

On the fundamental mechanisms & optimisation of ultrasonic-assisted liquid phase exfoliation of two- dimensional nanomaterials

By

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**On the fundamental mechanisms &
optimisation of ultrasonic-assisted liquid
phase exfoliation of two-dimensional
nanomaterials**

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Submitted in fulfilment of the requirements for the
Degree of Doctor of Philosophy

School of Engineering Computing and
Mathematics Oxford Brookes University



May 2023

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Abstract

The application of ultrasound and acoustic cavitation in liquid exfoliation of bulk layered materials is a widely used method. Ultrasonic assisted liquid phase exfoliation (ULPE) is a promising procedure for the large scale production of two dimensional (2D) materials. As of this date, toxic solvents such as N-Methyl-2-pyrrolidone (NMP) are commonly used for the production of graphene and other 2D layers. This research was intended to find a suitable eco-friendly liquid media alternative to NMP, such as water or water-based solutions for ULPE. However, in order to propose such a solution, the fundamental mechanisms pertaining to ULPE must first be fully understood.

There are a multitude of complexities of liquid exfoliation of bulk layered materials facilitated by ultrasonic cavitation. In addition to the solvent choice, other necessary factors to consider include the source material, solution temperature, input transducer power, sonotrode geometry and operating frequency.

Before these parameters could be considered, the first task was to interpret and understand the interactions between cavitation and bulk layered materials and hence to explain the mechanisms of ULPE. Unfortunately, most of the research currently reported has been ambiguous or inconclusive due to lack of direct real-time experimental evidence. Therefore, systematic work characterising cavitation emissions and observing the exfoliation of graphite *in situ*, in deionised water under the dynamic interaction with laser and ultrasound induced cavitation bubbles was conducted. Using ultra-high-speed optical imaging, we were able to determine the dynamic sequence of graphite exfoliation events on a time scale never reported before. Real-time observations revealed that shock wave surges predominantly with a pressure magnitude up to 5 MPa and liquid-jets secondary in the range of 80 ms^{-1} , from transient cavitation bubble implosions, were essential for the initiation and propagation of the exfoliation process. Additionally, bubble oscillations associated with stable cavitation were beneficial for promoting a gentler delamination of graphite layers. The evidence also demonstrated that proliferation of exfoliation occurred under the sonotrode within the cavitation zone.

With these fundamentals elucidated, the next step was to analyse solution temperature and input power on the developed pressure field, to optimise ULPE conditions. A high-

temperature cavitometer (calibrated in the National Physical Laboratory (NPL) UK) in the range of 8-400 kHz was used to measure the acoustic pressure generated from a 20 kHz acoustic source in different graphite solutions in deionised water at various temperatures (10-70 °C) and input power conditions (20-100%). In addition, high-speed optical imaging revealed insight on shock wave generation from transient bubble collapses in different sonication conditions. The optimal sono-exfoliation parameters were determined using 20% input power in 10 °C for a graphite flake solution, (of size 149 μm) and 100% input power in 40-50 °C for a graphite powder solution (of size 56 μm).

With the optimal temperature and power conditions identified, experiments were then conducted on solvent selection. Four solvents; three green solvents (water, ethanol and water/ethanol) plus NMP for comparison, were sonicated and examined in terms of their cavitation zone development, bubble dynamics, acoustic emissions and pressure distribution. Advanced fundamental analysis was conducted using high-speed imaging synchronised with acoustic pressure measurements complemented by shadowgraphic photography of the emitted shockwaves, in order to determine a suitable eco-friendly solvent medium from a cavitation bubbles dynamics perspective. Thereafter, ULPE of graphite in the optimum solvent took place for up to 2 h under controlled ultrasonication parameters of input power and solution temperature. The produced graphene samples were characterised by employing a series of techniques consisting of UV-Vis spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM). A mixture of deionised water and ethanol was shown to produce high quality graphene with a stability of $\sim 78\%$ for the duration of six months.

Further optimization of our ULPE procedure continued with analysis on the driving ultrasound frequency. We investigated the effect of implementing a dual-frequency system, where bubble dynamics, acoustic pressure, spectra and induced shock waves could be elucidated and compared with a single, low frequency sonotrode. Using ultra-high-speed imaging and synchronised acoustic pressure measurements, a dual-frequency system and its effect on bubble dynamics was investigated. A high frequency transducer (1174 kHz) showed that bubble fragments and satellite bubbles induced from a low frequency transducer (24 kHz) were able to extend their lifecycle sustaining an active cavitation regime in the bulk solution. In addition, this combination of ultrasonic frequencies generated higher acoustic pressures than the sum of the individual transducers, and enhanced the associated shock wave spectrum peaks, indicating an increase bubble activity with further collapses and the

generation of additional shock waves surges. The dual-frequency system also produced an enlargement in the cavitation zone size compared to the low frequency sonotrode. These data were put to the test where ULPE of graphite was conducted using a low frequency source of either a horn (22 mm diameter) or larger bell (40 mm diameter) shaped sonotrode. The produced graphene samples were characterised by employing a series of techniques consisting of UV-Vis spectroscopy, Raman spectroscopy and TEM. DIW:EtOH produced an average area of $1.5\ \mu\text{m}$ with 10 ± 5 layers and 5.8% yield with the horn sonotrode. When using the bell sonotrode the yield was approximately the same (5.75%) in half the sonication duration, although, at the expense of smaller sized area flakes ($0.3\ \mu\text{m}$).

This research has led to a deeper understanding of the ULPE physics and dynamics that improved optimization and control of the exfoliation process for the generation of high quality 2D materials. The combination of parameters presented in this thesis additionally provides a promising eco-friendly substitute for future commercial manufacturing of graphene.

Acknowledgments

First and foremost I must thank my perspicacious supervisor and mentor, Professor Iakovos Tzanakis. You have been extremely attentive and provided me with support throughout my PhD (which still impresses me considering your constant involvement in a myriad of projects, with numerous responsibilities). Your knowledge and erudition, along with your guidance has greatly aided me during my research.

I extend my appreciation to Professor Dmitry Eskin for his consistent and prompt support in crafting and structuring manuscripts, in addition to leading our project to various successful outcomes.

Next I give a sincere thanks to Dr. Paul Prentice for the aid of his prestigious Cav lab, and contribution to experimental work, as well as providing useful insights into analysing data.

I would like to thank Professor Jiawei Mi for supporting this PhD research with guidance and insights into developing manuscripts. I also thank Professor John Durodola for mentoring and supporting me from the beginning of my research. The supervision has ensured I was able to fulfil my commitments and complete this thesis.

I cannot forget to show appreciation to my colleagues, Dr. Abhinav Priyadarshi and Dr. Mohammad Khavari, who were particularly supporting and deeply involved in the progression of my research. Additionally, my fellow project members Dr. Amanpreet Kaur and Dr. Anastasia V. Tyurnina, who had pivotal roles in the succession of our research. They have all been an important part of my research experience.

I must also give gratitude to the Brookes technical staff, notably, Mr. Ian Spaksman and Mr. Adrian Ward.

I deeply thank my family for their unwavering support and encouragement over my entire academic journey. Lastly, a heartfelt thanks to my partner Melika, for her continued support and help during my PhD.

To conclude, my final thanks are to the Engineering Physical Sciences and Research Council (EPSRC). I am deeply grateful for the financial support provided for this project, and to me, in the form of a bursary, allowing this PhD work to be carried out comfortably and successfully reach the project goals.

