one finally gets equation (2.2) stated earlier which is the generalized Rayleigh-Plesset equation.

When looking thoroughly at the R-P equation, and in the presence of an inviscid liquid such as water, one can see that terms (1) and (2), respectively the instantaneous tension and the temperature difference, dictate the behavior of the interface. In other words, the resultant bubble dynamics can be governed by either inertial or thermal effects.

Inertially controlled bubble dynamics are caused by pressure difference between the vapor pressure and the pressure in the far field. On the other hand, thermally controlled dynamics are a function of the temperature difference ($T_B - T_\infty$), which in turn is directly proportional to the vapor pressure. Hence, the vapor pressure does indeed monitor the bubble growth and collapse rates. Following this analogy, one can hypothesize that cavitation is inertially controlled whilst boiling is thermally controlled. This is a fair assumption since cavitation and inertially controlled bubble dynamics are quite fast, compared with boiling and thermally controlled bubble dynamics which are often less rapid (but could in some rare cases be as fast). Nonetheless, it is argued by Brennen [1] that bubble dynamics are, to a certain extent, resultant from both inertial and thermal effects. This hypothesis is more obvious and likely more prominent in the presence of extreme thermodynamic conditions. This indeed is the case for laser induced cavitation where pressures can reach a magnitude of $10^6 Pa$ and temperatures $10^4 K$ [6].

Since pressure change happens faster than a temperature change does, the interface behavior at the initial stages of the growth phase, for a LIC case, is arguably governed by inertial effects. Furthermore, the liquid which has a higher density than vapor needs to be displaced and accelerated in the outward direction in order for the interface to advance. Unarguably however, the final stage of collapse is also governed by inertial effects. The liquid is accelerated in the inward direction, bringing the bulk of its weight towards the shrinking interface leading to a collapse or in some cases a rebound. Excluding these two moments of the bubble life cycle, namely the initial stage of growth and the final moments of collapse, the relative dynamics are governed by thermal effects and the ability of the condense to bring heat to the interface to sustain phase change. Consequently, the departure of the vapor temperature T_B from the temperature in the remote liquid T_∞ will dominate the mass exchange rate and thus the bubble evolution. Hence a proper evaluation of the temperature T_B is necessary in order to capture the right dynamics. T_B can be obtained following two procedures. The first consists of a resolution of the temperature distribution in the interfacial liquid, followed by a resolution of the temperature distribution within the interface itself. For the temperature distribution in liquid,

one can use a transport equation where both advection and diffusion are considered such that:

$$\frac{\partial T}{\partial t} + \frac{dR}{dt} \left(\frac{R}{r} \right)^2 \frac{\partial T}{\partial r} = \frac{\alpha_L}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \quad (2.10)$$

Where α_L is the thermal diffusivity of liquid.

The next task is to perform an energy balance across the water-vapor boundary to relate the heat supplied to the interface to the rate of production of vapor. Hence, the heat supplied to the interface can be expressed as follows :

$$4\pi R^2 k_L \left(\frac{\partial T}{\partial r} \right)_{r=R} \quad (2.11)$$

Where k_L is the thermal conductivity of liquid and $(\partial T / \partial r)_{r=R}$ is the temperature gradient at the interface.

Assuming all provided heat is used to evaporate the liquid, which is a fair assumption since $k_L \gg k_v$, one can relate the mass rate of production of vapor to the rate of increase in bubble volume, and this yields :

$$\frac{dR}{dt} = \frac{k_L}{\rho_v L} \left(\frac{\partial T}{\partial r} \right)_{r=R} \quad (2.12)$$

Where L is the Latent heat of evaporation.

Now the final step is to relate and re-write the thermal term, (2), in the R-P equation (2.3) in function of the rate of evolution in bubble volume $R(t)$. First, equation (2.12) is used to relate the temperature gradient at the interface $(\partial T / \partial r)_{r=R}$ to $R(t)$. Secondly, equation (2.10) is used to relate $(\partial T / \partial r)_{r=R}$ to the temperature difference $(T_B(t) - T_\infty)$. Unfortunately, these maneuvers do not solve all our problems, certain restrictions still prevail. The non-linear nature of the diffusion equation makes it hard to obtain a highly accurate solution since no analytical solution does exist. Furthermore, the lack of understanding of what a bubble interface is from a physical point of view is also an issue. Nevertheless, many approaches and approximates solution with varying levels of accuracy and simplifying assumptions have been introduced to solve the temperature distribution and obtain an estimation of T_B , see [1, 2, 4, 8, 10] for more details.

2.5 Compressibility Effects

A question that is commonly asked, *are liquids truly compressible?* Can the density of water for example change and if so, how does that affect the properties of water. For instance, if you take a cylindrical container, fill it with water, then use a hydraulic piston to push down starting from the surface of the liquid...What will happen?

Compressibility is a feature of local density change with respect to the mean density[23]. How much can the density of a liquid change though? There's indeed a difference between compressible, slightly compressible, and incompressible. Incompressibility is more of an approximation rather than a physical state. It is in fact defined as an operating regime where compressibility effects are negligible[22]. When assumed of significant influence, compressibility effects should be included as they bring prominent thermo-dynamical properties changes to the domain in question. Furthermore, and generally speaking, the compressibility feature of any fluid may give rise to shock waves.

2.5.1 Shock Waves

An energy release, often generated by a sudden and significant increase in temperature, will eventually be absorbed by the surrounding molecules. This increase in energy will in turn increase the vibratory motion of the molecules hence their mean velocity. The mean molecular velocity of liquids and particularly of water is defined as a quadratic function of the temperature[23]. These intensely vibrating molecules will collide with their neighboring ones and transfer a major part of their newly acquired energy. This collisional process will carry on resulting in a net transfer of energy, also known as propagation of energy through space. This wave of energy will propagate through space at a speed proportional to the mean molecular velocity. Hence wave propagation is a virtue of molecular collisions. This is the definition of a shock wave from a kinetic theory point of view[14].

The shock wave losses energy as it propagates through space. Across the shock interface itself however, energy is larger in the front of the shock and lower behind it i.e. a shock interface is characterized by a jump in energy. As the pressure wave travels (i.e. shock wave), it will compress the molecular structure in front of it. This will lead to a higher density which in turn, and by virtue of state and conservation laws, will induce a drastic and instantaneous change in pressure, temperature and velocity. Inversely, behind the shock, the molecular structure will be stretched out, decreasing the density. Following the same analogy, this will as well bring significant changes to the thermo-dynamic properties behind the shock. An important property to investigate and take into consideration when studying such a phenomenon is the speed of sound. The speed of sound in water as well as the propagation and attenuation of pressure waves in water have been a heavily discussed topic since the mid 19th century. It is indeed of high relevancy for many topics, including hydroacoustics, design and construction, underwater explosions, and process and biomedical engineering. Unfortunately we still rely on imperial relations and models. No exact theory yet exists.

2.5.2 Compressibility Effect and Cavitation

When the R-P equation (2.2) was first derived, incompressibility of the liquid was one of the main and most important assumptions. This assumption did largely sim-

plify the problem of bubble dynamics and permitted Rayleigh (1917), Plesset (1949), and Winick (1957) to model the dynamical behavior of a bubble interface with a certain level of accuracy. Many studies have been performed since using this approach and produced relatively satisfactory results, *Wilson et al.* [7] and *Akhatov et al.* [2]. A common factor among these studies is that the pressure and temperature values do not or barely exceed the critical point, respectively being 22.10^6Pa and 647K .

From one end, as mentioned earlier, shock wave initiation, formation, and propagation is a virtue of mean molecular velocity (vibratory motion of molecules), which in turn is a virtue of the temperature within the fluid domain. On the other end, it is agreed upon that the speed of sound, particularly in liquids, is heavily dependent on pressure [14, 20, 24, 25]. Under these arguments, one can safely hypothesize that if the pressure and temperature values depart largely from the saturation conditions, one should not only consider the magnitude of such departure, but further investigate its influence on the bubble dynamics.

Shock waves have been experimentally observed during two time periods of the bubble life cycle [6, 8, 10], the initial moments of the growth phase and the final instant of the collapse. We can already identify these two periods to be inertially controlled dynamics. Also, these two periods are known to display extremely fast dynamics compared with the rest of the bubble life cycle and hence deemed to be very important.

A bubble expands by virtue of potential energy. In the case of the presence of a shock however, the wave will carry away some of that energy. The bubble will be left with lesser amount of energy to expand which will result in relatively slower dynamics i.e. a lower maximum radius and a shorter life span. Similarly, during the end of collapse, the inward velocity of liquid is large [1] and the thermodynamic conditions reach the so called super-critical conditions [2][4][11]. These conditions are favorable for an even more violent shock wave to form (which in experiments was often more visible and prominent compared with the shock wave observed during the growth phase). Thus dissipating even more energy to the surrounding liquid. This further loss in energy will in most cases result in a less dramatic collapse or also in a smaller rebound, if such applies. In this case, the second bubble (after rebound) will have a smaller initial radius compared with the initial radius of the first bubble, where roughly $R_0 = 2.5R_0^*$ where R_0 is the initial radius of the first bubble and R_0^* is the initial radius of the second [2]. This is a property of the dissipative nature of pressure waves.