Publications Resulting from Thesis

- **J.A. Morton**, M. Khavari, L. Qin, B.M. Maciejewska, A. V. Tyurnina, N. Grobert, D.G. Eskin, J. Mi, K. Porfyrakis, P. Prentice and I. Tzanakis, *New insights into sono-exfoliation mechanisms of graphite: In situ high-speed imaging studies and acoustic measurements*, Mater. Today. 49 (2021) 10–22. <https://doi.org/10.1016/J.MATTOD.2021.05.005>.
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Contributing Author:

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<https://doi.org/10.1016/j.carbon.2023.01.062>
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<https://doi.org/10.1016/j.ultsonch.2023.106328>

Conferences Attended

- **CAV 2021**, 11th International Symposium on Cavitation. May 9-13, 2021, Daejeon, Korea. *Effect of Temperature on the Ultrasonic Exfoliation of Graphite*. J. A. Morton, L. Qin, B. M. Maciejewska, A. V. Tyurnina, K. Porfyrakis, N. Grobert, D. G. Eskin, J. Mi and I. Tzanakis.
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Declaration

I hereby declare that this thesis titled, “**On the fundamental mechanisms & optimization of ultrasonic-assisted liquid phase exfoliation of two-dimensional nanomaterials**” has been prepared by me, under the direct supervision of Prof. Iakovos Tzanakis, and Prof. John Durodola as a part of my research for the award of Doctor of Philosophy degree at Oxford Brookes University, Oxford, England. I have not submitted this thesis previously for the award of any degree or diploma at any other institution.

Signed: 

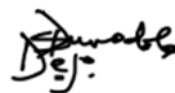
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Certificate

This is to certify that Mr. Justin Morton has done his research under my supervision and complied with all the requirements for the submission of this Doctor of Philosophy thesis to Oxford Brookes University, Oxford, England.



Prof. Iakovos Tzanakis



Prof. John Durodola

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List of Symbols

λ	wavelength of sound wave
T_a	acoustic period
f	frequency of oscillation
P_∞	ambient pressure
P_a	amplitude of acoustic pressure
$^{\circ}\text{C}$	temperature, Celsius
c	velocity
f_0	driving/fundamental frequency
n	integer
n/m	non-integer
Y	solvent surface tension
E_{Sol}	solvent surface energy
t	period
P_{Max}	maximum acoustic pressure
P_{RMS}	root mean square acoustic pressure

P	splitting force
δ	split length
E	Young's modulus of graphite
a	split depth
h	height
b	base
P_A	splitting pressure
τ	shear stress
F	transverse shear force
δ_{max}	maximum deflection of cantilever
Q	first moment of area
I	moment of inertia
r	distance
D	diameter

List of Abbreviations

2D	two dimensional
3D	three dimensional
vdW	van der Waals
LPE	liquid phase exfoliation
ULPE	ultrasonic-assisted liquid phase exfoliation
CVD	chemical vapour deposition
ALD	atomic layer deposition
ALD	atomic layer deposition
CO ₂	carbon dioxide
ITO	Indium tin oxides
SW	shock waves
NMP	N-Methyl-2-pyrrolidone
TEM	transmission electron microscopy

LF	low frequency
HF	high frequency
DF	dual frequency
GP	graphite powder
GF	graphite flakes
DIW	deionised water
HOPG	highly oriented pyrolytic graphite
AFM	atomic force microscopy
DMA	N,N-Dimethylacetamide
FOH	fibre-optic hydrophone
DMF	Dimethylformamide
SC	sodium cholate
NaDC	sodium deoxycholate
SDBC	sodium dodecylbenzene sulfonate
PCz	Poly[9-(heptadecane-9-yl)-9H-carbazole]
EtOH	ethanol
DIW:EtOH	deionised water:ethanol
DIW:IPA	deionised water:isopropanol
SLG	single layer graphene
FLG	few-layer graphene
MLG	multi-layered graphene
LIB	laser induced bubbles
VOF	volume of fluid
DCB	double cantilever beam
PCI	Peripheral Component Interconnect

Chapter 1

Introduction

1.1 Research Background

Over the last decade there has been a rapid growing interest into the production of two dimensional (2D) materials. A multi-layered bulk material can be exfoliated in order to produce few/mono-layer nanosheets, more commonly referred to as 2D materials. This phenomenon was first identified by Geim and Novoselov in 2004 with the successful isolation of graphene using a scotch-tape technique, for which they received the Nobel Prize in physics [3].

Only layered materials are capable of exfoliation to become 2D. Layered materials are comprised of 2D platelets that join and stack together, therefore, producing a three dimensional (3D) structure. For the most part, layered materials are held together by strong in plane chemical bonds and weak out of plane van der Waals (vdW) bonds. These 2D layers are subject to exfoliation by applying sufficient shear forces to overcome the weakly held vdW's forces, hence, producing an atomically thin material.

Subsequent to this, the existence and preservation of a 2D material was thought impossible due to thermal instability [4]. To scientists and academicians great surprise, this was not the case. Even more astonishing was the exceptional physical properties exhibited by 2D materials. For instance, graphene was quickly demonstrated to possess record high thermal conductivity at room temperature ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$) [5] in addition to an extraordinarily large electron mobility ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [6].

Consequently to these discoveries, research into 2D materials became vastly funded with a myriad of studies taking place worldwide. However, various issues surrounding the process of exfoliation and production of the 2D materials still present a problem hindering a broader exploitation and scaling up. These include production method efficiency, cost, quality of the nano materials, overall yield, size and more. To ameliorate these issues several exfoliation methods (characterised as “top-down” or “bottom-up”) remain under research.

Additionally, certain criteria must be adhered to in order to generate different kinds of 2D materials, whereby utilizing a different exfoliation method may be necessary. “Top-down” methods include mechanical exfoliation, liquid phase exfoliation (LPE) and shear mixing. On the other hand, “bottom-up” methods include chemical vapour deposition (CVD) and atomic

layer deposition (ALD). Each method includes its own advantages and drawbacks. For example, mechanical exfoliation can produce pristine 2D materials, but suffers from scalability; conversely, LPE has the potential to be scalable yet remains unable to produce consistently pristine 2D materials. Alternatively, CVD is capable of generating high quality 2D materials, but quantity suffers from large costs and energy consumption. These complexities have led to manifold research projects on the subject matter.

Due to the concerns surrounding the planet's climate, with particular focus on CO₂ emissions and preserving the environment, the necessity to reduce our energy output and find alternatives for emitting toxins into the atmosphere is more apparent than ever. In the case of generating 2D materials, LPE has been proposed as a viable and sustainable production method. In addition to the capability of producing high quality 2D materials with large surface areas, LPE is also a cost effective, environmental friendly and low energy alternative to other exfoliation methods [7]. First tested by Coleman *et al.* in 2008 [8], the principle to LPE is utilising liquid media for dissolution of layered materials. The exfoliated 2D materials are then stabilised.

The method has since grown in success with additional complementing techniques such as high-shear mixing [9] or ultrasonication (ULPE) [11, 12]. In most cases these complementary techniques are used for dispersion of chemically exfoliated graphene, although ULPE was demonstrated to be a powerful means for exfoliation by itself [12].

ULPE utilises energetic cavitation bubbles to facilitate material exfoliation. Shear forces are provided via transient cavitation (generating powerful shock waves (SW) and high speed liquid-jets from bubble implosions) and stable cavitation (generating rapid oscillating forces).

The core focus of this research thesis was to elucidate the fundamental mechanisms occurring during ULPE and identify the best ultrasonication settings, in order to control and optimise the process for large-scale production. This was to be achieved using high-speed imaging, complemented by the use of a range of calibrated sensors to detect acoustic emissions and relate the quality with the generated graphene via characterisation methods. As graphene is arguably the most demanded 2D material, with the largest amount of research into its generation, this research focused on ULPE of graphene.

Firstly, experiments were conducted to understand the interactions between the cavitation bubbles and the bulk layered material (graphite flakes). Next, investigating the bubble dynamics of various eco-friendly solvents, in addition to how different temperatures, acoustic

intensity and ultrasonic frequencies would affect acoustic emissions and pressure fields. These data sets would reveal optimal parameters for ULPE, whereby qualitative and quantitative exfoliation of graphite would then be characterised using various state of the art techniques. Hence, the aim of the research would propose an eco-friendly, scalable method for generating high quality of high yield few-layered graphene.