In conclusion, the larger are the pressure and the temperature in the liquid domain the more important it is to consider compressibility effects in order to capture the correct dynamics. This is the first milestone in this thesis work.

2.6 Plasma

As mentioned before, LIC is, among other factors, characterized by the formation of plasma, the so-called fourth state of matter; alongside gases, liquids, and solids. It won't however be explicitly modeled as it is a very complex and cumbersome topic. As we will see throughout this section, a proper modeling of the formation and the induced dynamics is indeed necessary in to order produce satisfactory results, this work should be included in future studies. Nevertheless, for now, a brief introduction would be useful in order to better understand the events leading to LIC. We will shortly introduce plasma physics, elementary definitions, and basic properties. We will furthermore discuss optical breakdown, particularly, within condensed media to provide a better understanding of the coupling between plasma formation and LIC.

Matter exists in three different phases, solid, liquid, and gas... This was the case until 1879 when Sir William Crookes identified a new phase in his Crookes tube (an experimental set-up) and named it “radiant matter”. Later in 1927 Irving Langmuir became a Nobel laureate for pioneering the scientific study of ionized gases. He gave this new medium the name *Plasma*, which comes from Greek and stands for “moldable substance”[26]. After its discovery, and throughout the years, we realised plasma is rather ubiquitous, it in fact makes up 99% of the visible universe[27], including stars, various astrophysical objects as well as the interstellar medium. At home, here on earth, the ionosphere provides us with protection from the lethal solar radiation. It is as well, as the name ‘iono’ suggests it, a plasma state and it extends roughly from 50km to 1000km[27]. Terrestrial plasmas do also exist, they can be found in streetlights, industrial plasma torches, etching processes, fusion machines (devices designed to confine and extract energy using nuclear fusion), lightning discharges, as well as high precision surgical procedures including organ ablation, Lithotripsy, Ophthalmic Keratomileusis and many others involving laser usage.

A simple textbook definition of plasma is, *a quasi-neutral gas of charged particles displaying a collective behaviour*[28]. Thus, plasma has two main properties, the first, defined by the term quasi-neutrality, means even though plasma consist of free negatively and positively charged particles, namely electrons or ions, their overall charge densities cancel each other in equilibrium. Quasi-neutrality is a state plasma actively tries to achieve by readjusting the local charge distributions. The second property, collective behaviour, means that local disturbances in equilibrium state can have a strong influence on remote regions in the plasma. In other words, macroscopic fields are usually dominated by microscopic fluctuations, and a local net charge imbalance will immediately give rise to an electrostatic field. Furthermore, different particles velocities within in the same set of particles will give rise to a current density. This in turn induces a magnetic field[27]. The type of plasma is mainly determined by its density and temperature which is fairly similar to the three familiar states of matter. However, and unconventionally, its behavior is determined by the latest mentioned internal electric and magnetic fields. Also, plasma dynamics is heavily influenced by their interactions with laser beams and particle collisions.

Plasmas are created through ionization. This can occur either through thermal motion i.e. collisions of intensely vibrating particles with one another (this approach can require a heating temperature of up to $10^6 K$ [29]), or through photo-ionization using electromagnetic radiation or via optical breakdown in intense electric fields. As our topic is LIC, we will only focus on photo-ionization by means of optical breakdown.

2.6.1 Optical Breakdown

Optical breakdown, also called dielectric breakdown, is a process that often proceeds the formation of plasma. It is a phenomena that occurs when an electrical insulator suddenly and instantaneously becomes an electrical conductor when provided with a sufficiently high electrical potential (In our case, through optical absorption of laser radiation) [31]. In addition to a change in polarity, breakdown is also defined by the partial or complete field ionization of the medium [30]. For a field ionization to occur, a certain threshold needs to be reached. This threshold is characterized by the electric field strength which is mainly a function of the atomic intensity. Its value is different with different atom and within different conditions. Consequently, to strip atoms of their electrons and guarantee ionization for the targeted medium, the laser intensity needs to reach and often exceed the atomic intensity. However, ionization can also occur well below this threshold due to multiphoton effects (this phenomenon will be discussed shortly in this section).

So that plasma formation can correspond to an optical breakdown it needs to reach extremely high temperatures ($<10^5 K$ [28]) as well as high density, and this is achieved by reaching a high levels of ionization. To do so, it needs to interact with the laser beam for a finite amount of time to reach a certain electron density through absorption of laser radiations. This duration can be extremely short, it can be as short as femtoseconds $10^{-15} s$ [31], and the required electron density roughly values for $10^{18} \text{electron}/\text{cm}^3$ [30]. After reaching this state, plasma will further on absorbing the optical radiation much more effectively than ordinary matter. This stronger absorption rate will rapidly heat plasma to extremely high temperatures which will drive it to expand producing a loud audible acoustic wave and a visible light emission. Inversely, some plasmas are considered cold and diffuse and therefore don't correspond to an optical breakdown. This type of media is called under-dense plasma and this usually is the case for a gas when it is partially ionized. This type of plasma 'barely' reaches a temperature of $10^5 K$ at most [28]. To sum it up, optical breakdown stands for the total ionization of a diffuse medium such as gases or for the partial or total ionization of a condensed medium such as water, using intense laser radiation.

There are two different mechanisms that can lead to breakdown, direct ionization by multiphoton absorption or cascade ionization, also called avalanche ionization. The latter process requires one or more free electrons, called seed electrons, to be present

in the medium at the beginning of the pulse. These seeded electrons will absorb light photons through collisions with atoms or molecules, a complex process called collisional absorption, or better known as inverse Bremsstrahlung absorption. After reaching greater energy than the required ionization potential, a free electron may ionize another particles. This produces two free electrons of lower energies (and an ion), which in turn further absorb energy from the laser pulse and ionize two more, and so forth. This process will continue as an electron cascade leading to an optical breakdown[32]. Multiphoton ionization is on the other hand a stochastic process. It usually requires larger laser energies and occurs for wavelengths in the near-IR. In multiphoton breakdown each electron is separately ionized. This approach requires no seed electrons nor collisions or interactions. It is much faster since it doesn't require the buildup of an electron cascade and therefore occurs for the shorter laser pulses[32].

In impure media, contaminants and impurities are usually present, such as micro-cracks or micro-bubbles. In this case, seed electrons are likely to come from these undesired additions and constitute a local weakness in the electrical field strength. They are arguably the locations where ionization begins, and thus do not require a high ionization potential. In contrast, in pure media, a high ionization potential is needed. Therefore, ionization of a few molecules by multiphoton absorption may be necessary to produce seed electrons and start a cascade. The breakdown process is hence independent of impurities and can occur even in media too diffuse to allow enough collisions during the pulse duration. To conclude, it is safe to assume, LIC events within condensates are initiated after plasma forms by virtue of optical breakdown through cascade ionization at the location of a micro-bubble.

2.6.2 Plasma and LIC

Plasma formation as well as recombination were experimentally observed during LIC events [2, 6, 7, 10, 11]. Focusing a laser pulse with a large enough energy often introduces ideal conditions for optical breakdown to occur. At the site of the pulse, and by virtue of laser radiation, an electric field with large fluctuations arises leading to plasma forming with different shapes and different levels of intensity. *Sinibladı et al.* and *Vogel et al.* experimentally captured the presence of plasma for a duration of 10 – 20ns[6, 11]. *Vogel et al.* studied the presence of plasma prior to the expansion of the bubble, particularly the concurrent shockwave system and the energy budget between laser energy absorbed (assuming 50% conversion efficiency between laser energy deposited and absorbed), shockwave energy, and bubble potential energy. *Sinibladı et al.* however studied the influence of plasma properties on the succeeding bubble dynamics, particularly the shape. It was determined that the less spherical the plasma is the more asymmetry there is within the induced bubble, and that different plasma shapes will produce different shockwave system thus resulting in different potential energies for the bubble to expand. Different plasma shapes can be seen in figure (2.4). Furthermore, plasma was also observed during collapse. It was identified by *Akhatov et al.* and *Wilson et al.* as a sonoluminescent point-like structure in the center of a collapsing bubble during re-bound scenarios.

The thermodynamic conditions within the cavity often exceed the critical point and record extremely large values during collapse, especially when violent. This introduces the right conditions for plasma to form. This plasma is however considered a recombination. It has different properties and virtues and is not characteristic of an optical breakdown. This phase is of no interest to us. We do not study plasma dynamics in this thesis work but rather the influence of the presence of plasma, and plasma recombination takes place at the end of the event which is of interest to us. Nevertheless, for this study, we will focus on the shockwaves interactions, the energy conversion, and how these two influence the bubble dynamics.

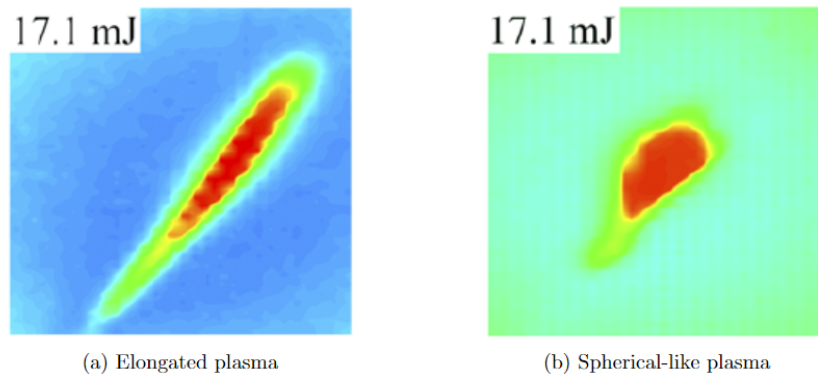


Figure 2.4: Two different plasmas color maps of the normalized gray scale of electron intensity (plasma density) averaging 64 recordings for a laser pulse of 17mJ. High speed imaging was used with a 160 kfps. The action of taking the photo was however initiated roughly $100\mu\text{s}$ before the laser pulse[11]

3

Methodology

In this section we introduce the steps followed to develop the in-house numerical tool that was used, and how it functions. We also briefly discuss certain theoretical aspect and necessary derivations. Furthermore, the modification brought in to model the compressible liquid will be outline.

3.1 Numerical Framework I

A numerical tool was developed at Chalmers to model the dynamical behavior of thermo-cavitation induced by a laser pulse. This tool was used and further developed to numerical investigate our hypotheses. A 1D framework is deemed computationally friendly to investigate a wide range of parameter and accordingly understand the conditions within and surrounding the cavity. This framework was initially intended for thermo-cavitation (a laser induced cavity that doesn't involve optical breakdown). Hence, The first stage of this study is to investigate the possibility of using the same code to model the life cycle of LIC. This approach is used in order to assess the shortcoming of the existing numerical tool in capturing accurate dynamics. We do already assume the shortcoming to be the inability to account for density variation in the liquid region (compressibility effects) and the absence of irradiation phenomena (breakdown of liquid). This first milestone will determine how important these two latter mentioned physical phenomena are, and if they are necessary to be included.

Our simulation takes place in an unbound domain to exclude the influence of surrounding solid walls. Spherical-symmetry of the LIC is assumed, as seen in figure (3.1). This assumption is justified for thermo-cavitation, however for LIC, we would need to restrict the set of laser parameters used in order to theoretically insure sphericity of the bubble after the laser pulse. The material properties used are those of pure water for the liquid region and accordingly for vapor for the gas region. In most numerical studies [2, 6, 7, 8, 12] only the collapse period is modeled. Our framework however does simulate the entire cavity life cycle including expansion, collapse, and potentially possible re-bounds. The rupturing process of the liquid is not considered and the bubble expands starting from a micro-bubble which already exists in the domain after the laser pulse begins. This occurs under the assumption of the existence of a contaminant gas (i.e. micro- and nano-bubbles) in the liquid. Despite the assumption of the existance of a non-condensable gas in the liquid, it's diffusion into the bubble is disregarded. *Akhatov et al.* and *Ki-Taek et al.* evalu-

ated the influence of non-condensable gas, with different levels of concentration, and deemed it negligible. Therefore our bubble will only contain vapor. The computational domain is divided into two regions, (1), the compressible region, inside the bubble $0 < r < R$ where vapor lies, and (2), the incompressible region $R < r < \infty$ where pure liquid water is; We evidently use spherical coordinates which narrow down to radial coordinates under the assumption of spherical-symmetry, hence r is the radius to solve for starting from the bubble radius and R is the radius of the bubble interface.

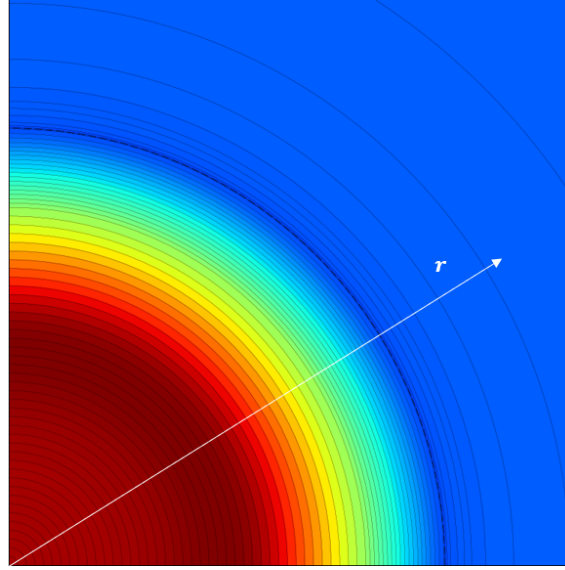


Figure 3.1: Temperature contour of our computational domain at the beginning of the simulation as the laser pulse begins.

3.1.1 Compressible Region

Before the beginning of the pulse, the system is in dynamic equilibrium, and once the liquid starts to heat the bubble will start to expand. For the bubble interior as well as the surrounding liquid, all variables are a function of time and space. However, accurate predictions of the pressures and temperatures in both regions are essential during the laser pulse and bubble expansion phase to get accurate evaporation rates. These rates will primarily determine the bubble evolution rate and are thus fundamental to obtain good results. Vapor dynamics on the other hand are quite fast and its properties change rapidly. Therefore, we use a compressible formulation of the conservation equations for the vapor region. The conservation equations of mass, momentum, and energy for the vapor phase are used as follows[5]:

$$\frac{\partial \rho_v}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_v u_v) = 0 \quad (3.1)$$

$$\frac{\partial}{\partial t} (\rho_v u_v) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_v u_v^2) + \frac{\partial p_v}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} = 0 \quad (3.2)$$

$$\frac{\partial}{\partial t} (\rho_v e_v) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho_v u_v (e_v + p_v / \rho_v) - r^2 \lambda \frac{\partial T_v}{\partial r} - r^2 u_v \tau_{rr} \right) = 0 \quad (3.3)$$

Here the index v denotes the vapor phase, ρ the density, u the radial velocity, p the pressure, T temperature, and λ the thermal conductivity. Furthermore, the total energy per unit mass is defined with $e_v = \epsilon_v + u_v^2/2$, with ϵ_v being the internal energy.

The viscous effects described by τ are often negligible compared to the other terms in the set of equations above (3.1)-(3.3)[4], they are nevertheless included to increase numerical stability, particularly when dealing with fast dynamics. The viscous effects are thus formulated as follows[5]:

$$\tau_{rr} = -\mu_v \left(2 \frac{\partial u_v}{\partial r} - \frac{2}{3} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_v) \right) \quad (3.4)$$

And

$$\tau_{\theta\theta} = \tau_{\phi\phi} = -\mu_v \left(2 \frac{u_v}{r} - \frac{2}{3} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_v) \right) \quad (3.5)$$

Which are the radial components of the shear stress tensor, and μ_v the dynamic viscosity of vapor.

3.1.1.1 Equation of State

We use a Hardcore Van Der Waals gas equations to model the internal energy and pressure within vapor. This equation of state can sustain minor compressibility[2] and low magnitude density variations, and are determined by:

$$\epsilon_v = \frac{B_v T_v}{\gamma - 1} - b_2 \rho_v \quad (3.6)$$

$$p_v = \frac{\rho_v B_v T_v}{1 - b_1 \rho_v} - b_2 \rho_v^2 \quad (3.7)$$

Where $B = 459.9 \text{ J/kgK}$, $b_1 = 1.694 \times 10^{-3} \text{ m}^3/\text{kg}$, $b_2 = 1708.6 \text{ Jm}^3/\text{kg}^2$ are gas constants determined imperically for water vapor within thermodynamic conditions that do not exceed the critical point, and $\gamma = 1.3$ is the adiabatic exponent of vapor.

3.1.2 Phase Change Model

The rate of phase change at the bubble interface is determined by the Hertz–Knudsen–Langmuir[3], also called Schrage model in other papers[4, 5]. It uses concepts from the kinetic theory of gases to compute fluxes of molecules across the interface using the temperatures and pressures of both phases as well as saturation conditions according to:

$$j = \frac{\alpha}{\sqrt{2\pi B_v}} \left(\frac{p_{\text{sat}}(T_l|_{r=R})}{\sqrt{T_l|_{r=R}}} - \frac{\Gamma_v p_v|_{r=R}}{\sqrt{T_v|_{r=R}}} \right) \quad (3.8)$$

Where j is the mass exchange flux per unit surface at the bubble interface. It is positive when evaporation takes place and consequently negative when condensation is occurring. Here α is the accommodation factor that determines the portion of molecules that traverses the interface during the phase change process compared with the ones that are mirrored. There are contradictory data in literature concerning the value of this coefficient, we thus select a high value so it doesn't affect our results i.e. $\alpha = 1$. Furthermore, Γ_v is a correction factor given by:

$$\Gamma_v = \exp(-\omega^2) - \omega\sqrt{\pi} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^\omega \exp(-y^2) dy \right) \quad (3.9)$$

With

$$\omega = \frac{j\sqrt{B_v T_v|_{r=R}}}{p_v|_{r=R} \sqrt{2}} \quad (3.10)$$

The inclusion of the correction factor Γ_v is necessary as it is needed when the vapor phase departs considerably from equilibrium. Such a departure certainly occurs during the intense heating during the laser pulse and during the collapse phase where conditions reach and often exceed the critical point[2].