1.2 Global Significance

2D materials have only been successfully generated for just under two decades, and hence, are a newly booming research industry. As noted in the Research background Section, the exceptional properties of these materials are the driving force behind their demand. The University of Manchester, UK (where graphene was first isolated) predicted an estimated global investment of 2.4 billion dollars in 2015 [13]. Despite such a large financial interest into this particular 2D material, the projected sales of graphene manufacturing businesses were just 3.5 million dollars. This financial disparity is mostly a consequence of production cost, quality and scalability. China has been responsible for approximately twice as many patents as the United States for graphene related applications, however, due to a lack of compelling technologies, and non-competing prices, demand for commercial sales are low. For instance, around 2000 graphene phone screens were produced in China in 2014, but failed to make a large impact. Indium tin oxides (ITO's) are approximately half the cost, therefore, remaining a high demand for the consumer [13]. The necessity for improved, economically viable production methods for 2D materials is on the rise, and likely to continue this upward trend. In particular, due to energy and cost dependant methods such as CVD, ULPE is a promising alternative to ameliorate these limiting factors to graphene's, as well as other 2D materials worldwide commercial success.

It is worth noting that this PhD project has been funded by the Engineering and Physical Sciences Research Council (EPSRC) UK, providing another stepping stone in the endeavour for graphene's global success, and I hope, humbly, that the experimental research presented in this thesis contributes to the development of such a monumental scientific venture.

1.3 Project Objectives

The vision of this project was driven by the extremely high demand and technological necessity to upscale the production of 2D materials, where the focus was placed on generating graphene. Specifically, the aim was to produce graphene via ULPE without the addition of harmful chemicals, but rather through the use of pure water with eco-friendly

surfactants. Below is a summary of the succinct project objectives, followed by the experiments conducted to fulfil the project goals.

1. The first objective (O1) was to understand the interactions between layered materials and acoustic cavitation. For this, the sono-exfoliation mechanisms needed to be fully understood.

Action: Experiments were undertaken using ultra-high speed imaging to observe acoustic multi-bubble formations, and laser induced single bubble cavitation interactions with graphite flake samples. From this testing, sono-exfoliation mechanisms were elucidated.

2. The second project objective (O2) was to optimise ultrasonication conditions in a low frequency reactor based on solution temperature and transducer input power, which would facilitate exfoliation.

Action: A high-temperature calibrated in the NPL in the range of 8-400 kHz cavitometer was used to measure the acoustic pressure generated in different graphite solutions in deionised water at various temperatures (10-70 °C) and input power conditions (20-100%). In addition, high-speed optical imaging revealed insight on SW generation from transient bubble collapses in different sonication conditions.

3. The third project objective (O3) required the bubble dynamics investigation of various eco-friendly solvents to find a suitable replacement for N-Methyl-2-pyrrolidone (NMP) (currently the most proficient liquid medium for graphene exfoliation via ULPE) using the optimum ultrasonication conditions identified in O2.

Action: Four solvents; three green solvents (water, ethanol and water/ethanol) plus NMP for comparison were investigated. They were sonicated and examined in terms of their cavitation zone development, bubble dynamics and acoustic emissions. Advanced fundamental analysis was conducted using high-speed imaging synchronised with acoustic pressure measurements complemented by shadowgraphic photography of the emitted SWs, in order to determine a suitable eco-friendly solvent medium from a cavitation bubbles dynamics perspective. Thereafter, ULPE of graphite in the optimum solvent took place for 2 h under controlled ultrasonication parameters of input power and solution temperature. The produced graphene samples were characterised by employing a series of techniques consisting of UV-Vis spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM).

4. The final project objective (O4) was to optimise exfoliation efficiency (size, thickness, quality, yield) for ULPE, utilising a dual-frequency (DF) setup based on the new knowledge acquired from the completion of O1, O2 and O3.

Action: The experiments investigated the bubble dynamics, acoustic pressure, spectra and induced SWs using a single, low frequency (LF) sonotrode (24 kHz) and a DF setup consisting of a LF (24 kHz) and high frequency (HF) source transducer (1174 kHz). Using ultra-high-speed imaging and synchronised acoustic pressure measurements, a DF system and its effect on bubble dynamics were investigated. The produced graphene samples were characterised by employing a series of techniques consisting of UV-Vis spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM).

1.4 Contribution to Knowledge

This research addresses and underpins some of the most important and novel contributions made in relation to the above objectives. These include:

- Identified real-time sono-exfoliation mechanisms during ULPE of graphite.
- Identified suitable solution temperatures and transducer input powers conditions for ULPE of graphite by understanding/elucidating bubble dynamics and acoustic pressures.
- Identified how to regulate and optimise cavitation development and bubble dynamics for use of appropriate eco-friendly solvents as a replacement for NMP. Controlling the cavitation zone during ULPE was shown to facilitate the production of high quality graphene.
- Identified a quantifiable demonstration that the use of a DF system generates a range of benefits for cavitation activity, whereby the enhancement of SW generation was shown to facilitate the delamination of layered materials during ULPE and cut down processing times.
- Developed technological guidelines and reproducible protocol for ULPE and ultrasound-assisted technologies.

The research presented in this thesis provides a strong foundation for ULPE, by first establishing the precise mechanisms of ultrasonic exfoliation. The technological step-change advance lies in developing a systematic, scalable and environmentally friendly process for

ULPE of graphene that reduces the processing time from tens of hours to only a couple of hours whilst increasing yield, quality and size of the 2D sheets.

1.5 Thesis Outline

A scrupulous effort has gone into the research, writing and structuring of this thesis. The overarching structure and narrative provide a coherent and cohesive flow of topics, with the intension of delineating the research with brevity.

This thesis primarily focuses on the influence of ultrasound in various liquids, generating acoustic cavitation, whereby the analysis of the acoustic emissions and bubble dynamics (in addition to fundamental studies of their interaction with graphite) led to developing an eco-friendly ULPE method to produce high quality 2D materials.

The following chapter (Chapter 2) presents an extensive literature review on recent and relevant topics pertaining to ULPE and acoustic cavitation, specifically delving into solvent and frequency studies. This basis will aid the reader to familiarize or highlight important concepts, useful to understand the subsequent results and discussion chapters.

Chapter 2 begins with a basic overview of the discovery of 2D materials, highlighting their importance, benefits and current limitations. The chapter continues by explaining the various exfoliation methods and delineating their benefits and drawbacks. Next, acoustic pressure and streaming are discussed, which regulates recirculating flows and borders of the cavitation zone. These important factors affect bubble activity, acoustic emission spectra and the cavitation zone. A thorough and fundamental review on acoustic cavitation is provided for the reader, as this knowledge is no doubt necessary to understand the mechanisms of cavitation induced exfoliation process of layered bulk materials as discussed in Chapter 3. Finally, specific attention is given to ULPE, using existing research to provide context as to why this particular method is the focus of the thesis.

The subsequent chapters (3-7) document all the important experimental work carried out during this research project. The chapters begin with a brief introduction, followed by methods, materials & experimental setup, results & discussion and finally concluding remarks.

Chapter 3 begins with an investigation and experimentation into the sono-exfoliation mechanism of graphite. This fundamental study was imperative to determine the most salient exfoliation mechanisms at play during ULPE. Ultra-high-speed shadowgraphic imaging of

laser induced single bubble interactions with fixed graphite flakes were recorded at 1 Mfps. High-speed imaging of bubble cloud interactions with fixed graphite flakes induced via an ultrasonic probe were recorded at 100 kfps. SW impact was monitored while acoustic measurements, taken using calibrated sensors, allowed us to estimate the required pressures to initiate and propagate delamination of layered graphite.

Chapter 4 presents a systematic study to determine optimum solution temperature and transducer input power conditions for ULPE. A calibrated cavitometer was used to measure the acoustic pressure of graphite powder (GP), graphite flakes (GF), and deionised water (DIW) solutions between temperatures of 10-70 °C, using three input powers (20, 50, 100%).