The phase change model described above is only valid below the critical point where a thermodynamic difference between water and vapor still exists. Beyond that state, the model is explicitly turned off ($j = 0$) and no phase change further occurs.

3.1.3 Incompressible Region

The motion of the bubble interface is governed by a Rayleigh-Plesset type-equation, (2.3), the derivation process is neatly discussed in section 2. In our tool though we also include mass transfer across the interface which is usually not the case for the generalized form. Thus one gets:

$$\begin{aligned} 2\dot{R}(\dot{R} - j/\rho_l) + R(\ddot{R} - \dot{j}/\rho_l) - \frac{1}{2}(\dot{R} - j/\rho_l)^2 + \frac{2\sigma}{R\rho_l} + \frac{4\mu_l}{R\rho_l}(\dot{R} - j/\rho_l) \\ = \frac{p_v|_{r=R} - p_\infty}{\rho_l} \end{aligned} \quad (3.11)$$

To compute the pressure in the liquid phase $p_l(r)$, as a function of the interface motion, a similar procedure can be used, details can also be found in section 2 on how to perform this derivation. However, the integration in this case is performed from a radius r in the liquid phase to the far-field liquid compared with R-P equation where the derivation is performed from the center of the bubble all the way to the far-field liquid. Thus, one gets:

$$-\frac{R}{r} \left(2\dot{R} \left(\dot{R} - j/\rho_l \right) + R \left(\ddot{R} - j/\rho_l \right) \right) - \frac{R^4}{2r^4} \left(\dot{R} - j/\rho_l \right)^2 = \frac{p_\infty - p_l(r)}{\rho_l} \quad (3.12)$$

3.1.4 Boundary Conditions

The vapor and liquid velocities at the interface as well as the velocity of the interface itself differ at the bubble wall due to phase change mechanisms. Boundary conditions are used to account for such phenomena according to:

$$u_v|_{r=R} = \dot{R} - \frac{j}{\rho_v} \quad (3.13)$$

$$u_l|_{r=R} = \dot{R} - \frac{j}{\rho_l} \quad (3.14)$$

Where $\dot{R}$ is the velocity of the interface and j is the phase change rate.

Furthermore, the conservation of mass (volume since in spherical coordinates) in incompressible liquid was used to produce an exact solution for the liquid velocity distribution at the interface as follows:

$$u_{l,int}(r, t) = \frac{R^2 \left(\dot{R} - j/\rho_l \right)}{r^2} \quad (3.15)$$

Here we include the rate of the phase change j in the liquid velocity formulation. This effect is often negligible for liquids with high density, it is however significant at high evaporation rates. These conditions are usually present during and after the laser pulse until the cavity reaches its maximum radius.

The pressure is also discontinuous across the interface due to surface tension and viscous effects. The pressure jump is thus implemented following the Laplace formulation such that[1]:

$$p_v|_{r=R} = p_l|_{r=R} + \frac{2\sigma}{R} + \frac{4\mu_l u_l|_{r=R}}{R} \quad (3.16)$$

Where σ is the surface tension coefficient and μ_l the dynamic viscosity of pure water. A pressure jump takes place across the interface. Its influence is taken into account by incorporating the phase change rate into the liquid velocity at the interface $u_{l,int}$

in equation (3.15).

At the bubble center, symmetry boundary conditions are specified for all variables, and in the far-field, Neumann is implemented for velocity and Dirichlet for the pressure and temperature.

3.1.5 Temperature Distribution

The phase change rate at the bubble wall, and thus the bubble growth rate, is governed by the liquid temperature at the interface. To determine the latter, we need to accurately resolve the temperature distribution within the liquid region, and particularly at the vicinity of the interface. This is achieved by solving the following equation of conservation of energy (the derivation process was also discussed in the theory section):

$$\frac{\partial T_l}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_l T_l) - \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \alpha_l \frac{\partial T_l}{\partial r} \right) = \frac{P_{las}}{\rho_l c_{p,l}} \quad (3.17)$$

Where α_l and $c_{p,l}$ are respectively the thermal diffusivity and specific heat capacity at constant pressure for liquid, and P_{las} is the energy source from the laser pulse.

At the bubble interface, a thermal boundary condition is implemented in a manner to account for the latent heat of evaporation using the following:

$$\lambda_l \frac{\partial T_l}{\partial r} \Big|_{r=R} - \lambda_v \frac{\partial T_v}{\partial r} \Big|_{r=R} = j \mathcal{L} \quad (3.18)$$

Where $\mathcal{L}$ is the specific latent heat of evaporation, evaluated using the temperature at the interface. On the other hands, the thermal boundary condition in the far-field is:

$$T_l|_{r=\infty} = T_\infty \quad (3.19)$$

Similar to the pressure, the temperature also undergoes a jump. It is in this case a more delicate issue since the temperature distribution at the vicinity of the interface drastically impacts the the bubble evolution during expansion. The temperature of the interface is unfortunately still an unresolved issue. Many approaches have been suggested with varying level of accuracy... The totality of these studies had however determined that the value of the temperature jump has insignificant influence on the induced bubble dynamics[1, 2, 8, 10]. Therefore, in this framework, we assume a continuous temperature across the interface as:

$$T_v|_{r=R} = T_l|_{r=R} \quad (3.20)$$

3.1.6 Source Term

The energy source term $P_{las}(r)$ is used to model the liquid heating. This term values for the laser power density absorbed by the liquid during the pulse duration t_{las} . The

conversion between laser energy applied and absorbed is disregarded (rate of optical absorption is neglected). Additionally, the absorption of laser irradiations in vapor is negligible (Unless an extremely high laser energy is used, see Plasma in Theory Section to better understand the difference between optical absorption in liquids and gases), hence the laser pulse is only applied in the liquid region. Furthermore, we assume the beam profile to have a Gaussian distribution (Bell-shaped profile) according to:

$$P_{\text{las}}(r) = P_{\text{max}} \exp\left(-2r^2/r_{\text{las}}^2\right) \quad (3.21)$$

Where r_{las} is the radius of the laser beam and P_{max} the maximum power density which lies in the center of the beam. The laser power density P_{las} is assumed constant during the laser pulse duration t_{las} , thus the total laser energy E_{las} absorbed by the liquid can be determined by:

$$E_{\text{las}} = \int_{R_{\text{las}}}^{\infty} e_{\text{las}} 4\pi r^2 dr \quad (3.22)$$

Where $e_{\text{las}} = t_{\text{las}} P_{\text{las}}$ is the laser energy density, and R_{las} is the radius of the heated liquid.

3.1.7 Numerical Parameters

The governing equations for the compressible region are solved in a stationary coordinate system with the origin being the centre of the bubble, whilst the incompressible region uses a moving coordinate system with the origin lying at the bubble interface. For time discretization, the Implicit Crank-Nicolson Scheme was used, whilst for spatial discretization the Cell Centered Finite Volume Scheme was resorted to.

During simulation, the pressure and particularly the temperature vary by more than 2 orders of magnitude due to the intense evaporation rates. Similarly, the bubble radius can vary with more than 3 orders of magnitude. Thus, to accurately resolve the domain during the entire bubble life cycle, and reducing the simulation time, an adaptive mesh is implemented. The adaptive grid refinement works using gradients and curvatures of the fluid properties. It can ensure a sufficiently refined grid, splitting cells when the gradients are high and/or curvature is large, or joining cells when the opposite applies. This approach can help reduce the computational cost while maintaining a high enough accuracy. The time step is also set variable to avoid excessively small time steps during the simulation. It is determined and restricted by the cell size, the velocity, the magnitude of change in fluid properties, the speed of sound in air, and the Courant number which is usually below 1.

Before the laser pulse, the initial pressure and temperature in the liquid region are the ambient values, respectively, $p_{\infty} = 101325$ Pa and $T_{\infty} = 293$ K. On the vapor side however, pressure is initialized using the Laplace formulation (3.16) and thus values for 392329 Pa corresponding to a saturation temperature of 416 K (under the assumption of thermodynamic equilibrium within the bubble). The nucleation

3. Methodology

mechanism is not considered in this study, hence the simulation starts from a micro-bubble with an initial radius of $1\mu\text{m}$. The simulation time t_{sim} as well as the laser energy and pulse, respectively, t_{las} and E_{las} , are variables and hence adjusted according to the cases. Simulations were performed for durations varying between $10\mu\text{s}$ and $60\mu\text{s}$ and using laser energies and pulses between 0.1mJ and 30mJ , and 1ns and 6ns , respectively.

3.2 Numerical Framework II

Compressible liquid is the second step in this study. As we have motivated numerous times throughout this report, compressibility effects is an important feature that needs to be accounted for when the incompressibility assumptions can no longer be valid and the liquid domain undergoes a local change in density, such is the case during LIC events. Being able to capture the variation in density, regardless of its significance, and consequently the shockwaves, will increase the accuracy of results and permit us to conclude the correct bubble dynamics.

The initial tool was developed to test a Crystallization hypothesis. It states that crystals are nucleated at the vicinity of the bubble interface during the first stages of growth due to high levels of supersaturation. A good understanding of the thermo- and dynamic conditions was assumed sufficient to investigate our assumption. However, shockwaves often present during LIC events do bring drastic changes to the conditions within our domain. Therefore compressibility effects need to be included. Regardless, the new tool, which resolves compressible liquid, is an integral tool. The scope of the numerical framework widens to include biomedical applications, particularly, high precision medical surgeries involving the usage of lasers. When a laser beam is subjected into the human eye to re-adjust the shape of the cornea (Keratomileusis), or into the kidney to remove stones (Lithotripsy), a LIC event occurs. In this scenario however, the most important feature are the expanding and propagating shockwaves which damage the organs internal tissues. This increases the recovery time needed and can also introduce complications which can lead to the failure of the medical procedure. Therefore, a good understanding of the shockwave system and how it is influenced by the laser parameters is essential to avoid such dilemmas. Our tool can now do that.

To develop this second numerical framework, the first, initially developed at Chalmers, is used as base. Numerical as well as theoretical modifications and improvements are incorporated to resolve compressible liquid.

3.2.1 Compressible Liquid

To model the liquid domain, instead of relying the conventional R-P equation (2.2), the bulk of water is resolved using conservation laws, similar to the compressible vapor phase formulations. Hence, in the absence of viscosity effects and neglecting mass diffusion, the conservation equations for mass, momentum, and energy read as follows:

$$\frac{\partial \rho_l}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_l u_l) = 0 \quad (3.23)$$

$$\frac{\partial}{\partial t} (\rho_l u_l) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_l u_l^2) + \frac{\partial p_l}{\partial r} = 0 \quad (3.24)$$

$$\frac{\partial}{\partial t} (\rho_l e_l) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho_l u_l (e_l + p_l / \rho_l) - r^2 \lambda \frac{\partial T_l}{\partial r} \right) = 0 \quad (3.25)$$

Here the viscous effects are obviously minor as we do use the properties of pure water, and were considered negligible. We further neglect mass diffusion (the presence of contaminant gas) as its influence is insignificant in inviscid media, so do suggest the analytical results of *Akhatov et al.* as well as *Ki-Taek et al.* [2, 10]

3.2.2 Equations of State

3.2.2.1 Mie–Grüneisen model

To account for density variations in our numerical tool, we use the Mie–Grüneisen model[2, 3]. However, we rely on a re-formulation of the original set of equations. This new form of the Mie–Grüneisen model was derived empirically approximating experimental data with conditions that far exceed the critical point, and thus can handle events that include such scenarios. It uses concepts from kinetic theory to model the pressure and internal energy as the sum of a cold and a hot component. The cold components, p_c and ϵ_c , describe the elastic properties, whilst the hot components, p_h and ϵ_h represent the oscillation effects within the atomic lattice. The latter components read as follows[2]:

$$p_l = p_c(\rho_l) + p_h(\rho_l, T_l) \quad (3.26)$$

$$\epsilon_l = \epsilon_c(\rho_l) + \epsilon_h(T_l) \quad (3.27)$$

Where the hot components as described as:

$$p_h = \Gamma(\rho_l) \rho_l \epsilon_h \quad (3.28)$$

And

$$\epsilon_h = T_l c_v(\rho_l, T_l) \quad (3.29)$$

Here, c_v is the specific heat capacity at constant volume and $\Gamma(\rho_l)$ the Grüneisen correction coefficient, which values for:

$$\Gamma(\rho_l) = 0.57 + \frac{0.95}{1 + (\rho_l/\rho_{l0} - 1.65)^2/0.12} - \frac{0.28}{1 + (\rho_l/\rho_{l0} - 1)^2/0.07} \quad (3.30)$$

The equation above, (3.30), satisfies experimental data from isothermal acoustic propagations in pure water. It describes the properties of the liquid when $\rho_{l,o} < \rho_l$, where ρ_l and $\rho_{l,o}$ respectively are the density and the initial density in water. When $\rho_{l,o} > \rho_l$ however, a different set of experimental data is used that satisfies the properties of saturated water on the binodal curve, and the correction coefficient then reads:

$$\Gamma(\rho_l) = 0.24 + 1.9 \times 10^{-4} \rho_l + 0.07 \exp[-0.004(\rho_l - \rho_{l0})^2] \quad (3.31)$$

On the other hand, the cold components in equations (3.26) and (3.27) represent the Born–Mayer potential[2] which accounts for the intermolecular properties of the condensed medium in question, such that:

$$p_c(\rho_l) = A \left(\frac{\rho_l}{\rho_{l0}} \right)^{2/3} \exp \left[b \left(1 - \left(\frac{\rho_l}{\rho_{l0}} \right)^{-1/3} \right) \right] - K \left(\frac{\rho_l}{\rho_{l0}} \right)^{4/3} \quad (3.32)$$

$$\epsilon_c(\rho_l) = \frac{3A}{\rho_{l0}b} \exp \left[b \left(1 - \left(\frac{\rho_l}{\rho_{l0}} \right)^{-1/3} \right) \right] - \frac{3K}{\rho_{l0}} \left(\frac{\rho_l}{\rho_{l0}} \right)^{1/3} \quad (3.33)$$

Where the first terms (before the minus sign) stand for the repulsive forces and the second terms describes the attractive forces in between atoms in the lattice. A , b , and K are constants, which have been determined from experimental data, also from isothermal acoustic propagations in water, where $A = 3.492 \times 10^8 Pa$, $b = 16.0558$, $K = 8.283 \times 10^8 Pa$.

Another correction factor is required when the conditions in simulation exceed the critical point, and it is related to the internal energy. Thermodynamic basic theory states that there's no difference in between vapor and water after the critical point and hence their internal energies must be equal. Furthermore, the properties of vapor and water are described with different equations of states. Therefore their internal energies must be matched on the binodal curve with a correction factor accordingly[2]:

$$\epsilon_l = \epsilon_c(\rho_l) + \epsilon_h(T_l) + \epsilon_{l0}(T_l) \quad (3.34)$$

Where the equation above, (3.34), is the new formulation for the internal energy with $\epsilon_{l0}(T_l)$ being the new correction factor such that:

$$\epsilon_{l0}(T_l) = 0; \quad \text{if } T \geq T_{cr} = 647 \text{ K} \quad (3.35)$$

And

$$\epsilon_{l0}(T_l) = -1.207 \times 10^3 T \text{ J/(kgK)} + 7.793 \times 10^5 \text{ J/kg}, \quad \text{if } T < T_{cr} \quad (3.36)$$

With $T_{cr} = 647K$ being the critical temperature, and the critical pressure is $p = 22 \times 10^3 \text{ MPa}$.

3.2.2.2 Modified Tait model

In order to increase the computational efficiency of our framework, and at the risk of decreasing the accuracy of the results, we investigate the possibility of using the Tait equation. This equation of state is conventional for pure water but doesn't usually account for density variation[23]. We thus use a modified form. This version was derived using experimental data that are fairly modest and are far from reaching the critical point, roughly, $p = 2400 \text{ MPa}$ and $T = 440 \text{ K}$ [22]. The modified version of the Tait equation reads as follows:

$$\frac{p_l + B}{p_{0l} + B} = \left(\frac{\rho_l}{\rho_{0l}} \right)^n \quad (3.37)$$

And

$$c = c_{\infty} \left(\frac{p_l + B}{p_{ol} + B} \right)^{\frac{n-1}{2n}} \quad (3.38)$$

Here $B = 303975\text{MPa}$ and $n = 6.7$ are material constants determined analytically. The speed of propagation of sound in undisturbed water however, $c_{\infty} = 1408\text{m/s}$, was determined from experimental data of spherical propagating shockwaves in pure water.

The Tait equation doesn't offer an alternative to model the internal energy and account for conditions beyond the critical point, the so-called super-critical conditions. When using this approach, we will thus follow the procedure used by Mie–Grüneisen to model the internal energy, whilst for pressure, modified Tait should be sufficient.

3.2.2.3 Numerical Parameters

The governing equations for both compressible vapor and compressible liquid are solved in a stationary coordinate system with the origin being the centre of the bubble. For time discretization, the Implicit Crank-Nicolson Scheme was used, whilst for spatial discretization the Cell Centered Finite Volume Scheme was resorted to.

The adaptive mesh refinement is also used here to reduce computational cost as well as a variable time step. This variable time step works similarly as it does for the vapor phase, however, it uses the speed of propagation of sound in pure liquid water and a higher Courant number (This choice will be discussed in the Results Section).