Chapter 5 experiments consisted of analysing solvents bubble dynamics and acoustic emissions to identify a suitable eco-friendly solution for ULPE. Synchronised high-speed imaging with acoustic pressure measurements were taken for potential green solvent candidates. Additionally, shadowgraphic high-speed imaging was taken to analyse SW generation of the solvents. Brief graphene characterisations demonstrated the success of the solvent bubble dynamics experiments.

Chapter 6 presents an investigation of the effect of dual-ultrasonic frequencies on eco-friendly solvents bubble dynamics and acoustic emissions. Comparison of a single frequency probe (24 kHz) and a DF setup (24 kHz + 1174 kHz) was carried out using synchronised high-speed imaging with acoustic pressure measurements in conjunction with shadowgraphic high-speed imaging. Graphene characterisations using the established DF setup demonstrated the success of the solvent bubble dynamics experiments.

The final chapter (Chapter 7) summarises the important findings from the aforementioned experimental studies, followed by the potential future work as a consequence of the research results from Chapters 3-6.

Chapter 2

Literature Review

2.1 Two Dimensional Materials & Exfoliation Methods

The importance and utility of layered materials has long been known, far before the concept of scientific analysis. At the height of the Mayan civilisations (after 250 AC), layered materials were being used to create layered clays and dyes. With the development of scientific research, the properties of these materials were identified and hence, the applications of layered materials grew. These uniquely structured materials consist of 2D plates stacked together producing a three dimensional (3D) crystalline structure. Layered materials interesting properties are a consequence of their atomic bonding and the forces which keep the atoms in formation. In general, layered materials can be categorised as having strong in-plane chemical bonds (i.e. covalent or ionic bonds) and weak out-of-plane forces (vdW's) which hold the stacked layers together. These vdW's forces require small distances between the 2D layers in order to remain stable. Due to the instantaneous dipole-induced dipole interactions, whereby apolar atoms can either be attractive or repulsive (hence, lack a permanent electric dipole moment) one orientation of the molecule becomes somewhat positive or negative [14]. The proclivity of these dipoles to align with each other is sufficient to generate a weak positive force, holding the layers together.

The disruption of this interaction between the stacked layers is what gives rise to the phenomenon called exfoliation. Exfoliation is the removal of layers from the bulk 3D material by overcoming the respective vdWs forces in place. This process can also be called delamination. Given sufficient force and persistence, a 3D material can be exfoliated all the way down to only a single layer, also called a mono-layer, therefore generating a 2D material (i.e. a one atom thick material). One way to conceptualize this phenomenon is to think of a bulk layered material like a book made up of many pages (atomic layers), whereas an individual page would represent only one atom thickness.

The archetype of 2D materials is graphene, the first ever isolated 2D material exhibiting a multitude of exceptional properties. Graphene is a mono-layer of graphite, which features carbon atoms covalently bonded in a hexagonal honeycomb lattice. Novoselov and Geim from the University of Manchester first successfully isolated graphene in 2004 [3] using a “top-down” exfoliation method called mechanical exfoliation. This process was wonderfully

simple and exceptionally effective, with scientists praising the method for its ingenuity. For this experiment, a synthetic material called highly oriented pyrolytic graphite (HOPG) was used. The benefit of HOPG is that it features an ordered crystalline structure enabling heightened physical properties when exfoliated to nanosheets. Using scotch tape, layers were peeled from the HOPG whereby atomic force microscopy (AFM) was used to characterise the decreasing layer count. This arduous and repetitive process of cleaving layers and characterising was conducted until a single layer was observed. Using acetone, the graphene was successfully removed from the tape and placed onto a silicon substrate to determine its properties using a range of characterisation techniques.

Despite the successful experiment, the limitations were evident. In a laboratory scenario the method was appropriate (despite being time consuming and tedious) for generating 2D materials, however, for a commercial setting, demand would never be met. In the wake of this revelation, various exfoliation methods were pursued to extinguish the processing time and quantity limitations.

Some types of 2D materials can be built upwards as opposed to delamination. These are called “bottom-up” methods (essentially the opposite process of mechanical exfoliation, a “top-down” method). Chemical vapour deposition (CVD) involves a heated vacuum chamber whereby gaseous precursors react and deposit 2D layers on a substrate. The upside is that having such control over the generation of the material, the quality can be exceptional. However, the downsides are to be expected; with high energy demands (a consequence of extreme temperatures over 1000 °C and maintaining the vacuum chamber) leading to large production costs, and hence scalability issues [15], [16].

Liquid phase exfoliation (LPE) possesses the capability of producing high quality 2D materials with fairly large surface areas in addition to competing as a cost effective and low energy alternative to CVD [7]. About a decade ago, Coleman’s *et al.* initial research involved producing graphene dispersions with concentrations up to 0.01 mg ml⁻¹ using toxic solvents such as NMP and N,N-Dimethylacetamide (DMA) as liquid media for dissolution of bulk graphite [8]. This method has since developed successfully using additional complementing techniques such as high-shear mixing (providing additional shear forces to aid in delamination of layers during LPE) [9] or intercalation [17]. A high-speed mixer is used to subject the starting material to intense shear forces, causing it to exfoliate into thin layers. The process involves dispersing the starting material, such as graphite, in a suitable

solvent, which is then placed in the mixing vessel [18]. The mixer typically consists of a rotor and a stator, with the rotor rotating at high speeds to generate shear forces. As the rotor spins, it creates a turbulent flow in the solvent, which causes the layers of the starting material to be separated.

Intercalation works by inserting a guest molecule in-between the bulk layers of a material (providing certain criteria are met i.e. appropriate matching size, charge, etc.) consequentially inducing layer swelling therefore increasing the separation between the layers. This atomic layer separation increase allows for less chemical energy or agitation during LPE to facilitate exfoliation. This process often works via ion exchange, whereby the repulsion of oppositely charged ions in-between the layers increases layer separation distance [7], [19]. Despite producing high quality 2D materials, the drawback of LPE with intercalation comes at the complexity of the experiment, requiring various different guest molecules for intercalation, and the use of high energy equipment such as a cryo-pump, vacuum pump and furnace [17].

Another promising “top-down” exfoliation method is ultrasonic liquid phase exfoliation (ULPE) [11, 12], utilising energetic cavitation bubbles to facilitate material exfoliation. Powerful shear forces are provided via transient cavitation (shock waves (SW), liquid jets) and by rapidly oscillating cavitation bubbles (micro-streaming). Recently, ULPE was demonstrated to be a powerful method for exfoliation, generating 10% yield of high quality few-layered graphene under controlled and optimized experimental conditions [12], [20]. ULPE has the potential to become a competitive, scalable production method. The later section of the literature review will cover the utility of this method and up to date research, demonstrating the necessity of utilising this process, and in turn, lay out why this thesis research was predicated on ULPE.

2.2 Acoustic Cavitation

Before we delve into the literature and a detailed analysis of ULPE, it is first necessary to understand the background of acoustic cavitation. Cavitation is induced in liquids with the introduction of high energy longitudinal acoustic (ultrasound) waves which cause pressure fluctuations upon propagation. These fluctuations result in the formation and expansion (known as the rarefaction cycle) and subsequent collapse (known as the compression cycle) of the cavity, or bubble. The length of a fully complete pressure oscillation is considered the wavelength (λ). The duration of the time taken to complete one cycle of the wave is known as the acoustic period (T_a). Therefore, the frequency of the propagating wave is denoted as $f =$

$1/T_a$ (oscillations per second). Calculation of the velocity of the sound wave is derived from the frequency and the wavelength of the pressure oscillations; $c = f\lambda$.

The intensity of the pressure field (driven by rarefaction and compression cycles) is dependent on the frequency of the propagating wave. We consider an ultrasonic wave to be of an oscillating frequency larger than the human hearing range (20 kHz). If the acoustic pressure is greater than the ambient pressure (101.3 kPa) then the local pressure becomes negative during the rarefaction cycle. However, depending on the quantity of gas nuclei in the liquid, this pressure magnitude can be much smaller. The liquid is subject to expansion under this total pressure, therefore, these dissolved gases induce nucleation of tiny bubbles (cavities) which expands in the liquid medium until the bubble wall pressure exceeds the net pressure in the liquid [21]. When these bubbles grow to a threshold size (named the resonance size) and are unable to absorb additional acoustic energy, instability occurs and induces a localised high energy implosion during the compression cycle [22]. This cyclic phenomenon of bubble nucleation, expansion and subsequent collapse (causing implosions) occurring as a consequence of ultrasonic waves is defined as acoustic cavitation.

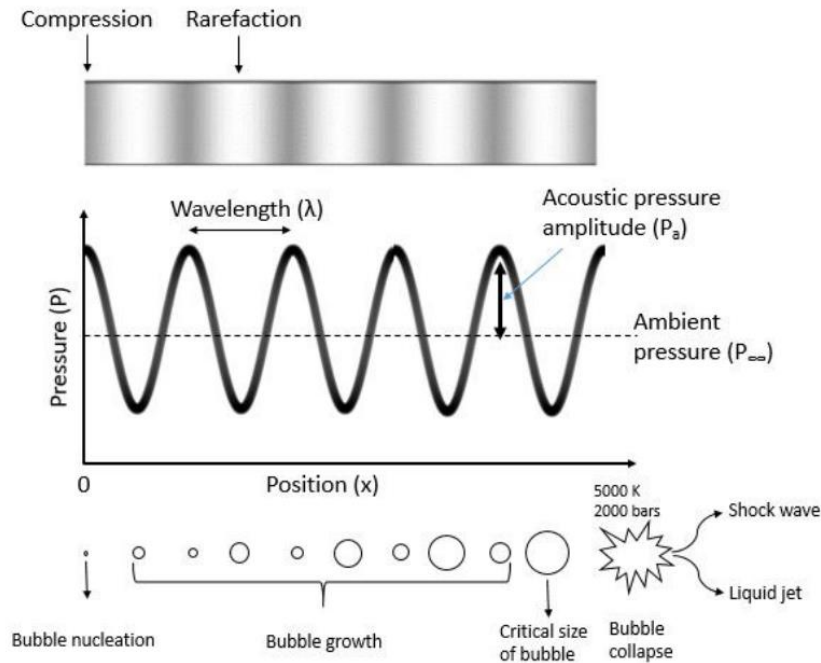


Fig. 2.1 Representation of acoustic cavitation displaying the rarefaction and compression cycles including bubble implosion [21].

There are two important mechanisms of acoustic cavitation, transient/inertial and stable/non-inertial cavitation. The former occurs due to bubble implosions generating extremely high localised temperatures (up to 5000 K) and impact pressures (up to 1 Gpa) [1], [23].

Consequently, these bubble implosions lead to the generation of SW and high-speed liquid jets that can also trigger formation of additional micro-bubbles in the vicinity that contribute to the cavitation regime. Transient cavitation, and the associated dynamic effects from the aftermath of the implosion are useful in a variety of applications. Some examples include emulsification, liquid melt processing, fragmentation, sonoluminescence, food and chemical processing, waste water treatment, a litany of medical uses (drug delivery, liposuction, lithotripsy, cancer treatment) and more [24]–[34]. Additionally (and of most relevant to this thesis), they are particularly useful in the facilitation of 2D materials through exfoliation [12], [20], [35]–[38].

On the other hand, stable cavitation are rapidly oscillating bubbles with small change in size and longer lifecycles that radiate low pressure amplitudes to the surrounding fluid generating micro-streaming phenomena around the bubble. They have lesser, but important uses such as cleaning surfaces [39] and again, have shown utility in exfoliation using less violent forces to gently scrub layers and can expedite exfoliation by fitting in-between layers and pulsating vigorously [37].

The distinction between the manifestations of these cavitation types lies in something called Blake's threshold. A collapsing bubble is dependent on reaching a critical radius (twice the equilibrium radius) [40]. This occurs at the peak acoustic pressure during the rarefaction cycle and is defined as Blake's threshold pressure. Some factors that affect this threshold include the driving frequency, vessel geometry and dissolved gas in the liquid medium. Research delineated by Nolting demonstrated that a cavitation bubble smaller than its resonance radius will experience smaller oscillations and may not collapse [41]. However, a bubble size greater than the resonance radius can still collapse, but the collapse is less violent, and the bubble may experience multiple cycles of expansion and contraction before collapsing completely. The Minnaert equation can also be used to estimate the size of cavitation bubbles in liquids. The equation relates the acoustic resonance frequency of the bubbles to their size, which allows for the estimation of the bubble size distribution in a liquid [42]. In general, the resonance frequency of a bubble is inversely proportional to its radius. This means that smaller bubbles will have a higher resonance frequency than larger bubbles.

Another interesting phenomenon to acoustic cavitation is acoustic shielding (and of great importance during the optimisation ULPE stage for this thesis). The cavitation index is a

useful definition for the population density of cavitation bubbles. We can describe this as the product of the number of bubbles formed in the unit volume and the maximum volume of a single bubble (volume at largest bubble size). As this ratio approaches 1, the bubbles formed per unit volume supersedes the liquid phase. This in turn reduces the transfer of ultrasonic energy into the liquid phase as it is absorbed by the gas phase, hence, the acoustic emissions are diminished [43].

Characterisation of acoustic cavitation can be achieved through various experimental methods. Analysis defragmentation or surface erosion of materials can provide an insight into cavitation intensity of bubble dynamics [44], [45]. High-speed optical imaging provides direct observation of cavitation events, which can be particularly beneficial for understanding the processes occurring in real-time [46]. Alternative methods of cavitation characterisation dynamics include analysing the sono-capillary effect [47], [48].

As there are various mechanisms and characteristics of acoustic cavitation it is often difficult or complex to describe the specific bubble dynamics occurring. Therefore, to provide clarity for the remainder of the thesis, the nomenclature used to describe the cavitation activity should first be defined. The “primary” cavitation cloud refers to the large bubble cluster formed directly under the sonotrode tip. The “secondary” cavitation cloud refers to bubbles that separate from the primary cavitation cloud. These consist of satellite bubbles and bubble clusters. The “cavitation zone” refers to the overall spatial distribution of the cavitation bubbles. These definitions will help to provide consistency when detailing cavitation activity hereafter.

2.3 Acoustic Streaming

One phenomenon that plays an important role and an effecting factor in ultrasonic cavitation is acoustic streaming. Acoustic streaming is the flow of fluid that is generated by an applied acoustic field. This phenomenon is caused by the interaction between the fluid and the sound waves, which results in the creation of vortices, micro-streamers and other flow patterns [49], [50]. Generally, acoustic streaming is mainly discussed under the conditions of either Eckart or Rayleigh streaming, with flow velocities of the magnitude cm/s for “fast” streaming and $\mu\text{m/s}$ for slower streaming [51]. Eckart streaming arises due to unbalanced radiation pressure leading to accelerated flowing of fluid in the direction of wave propagation. This results from the strong attenuation of ultrasound induced by cavitation bubbles. The direction and movement of the bubbles is a consequence of the primary and secondary Bjerkens forces.

The movement of the liquid is then consequentially controlled via the drag forces produced by the bubbles. Rayleigh streaming was discovered by Lord Rayleigh, who originally developed a solution that describes the steady vortices generated in the core of the fluid in a wide channel [52]. Rayleigh observed that the dissipation energy flux induced variations in momentum flux that caused streaming motions within the medium [53]. More recently, using advanced numerical modelling Lebon *et. al* showed that acoustic streaming is formed due to the formation of pressure zones across the bulk liquid that regulate the direction and velocity of the flow [54]. It was noted that the level of the streaming force and velocity depended on the properties of the liquid as well as the configuration of the external boundary field. The strength and direction of the streaming velocity is also dependent other factors including the frequency, amplitude and the surface area of the radiating source of the sound waves. Regarding the physical properties of the liquid, the attenuation coefficient (related to the inverse function of the sound velocity and viscosity within the medium) and bubble fraction volume effects the streaming velocity [55].