The initial conditions used in the numerical investigation using the second framework are roughly similar to the first, excluding some minor changes. This time, simulations were performed for durations varying between $50\mu\text{s}$ and $650\mu\text{s}$. The laser pulse time was set constant such that $t_{las} = 6\text{ns}$. The laser energy however was varied between 0.3mJ and 418mJ .

4

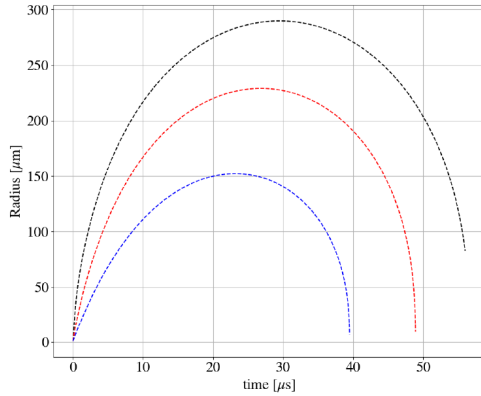
Results

4.1 Validation

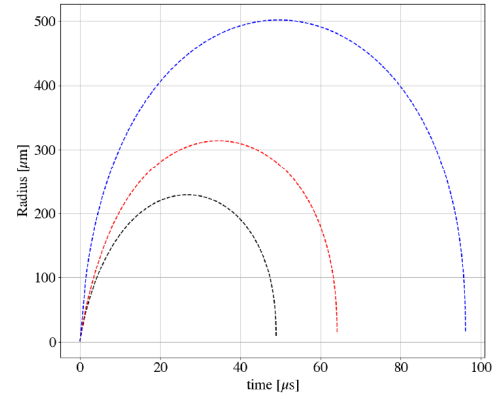
As mentioned before, the initially designed numerical tool was intended for thermocavitation events (without optical breakdown). This framework was used for a numerical investigation using parameters that in experiments induced optical breakdown and hence generated a LIC. The goal is to assess how well the LIC dynamics are captured, conclude the shortcomings, and the magnitude of their influence.

4.1.1 Case 1

The first step is to test the limits and the flexibility of the code. We do so by running simulations with different energy densities, varying the laser beam radius and the laser energy absorbed, and assess the influence of these variations on the bubble dynamics.



(a) Constant laser energy absorbed $E_{las} = 5\text{mJ}$ and varying the laser radius such that, (i) (- -) $r_{las} = 20\mu\text{m}$, (ii) (- -) $r_{las} = 30\mu\text{m}$, and (iii) (- -) $r_{las} = 40\mu\text{m}$.



(b) Constant laser radius $r_{las} = 50\mu\text{m}$ and varying the laser energy absorbed such that, (i) (- -) $E_{las} = 5\text{mJ}$, (ii) (- -) $E_{las} = 8\text{mJ}$, and (iii) (- -) $E_{las} = 12\text{mJ}$.

Figure 4.1: Different bubble dynamics induced with different laser parameters with increasing levels of energy densities where in (a) the laser energy deposited E_{las} was kept constant and the radius r_{las} varied, whilst in (b) the inverse took place.

Illustrated in the figures above, (4.1a-b), we have different bubble dynamics induced with different laser parameters. To produce these plots we used laser parameters

that in experiments induced optical breakdown. In figure (4.1a), we use an absorbed laser energy $E_{las} = 5\text{mJ}$ and vary the laser radius r_{las} , whilst in figure (4.1b), we vary the laser energy absorbed E_{las} for a constant laser radius $r_{las} = 50\mu\text{m}$. At first sight, we can see that the code captured realistic bubble dynamics. One can clearly distinguish the conventional shapes of both growth and collapse phases. We can also identify symmetry with respect to the maximum radius in all of the curves but the blue one in (4.1a), using $E_{las} = 5\text{mJ}$ and $r_{las} = 40\mu\text{m}$. The symmetry characteristic is a feature of the generalized R-P equation that excludes mass transfer. In this matter however, one can argue that the asymmetry feature in the blue line is a virtue of low energy density which produces a relatively low temperature and heats a larger portion of the liquid. This results in low evaporation rates that are probably less uniform compared with high evaporation rates. The laser beam profile is bell-shaped and its uniformity can be influenced by the laser intensity, as can be suggested from the laser power density formulation in equation (3.21). Compared with the blue line, which uses a less focused laser beam, the other two lines (red and black, still in figure (4.1a)) display a faster initial growth evidently caused by fast evaporation rates. On the other hand, In figure (4.1b), all curves are symmetric, also with respect to the maximum bubble radius. Comparing both plots (4.1a) and (4.1b), the simulation times are seen to be different. This is because we used increasing values of energy densities to test the limits of the code. Larger energy densities give rise to faster evaporation rates, which in turn induce a larger bubble with a longer life span. The step in energy density used for all curves is $e_{las} = 0.2\text{W}/\text{cm}^3$ (i.e. the difference in energy densities in between cases). The maximum energy density used in plot (4.1a) is chosen to be right below the minimum energy density used in plot (4.1b), respectively, $e_{las} = 0.5\text{W}/\text{cm}^3$ and $e_{las} = 0.7\text{W}/\text{cm}^3$. The energy density is equated in the method section, equation (3.22), and is, since the pulse time t_{las} is set constant, a function of the laser radius and the energy absorbed. Even though we use a constant energy density step in between the cases, we loose the symmetry feature in the blue curve in figure (4.1a), and then gain it back for the subsequent curves. One should run more simulations following the same approach (further increase the energy density using the same step, or even try smaller steps) in order to understand the dependence between the maximum bubble radius (bubble potential energy) and the energy density applied. We were unfortunately unable to perform this investigation since each simulation takes a very long time, roughly a week for a simulation time of $65\mu\text{s}$. We can further point that the difference in maximum radii is continuously non-linearly increasing as we increase the laser energy density, which can clearly been seen in the plots, particularly, in (4.1b). *Vogel et al.* investigated this matter and concluded an increasing optical absorption efficiency which increases with increasing laser intensity. It roughly varies between 18% and 72%[6]. We were unable here to compute the energy density for the data provided by Vogel since he doesn't provide the laser radius. This might be the first shortcoming of this numerical tool, since we do not account for the laser energy conversion between deposited and absorbed. This factor appears to be fundamental since with higher laser energies the bubble is provided with exponentially larger potential energies. Optical absorption is a stochastic process whose efficiency increases with increasing laser intensity[32]. Another shortcoming is also observed in the black curve in plot

(4.1a) where we use laser parameters such that $E_{las} = 5\text{mJ}$ and $r_{las} = 30\mu\text{m}$, which is the largest energy density used in this plot. Here, the simulation crashes and records pressure and temperature values exceeding the critical point. When these conditions are met, and based on theory, a shock is initiated and a rebound takes place. But not here, here the simulation crashes because of the absence of compressibility effects.

4.1.2 Case 2

The second step in this validation is to study the applicability of the present framework and identify differences due to optical breakdown by comparing our simulation results to ones that are experimentally produced. To do so we compare our results to *Wilson et al.* data[7]. Wilson investigated LIC experimentally and numerically, where he studied the entire bubble life cycle. Furthermore, to assess the difference in dynamics, we compare both sets of results (ours and Wilson) to the Rayleigh prediction of voids collapsing in an inviscid fluid.

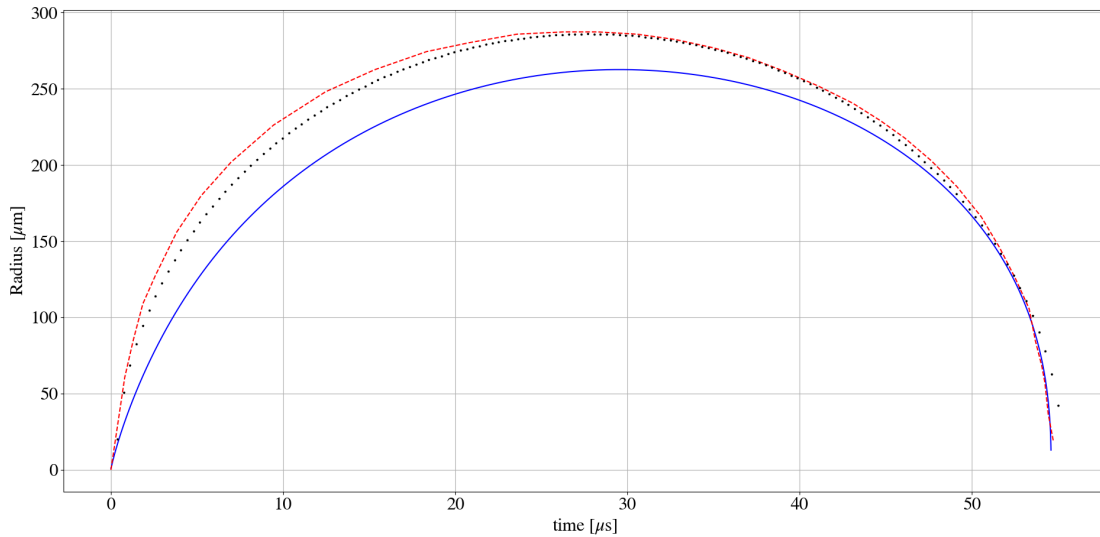


Figure 4.2: A single bubble life cycle evaluated using three different methods (a) Simulation (-) $E_{las} = 6\text{mJ}$ and $r_{las} = 40\mu\text{m}$ (b) Experimentally (- -) using the same parameters as in simulation, and (c) The theoretical Rayleigh collapse (**).