A variety of applications such as transport, separation and mixing of fluids are made possible by flow patterns generated by acoustic streaming [50]. Small scale acoustic streaming in a fluid is called microstreaming that is common in stable cavitation and occurs when the size of the cavitation bubble is smaller than the acoustic wavelength. As the bubble increases in size and eventually collapses the velocity of the microstream also increases.

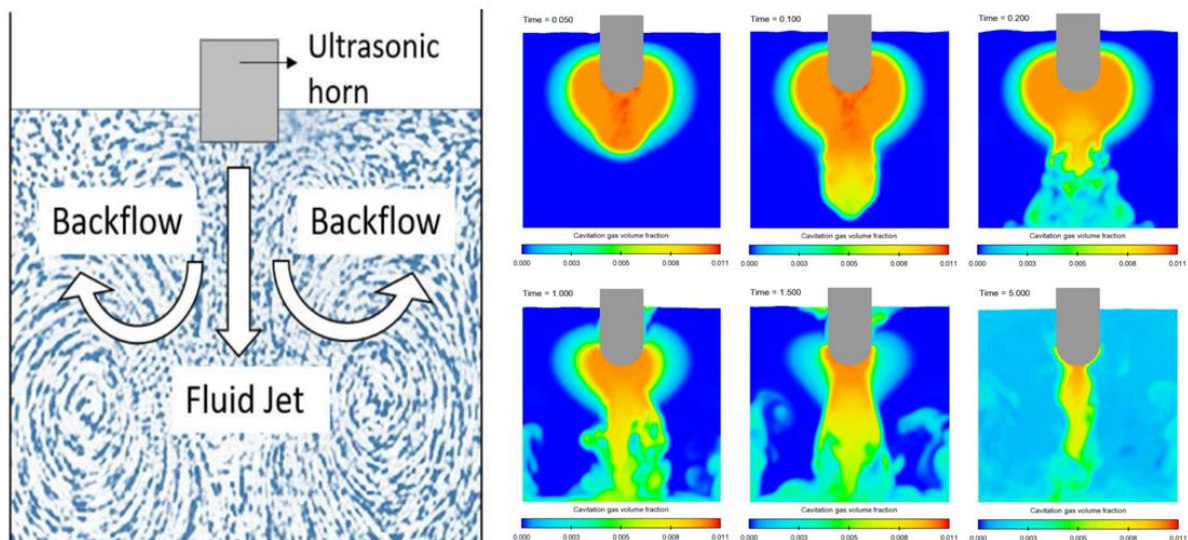


Fig. 2.2 Ultrasonic horn generating an acoustic streaming field. The recirculating back flow is observed, by an illustration on the Left, and simulation of acoustic flow on the Right. Adapted from [56], [57].

Fig. 2.2 shows an example of acoustic streaming. Once the ultrasonic horn is activated, a portion of its acoustic energy is absorbed within the liquid medium (whereby the rate of the absorption is proportional to the square of the introduced ultrasonic frequency). This absorption results in the amplitude of the ultrasonic wave dissipating in the liquid consequentially leading to a loss in momentum flux (and also acoustic pressure), which in turn generates the liquid flow in the direction of the wave propagation. For the case of Fig. 2.2 (whereby there are rigid walls contain the liquid) a vortex is induced producing liquid circulation back towards the ultrasonic horn. The horn in this environment produces an effect related to its size, which decreases with distance. After a sufficient distance is reached (a few lengths of the horn diameter) the streaming field negates due to geometrical spreading [37].

2.4 Acoustic Spectrum

It is paramount to the elucidation of cavitation phenomena to understand the experimental characterisation and theoretical analysis of ultrasonic emissions generated from an acoustic source. Ultrasonic cavitation has been demonstrated as a key process for a range of physical, chemical and biological applications [58]–[60]. Despite the litany of uses for this phenomenon, understanding cavitation characteristics still requires a great deal of research. For instance, it is pivotal for scaling up ULPE that acoustic cavitation must be controlled and optimised, and this is also the case for a variety of processes which utilise ultrasound in liquids [38], [61], [62].

Part of the complexity of analysing acoustic cavitation arises due to its stochastic nature in addition to producing a multi-bubble oscillating cavitating domain. The generated cavitation regime induces complex multi-bubble interactions which lead to non-linear acoustic behaviour. As expected, this phenomena means cavitation modelling and observation are particularly challenging [63]. We can, however, make use of various cavitation sensors which measure cavitation activity. These devices aid to characterise the acoustic emissions whereby analysis of the acoustic field, spectrum and intensity of oscillating bubbles can be achieved. Detection and characterisation of both low frequency (LF) (involving ultrasonic baths or sonotrode/horns) and high frequency (HF) (involving high intensity focused ultrasound or a membrane transducer) acoustic sources has been previously demonstrated [64]–[66].

Early experimental investigation into interpreting signals from cavitation include the detection and monitoring of cavities within glaciers with the aid of water tunnels [67]. This study utilised a cavitometer as its detection device, measuring velocity with two types of

acoustic signals. The first signal corresponded to the distance travelled, while the second measured the known time intervals. Then the height variations of the ice vault above the bedrock were recorded based on the distance signals, whose intensity was made to be a function of this height.

Modern day cavitometers can operate in a wide temperature range (up to 800 °C) and can be precisely calibrated to detect specific frequency ranges and work using the piezo electric effect. In regards to melt treatment research; they consist of an electronic block device and a hydrophone designed to protect against heat and cavitation erosion [35]. The hydrophone has a probe that is attached to a piezoceramic plate. The probe acts as a waveguide, coupling the acoustic signal from the cavitation zone to the piezoceramic plate. The waveguide is designed such that the distance between the heated metal and the sensitive piezoelectric element, as well as the casing of the latter ensures protection from heat. The piezoelectric crystals work by detecting the mechanical energy in the form of acoustic emissions, and converting this into an electrical signal which can be analysed via a PC. These signals can then interpret the acoustic spectrum and intensity.

Other important acoustic sensors include a needle hydrophone for directional detection of signal and a FOH for omnidirectional detections (ideal for SWs). The needle hydrophone works on the same principle as the cavitometer, utilising the piezo electric effect, whereby the pressure changes emitted onto the tip of the needle hydrophone (where the piezo electric element resides) are converted into an electrical signal fed to the PC. A FOH works by sending a laser through an optical cable. The acoustic vibrations are then converted into an optical signal whereby a signal processing system can be used to determine cavitation intensity or pressure. Many commercially available acoustic cavitation devices operate in low frequency ranges (20–400 kHz), however, acoustic emissions from collapsing bubble clouds encompass MHz frequencies. FOH's are beneficial due to their capability to be calibrated over a large MHz frequency range, while offering high sensitivity and precise detection of acoustic emissions due to exhibiting high spatial resolutions.

The uses of cavitation characterisation have evolved over a long period of research. Important research into ultrasonic cavitation by Young and Leighton in 1989 presented information on transient and stable cavitation emissions. An acoustically induced cavitation noise spectrum typically comprises of several peaks that are closely associated with the driving frequency field (f_0). In addition, other peaks arise as a consequence of harmonics (nf_0), subharmonics

(f_0/n) and ultraharmonics (n/mf_0) , whereby n and m are integers and n/m is a non-integer. A typical plot of acoustic cavitation signals is shown below (Fig. 2.3).

The driving/fundamental frequency (f_0) is generated by the driving acoustic field, hence it usually appears as the most prominent frequency peak, and features linearly cavitating bubble emissions [68]. The harmonic frequencies denote the integer multiple of the fundamental driving frequency, arising as a consequence of nonlinear bubble oscillations and distortion of the incident wave [69]. Ultraharmonic frequencies are a representation of the non-integral fraction of the fundamental frequency. Subharmonic frequencies are the fraction or integer submultiple of the driving frequency component, also denoted as cavitation inception [69]. This phenomenon can occur when the bubbles have an equivalent size to twice or more the resonance size, and reach the critical size in more than one acoustic cycle before collapsing [70], [71]. Additionally, subharmonic frequency peaks also correspond to the propagation of periodic SWs [72]. The low acoustic intensity across the frequency spectrum is called the broadband noise. This arises due to cavitation bubble collapses and SW generation [69].

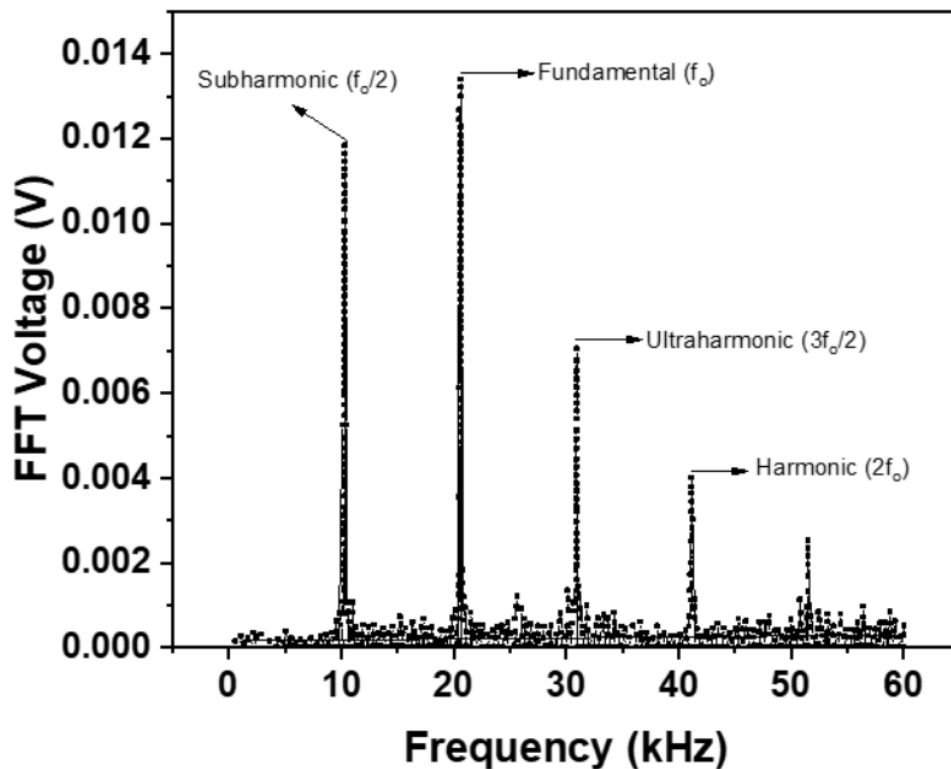


Fig 2.3 Acoustic cavitation noise against frequency, taken using a hydrophone [68].

Being able to resolve the acoustic spectrum in conjunction with elucidating the bubbles behaviour allows us to better understand the mechanisms behind exfoliation of 2D materials, and control the processing while also monitoring and optimising production at a large scale.

As previously mentioned, high-speed optical imaging is useful as it provides direct observation of cavitation events. Advanced analysis of cavitation activity can also include a synchronised process of observing bubble dynamics in real-time through a high-speed camera whilst also monitoring acoustic pressure simultaneously through a sensor. By using a Peripheral Component Interconnect (PCI) card both the camera and sensor can be linked together whereby a synchronised trigger system will activate an acoustic sensor as soon as the camera records the first frame. This technology allows observation of the acoustic spectrum in sync with the corresponding bubble dynamics. Therefore, the collapse of a cavitation cloud can be specifically mapped to an acoustic emission signal. This technique is useful when trying to analyse how layered materials are being interacted with in the cavitation zone (where the majority of exfoliation occurs).

2.5 Ultrasound Assisted Liquid Phase Exfoliation

2.5.1 Effect of Cavitation Dynamics

Without sufficient agitation, layered materials often lack the energy required to dismantle the vdWs forces holding them together. As mentioned, agitation in the form of acoustic cavitation is a resourceful and fairly efficient manner in which to exfoliate layers in LPE. However, that being said, the fundamental mechanics and interactions between the bulk layered material and cavitation bubbles were poorly understood. Various simulations have been produced to hypothesise these interactions. Transient cavitation bubble collapses inducing liquid jets were thought to be the driving force for exfoliation. These liquids jets are shown to penetrate the surface of the layered material (Fig. 2.4.1 (a)). As they do, localised high thermal energy is also released [36]. Schematics have also previously been produced presenting similar transient cavitation interactions. Fig. 2.4.1 (b) portrays a liquid jet penetrating in-between layers to “wedge” them apart and break the vdWs forces. The schematic also demonstrates how liquid jets making contact perpendicular to the vdWs forces induce exfoliation via a compressive stress wave which leads to shearing of neighbouring layers [73]. A large achievement of this thesis was taking the next step to elucidate these mechanisms in more detail. The experiments conducted using high-speed imaging in the following chapter demonstrate SWs from bubble collapses were found to be the driving mechanism of sono-exfoliation, in addition to liquid jets and stable cavitation oscillating forces playing a secondary exfoliation role [37].

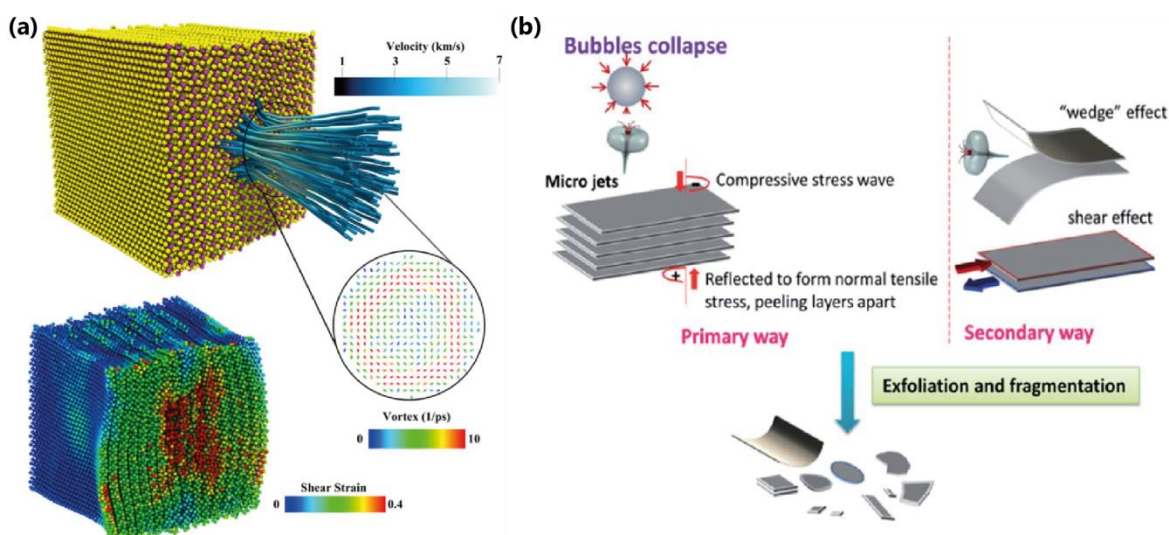


Fig. 2.4 Theorised interaction between cavitation bubble collapse and layered material. (a) A simulation of how a liquid jet induced via transient cavitation collapse penetrates the surface of the layers. (b) A schematic prediction of how liquid jets emit compressive stress force to shear layers, or alternatively induce a wedge effect to penetrate layers. Figures taken from [36], [73].