Illustrated in the figure above, (4.2), we have the life cycle of a single bubble evaluated until the first collapse using our simulation data, *Wilson et al.* results, and the Rayleigh cavitation collapse time. For our simulation we used the same parameters Wilson did, a laser radius $r_{las} = 40\mu\text{m}$ and a laser energy absorbed $E_{las} = 6\text{mJ}$. We do not model the optical absorption and fitted our data empirically, and hence conclude a laser energy conversion efficiency of 6%, whilst Wilson reported 9% based on his experimental data. The Rayleigh collapse time was evaluated using $t_c = 0.9148R_m\sqrt{\rho/p_\infty}$, with R_{max} the maximum bubble radius, and ρ and p_∞ respectively the local density of water and static pressure in far-field. One can already observe a qualitative agreement between our results, Wilson's, and the Rayleigh collapse, particularly during collapse. However, the Rayleigh curve and Wilson's are

almost identical, which was not expected. The Rayleigh collapse is characterized by its reversible nature i.e. absence of diffusion and dissipation as well as phase change. It is therefore evident for the bubble cycle to be symmetric. On the other hand, as mentioned in the previous discussion, the symmetric nature of a LIC, and in the case of Wilson’s curve also, is a virtue of fast evaporation rates which are resultant of the extra energy provided by the liquid breakdown. For ordinary bubble dynamics (without optical breakdown), ratios of 1/3 and 2/3 of the bubble cycle are respectively suggested for the growth and collapse durations[1].

All cavities collapse at the same time, roughly after $55\mu\text{s}$ and are therefore assumed to have equal potential energies when they had reached their maximum radii. Yet, despite using the same laser parameters, the initial growth phases are different when comparing our results and Wilson’s. Our bubble displays a slower growth and it reaches a lower maximum radius, $234\mu\text{m}$ compared with $287\mu\text{m}$ for Wilson’s bubble which was captured experimentally. This difference in results can be caused by the difference in conversion efficiencies that we and Wilson use, namely 3%. However, *Vogel et al.* reported that for similar pulse durations of 30ps (picosecond, 10^{-12}s) but two different laser energies, $50\mu\text{J}$ and 1mJ , the conversion efficiency almost tripled, respectively, 18% and 42%[6]. We however use a nanosecond pulse, but no similar data is available. We can nonetheless assume a similar trend. Furthermore, We can argue that the difference in bubble growth is a consequence of the extra energy provided by the optical breakdown, which we do not model. To quantify this energy we compute the bubble potential energies (ours and Wilson’s), and the difference is assumed to be the extra energy provided by the liquid breakdown. To do so, we use $E_B = (4/3)\pi R_{max}^3 (p_o - p_v)$ which equates a bubble potential energy, where p_v is the vapor pressure inside the bubble when it reaches its maximum radius. The extra energy provided by the breakdown process thus values for $36\mu\text{J}$ and makes up $< 1\%$ of the absorbed energy, compared with 23.2% being the total converted potential energy. The magnitude of the energy we don’t account for due to the breakdown process appear to be minor compared with the difference in conversion efficiencies. At such relatively low levels of laser energies, the energy conversion appear to influence the bubble dynamics more than the liquid breakdown process. A proper modeling of the optical absorption is necessary to get better results and fit a better match.

Even though, the two bubbles start collapsing withholding two different potential energies, they still collapse following the same trend and within the same duration. This is likely due to different liquid inertias. From one end, theory states that collapse is mainly governed by inertial effects. On the other end, *Vogel et al.* reported minor density changes in the liquid during collapse, even though no shockwaves were captured during that period[6]. Our numerical tool doesn’t account for density variation in the liquid region at this stage and can’t hence capture these minor dissipative effects. Additionally, the presence of non-condensable gas in Wilson experiments and its absence in our framework, could also be an additional factor which led to similar collapse times. Afterall, the collapse period is also heavily influenced by the ability of the vapor to condensate rapidly enough to keep up with

the shrinking interface, and the final amount of non-condensable gas that remains trapped. However, in their numerical study Wilson used the Keller-Miksis model which assumes the interface to be impervious to gas and disregards the vapor inside the bubble. He nevertheless managed to numerically capture the collapse better than the growth period comparing with his own experimental results. To conclude, the absence of modeling of optical breakdown initially resulted in different dynamics, it was however compensated by the inability of the framework to capture density variations. Incorporation of the optical breakdown, efficiency conversion, as well as compressible liquid seem to so far have equivalent importance.

4.1.3 Case 3

In this third and final step in this validation, we tried to reproduce the bubble dynamics induced using an extremely high laser energy. The intention is to study the effects of liquid compressibility during the collapse phase. The laser parameters we use are assumed to produce an energy density considerably higher than the optical breakdown threshold. This produces a denser plasma with higher temperature, and this results in higher evaporation rates. This produces larger bubbles and often leads to rebounds. We managed to numerically capture some rebounds and compare them with experimentally produced ones. To do so, we compare our simulation results to *Sinibaldi et al.* experimental data. Sinibaldi investigated LIC experimentally and focused mainly on the influence of plasma presence. The most extreme of their cases is used for comparison, which produced a bubble maximum radius of $1982\mu\text{m}$ as well as two subsequent rebounds.

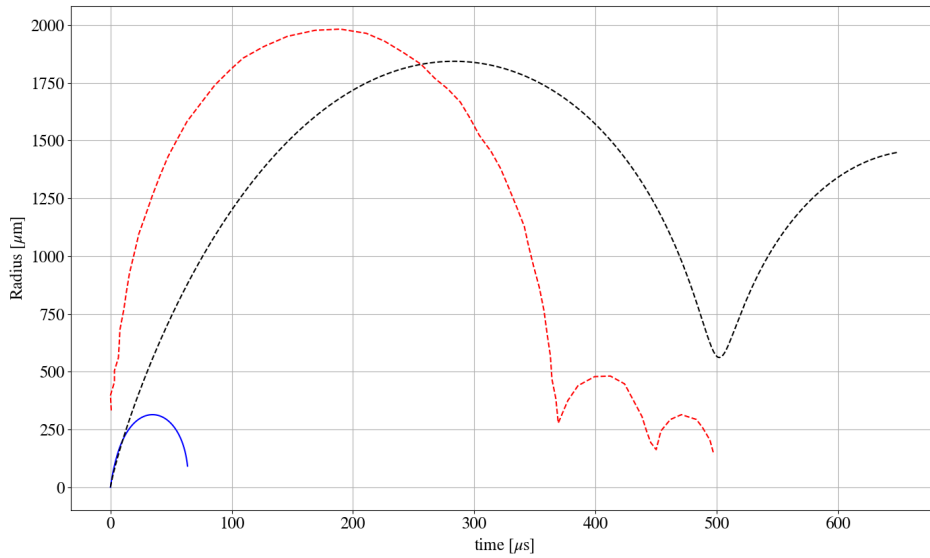


Figure 4.3: Three different bubble cycles induced with different parameters where a) and b) were numerically produced and c) experimentally such that, (a) Simulation I (-) $E_{las} = 27\text{mJ}$ and $r_{las} = 98\mu\text{m}$, (b) Simulation II (- -) $E_{las} = 193\text{mJ}$ and $r_{las} = 426\mu\text{m}$, and (c) Sinibaldi (- - -) $E_{las} = 27\text{mJ}$

Illustrated in the figure above, (4.3), we have the bubble life span of three differ-

ent cycles, two simulated numerically (continuous blue line and black dashed line) and one produced experimentally by Sinibaldi[11]. Sinibaldi used a deposited laser energy $E_{las} = 27\text{mJ}$, but reported no laser radius. They captured a bubble cycle that reached a maximum radius of $1982\mu\text{m}$ and produced two subsequent rebounds. For our simulations, we first tried to use the same laser energy Sinibaldi used and conclude the radius. Sinibaldi reported that when using such high deposited laser energy ($E_{las} = 27\text{mJ}$), the losses due to conversion efficiency are minor and the same value can be assumed to be absorbed[11]. Vogel however states that even with such high energy levels, there will always be 10-20% losses[6]. These inevitable losses are characterized by the time it takes plasma to form and reach a high enough density to fully absorb all of the laser radiation. Anyway, we used $E_{las} = 27\text{mJ}$ as an absorbed energy, and we managed to produce the bubble dynamics illustrated with the blue curve for a laser radius $r_{las} = 98\mu\text{m}$. The laser radius we used is abnormally large, it is yet the smallest we managed to use without facing numerical discrepancies. This laser radius is not only considered extremely large, but it is probably way larger than the one used by Sinibaldi. In their experimental set-up, they used many focusing and adjusting lenses to focus the laser beam furthermore and produce even higher energy densities. Nevertheless, even when using such a large laser radius, the numerical discrepancies still arise at the end of the collapse, when the conditions are assumed to be at the super-critical level. This is a similar scenario to that discussed in figure (4.1a) illustrated with a black line. The laser parameters we and Sinibaldi use are fairly different, but the difference in dynamics is even more pronounced. The bubble we simulate barely reaches $315\mu\text{m}$ as the maximum radius. Here, the absence of modeling of the breakdown process and the energy it releases is obvious at such high laser energies and the difference in dynamics is immense. We can also argue that our numerical tool is unable to handle extremely large energy densities and super-critical conditions.

Furthermore, we tried to match Sinibaldi maximum radius and asses the difference in laser parameters, this is also illustrated in figure (4.3) with the black dashed line. The fit produced an energy absorbed $E_{las} = 193\text{mJ}$ and a radius $r_{las} = 426\mu\text{m}$, and induced a bubble with a maximum radius of $1843\mu\text{m}$. Sinibaldi's bubble reached $1982\mu\text{m}$, the difference in bubble maximum radii is probably caused by the plasma formation and the extremely intense evaporation rates our numerical tool is unable to numerically reproduce. Sinibaldi used a highly focused laser beam to further increase the energy density. These high levels of energy density produce a denser and hotter plasma which results in higher evaporation rates. Here, the difference in dynamics is quite pronounced, the numerical tool is incapable of matching the maximum bubble radius Sinibaldi captured. Additionally, our respective bubbles, ours and Sinibaldi's, reach their maximum sizes at considerably different times, respectively, $287\mu\text{s}$ compared with $182\mu\text{s}$. The inability of the framework to handle extreme conditions is quite obvious and the consequences in dynamics are tremendous. At this stage, one can argue that the modeling of liquid breakdown and the energy conversion won't be sufficient. Consideration towards the handling of extreme conditions, particularly, extremely high energy densities in contrast to super-critical conditions, needs to be addressed.

In figure (4.3) we can also observe rebounds. It takes Sinibaldi's bubble $188\mu\text{s}$ to collapse, whilst ours does after $216\mu\text{s}$. Even though Sinibaldi's cycle withholds more potential energy and starts collapsing from a larger size, it does so in a shorter time compared with our cycle. If the liquid is displaced further due to a larger bubble size, the liquid inertia should theoretically be greater when it rushes back toward the interface when the bubble collapses. In addition to this theoretical aspect, one can argue that this difference is also influenced by the inability of the framework to capture density variations and hence the respective minor dissipative effects. After its collapse, Sinibaldi's cycle rebounds twice, producing two subsequent bubbles with smaller radii. This is a virtue of the dissipative effects of compressible liquid that are obviously part of the reality and hence the experiment. In contrast, our bubble does rebound but produces a bubble with a way larger radius than the ones produced by Sinibaldi. This is a fault of the incompressible assumption. The only dissipative effects we include are viscous and thermal to the surrounding liquid. The viscous effects we include in our tool are considered small and negligible, however, they were incorporated for numerical stability. This case is one of the few where we managed to capture rebound. The parameters we used for such an end were always extreme i.e. extremely high energy density. The physical phenomena behind rebounds are understood as well as their influence on the conditions surrounding the bubble but not of the vapor inside. However, we know from theory, before the rebound event, the conditions at the interface are at the critical point (and in some cases reach the super-critical level), and the liquid inertia moving toward the interface is immense. With no dissipative effects from pressure waves induced by compressibility effect, the difference in dynamics is quite noticeable as can be observed.

4.2 Compressibility

The dissipative nature of the compressible effects were shown to be important. The difference in dynamics was observed to be major especially during the collapse. The second step in this numerical investigation is to study the difference in results with and without dissipation in the liquid region. A compressible solver was implemented to resolve the liquid region. Also, a set of equations of energy and state were used to account for extreme conditions within and surrounding the bubble, particularly during the early growth and collapse periods. The implementation was partly successful, we did manage to capture oscillations in the pressure and density distribution in the liquid region at the vicinity of the interface. However, we continuously face numerical discrepancies. Indeed, some of these discrepancies are probably purely numerical. Yet, most of the issues we faced were related to the extremely fast nature and incredibly small time scale of the dynamics, that includes the speed of sound, the numerical damping needed when dealing with such fast dynamics, and the time step, which needs to be extremely small. The physical speed of sound in pure water in ambient conditions is roughly 1400m/s . However for the numerical damping, needed for the adaptive time step and the CFL criteria, we need the numerical speed of sound in water, and our literature survey wasn't successful since this value doesn't figure anywhere. We did however analytically conclude and averaged a nu-

merical speed of sound of $3.8 \times 10^5 \text{m/s}$ using a few relations empirically derived to account for this variable, one of them being the non-modified Tait equation. This high number and the very small cell sizes we use resulted in an extremely small time step, 10^{-21}s , to be used for most the simulation time. Using this time step and an substantial amount of numerical smearing, the simulation did run but was extremely slow. Even though we managed to capture the desired variations, it took more than a week to simulated less than a $1 \mu\text{s}$. Further consideration toward this issue should be addressed. One should pay attention to the purely numerical discrepancies, but we suggest to start looking at the numerical damping first. Another approach is to use better equations of state where we can compute and obtain a reasonable speed of sound.

5

Conclusion

This study was conducted to better understand the physics of Laser Induced Cavitation. A good understanding of the physical phenomena within and surrounding the bubble during and after the laser pulse was deemed necessary to test our crystallization hypothesis. Further development of an existent numerical tool and inclusion of additional relevant physical phenomena took place. By further developing the framework, we enlarge the scope of its usage to not only test the possibility to use LIC for crystallization, but other cavitation events such as high precision surgical laser procedures. This new tool can help shed light on cavitation scenarios within diverse conditions and for different dynamical behavior.

The inclusion of dissipative and diffusive effects through the implementation of a compressible solver for the liquid region was assumed to be the next step toward higher accuracy and more realistic dynamics. Our results do confirm our assumption. The lack of dissipative effects and the absence of diffusive shockwaves do largely alter the bubble dynamics in our simulations. However, our results also suggest that the explicit modeling of optical breakdown and optical absorption (the laser energy conversion efficiency between deposited and absorbed) are equally important, and they become more relevant for higher energy densities. First, the incorporation of the optical absorption event is necessary to get the correct parameters for our numerical investigation, especially when comparing to experimental results. In some cases, we managed to perform some comparison with a certain level of accuracy after introducing some assumptions and simplification. However, our results show these assumptions to be no longer valid at high energy levels. Optical absorption is a stochastic process whose likeability increases with larger energy densities (hotter and denser plasma), and we have concluded based on our results that its efficiency is exponentially growing. Secondly, the modeling of liquid breakdown and plasma formation is also a must. The developed framework is able to capture LIC events with high accuracy for moderate laser parameters only. When using extremely high energy densities, which are often used in experimental work, our framework is unable to resolve the extremely fast and intense evaporation rates and fails at predicting the growth period immensely. In addition to the inclusion of optical breakdown, one must also enhance the tool to permit it to handle extreme conditions. This includes the extremely high temperatures at the beginning of the growth phases, which was observed to dictated the entire growth phase, but also at the end of the collapse when conditions push beyond the so-called super-critical conditions. The inability of our tool to handle these circumstances was pronounced and shown to produce unrealistic results. Finally, the compressibility feature in the liquid region was as well

shown to be drastic. The ability to capture density variations and pressure waves can indeed help understand how the interface behaves under extreme conditions. However, our results and the literature survey we conducted suggest the presence of a system of shockwaves and not a single wave. This system of interacting shockwaves is present for an extremely small duration. It was not captured experimentally and it is probably quite challenging to capture numerically consideration the small time scale. However, the impact of its presence is obvious. A plasma that is characterized by optical breakdown releases a shockwave when it decays. Sinibaldi did identify two different shockwaves at the two separate ends of the plasma they captured. At the end closest to the laser pulse, where the energy density is relatively lower, a compression wave arose, however, on the other end, where the energy density is larger an expansion wave arose. Furthermore, the presence of plasma introduces extremely high and sudden temperature values. This generates very intense and violent evaporation rates, in addition to a shockwave. This system of shockwaves interacts before the cavity starts to expand, and needs to be considered and addressed. Shockwaves dissipate energy away leaving the bubble with lesser potential energy to expand, and a good resolution of this potential energy is necessary to produce correct results. Another shockwave is also initiated during the end of collapse, but it is less relevant for the purpose of this study.

Laser Induced Cavitation is a relatively new topic yet it is ubiquitous. Further studies should be conducted to better understand LIC dynamics. The development of a numerical tool that includes the theoretical ambiguities mentioned above should also take place. An integral framework can help understand and monitor engineering applications where LIC is governing.

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