2.5.2 Solvent Selection

As briefly laid out in the research background, LPE is based on the dismantling of layered materials using liquid media. By utilising ultrasonic cavitation, LPE can be expedited with the aid of acoustic cavitation and the resulting SWs, liquid jets, micro-streaming and acoustic flows facilitating the exfoliation of graphite (known as ULPE) [37].

Coleman *et al.* work has largely led the development of this method [7], [8], [19], [74]–[76], although most of the experimental process and investigation has been focused on the use of solvent rather than the exfoliation mechanisms and the use of an ultrasonic source, either sonic bath or sonotrode, as a complementing factor. The use of different liquid media (such as organic solvents (polar solvents), ionic liquids, aqueous solutions and surfactants) behaves differently in decreasing the potential energy barrier needed to delaminate layered materials. It was found that polar aprotic solvents such as NMP and Dimethylformamide (DMF) were especially suitable for exfoliation of graphene [77]. This was due to the surface energy of the solvents (40 mJ m^{-2}) being relatively close to the surface energy of graphene (35 mJ m^{-2}) (Fig. 2.4) [8]. This observation can be explained by Hansen’s solubility parameter, which is a method to predict the solubility of a substance in a particular solvent or a mixture of solvents [78]. It is based on the idea that substances with similar chemical structures and intermolecular forces dissolve well in each other. The solubility parameter measures the

energy required to break the intermolecular forces between molecules and is expressed in units of $\text{Mpa}^{1/2}$.

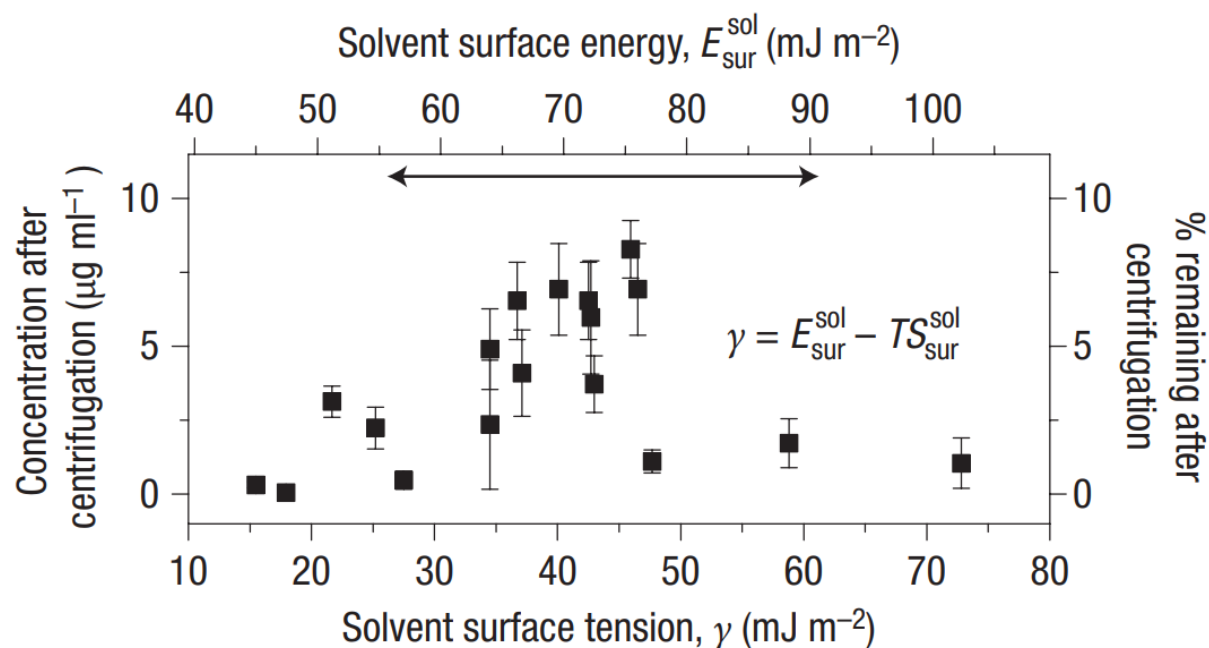


Fig 2.5 Plot showing surface tensions around 40 mJ m^{-2} being conducive to exfoliation of graphene [7].

Despite this successful correlation of suitable surface tension for exfoliation, the polar solvents such as NMP are harmful for the environment and pose some challenge to remove from the surface of the exfoliated nanosheets. In addition, the high boiling point causes complications whilst depositing individual monolayers on surfaces [79]. Therefore, other solvent types would need investigation to up-scale the graphene production in an eco-friendly manner.

Using DIW to exfoliate layered materials (such as graphite) would be an obvious choice due to its abundance, cheap cost and non-toxic nature. However, DIW presents strict limitations and lacks efficiency due to a surface energy disparity between the liquid and the layered material. This leads to dismantled layers re-agglomerating together shortly after the sonication ends. Surfactants can reduce the surface tension of DIW (initially 72 mN m^{-1}) to a lower value more suitable for graphite exfoliation (closer to a surface tension of graphene; 60 mN m^{-1}) acting as a stabiliser [8]. For instance, the surfactant sodium cholate (SC) in DIW has previously been used for these reasons [76], [80]. In addition, an appropriate solvent/surfactant such as SC can decrease the potential energy between adjacent layers in the bulk graphite, hence, overcoming the vdW interactions between layers [81].

Other solvents have also been investigated to improve the yield while using DIW for ULPE, in addition to the exfoliation quality. The aqueous solutions sodium deoxycholate (NaDC) and sodium dodecylbenzene sulfonate (SDBS) have been shown to improve yield and dispersion stability of graphene, due to charged nanosheets preventing re-agglomeration [10], [79]. Poly[9-(heptadecane-9-yl)-9H-carbazole] (PCz) with toluene was also demonstrated to facilitate exfoliation. As the PCz molecule contain a benzene ring, the large π bond in the conjugated structure interacts with the graphite lamellae, entering into graphite lamellae during ultrasonic cavitation, hence, promoting the exfoliation process in addition to stabilising the dispersion of graphene in toluene [10].

Ionic solvents have also demonstrated to aid in stabilisation of graphene dispersions in water. Ionic solvents are a type of organic salt which are beneficial for ULPE due to their high thermal stability, low melting point ($>100\text{ }^{\circ}\text{C}$) and importantly, low toxicity [82]. *Dai et al.* reported for the first instance that natural flake graphite can be directly exfoliated in 1-butyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide ([Bmim]-[Tf2N]) with probe sonication [82].

The choice of solvent is imperative to facilitate the exfoliation of layered materials and should be specially selected depending on the physical and chemical properties of the chosen bulk material. For ULPE the solvent choice is particularly important to enhance the cavitation zone and improve exfoliation efficiency. The above mentioned research examples demonstrate that a variety of potential eco-friendly solvents are available. However, further optimization of solvent selection is required to improve nano material generation, whereby additional parameters also play an important role.

2.5.3 Sonication Power and Duration

In addition to appropriate solvent selection for ULPE, sonication power and duration are also important parameters. For example, graphene concentrations of 1.2 mg mL^{-1} were previously recorded using a low-power sonication source in NMP but with a treatment duration of 460 hours (graphene concentrations up to 1.2 mg mL^{-1}) [83]. Concentration of graphene versus sonication time has been mapped (Fig. 2.5), whereby a proportionality relationship is observed. However, despite graphene yield increasing with sonication duration, this also gives rise to a reduction in flake size dimension, proportional to the reverse of square root of time ($t^{-1/2}$) [84]. Additionally, such long sonication durations also demonstrate resultant edge- and basal plane defects. These attributes are a consequence of repeated/continuous acoustic

cavitation, in the form of SWs, leading to long term exposure to acoustic emissions [37]. Thus, keeping time as short as possible by controlling the exfoliation process is a necessity i.e. monitoring the acoustic spectrum changes by using suitable sensors, while maximising yield is a desirable step forward.

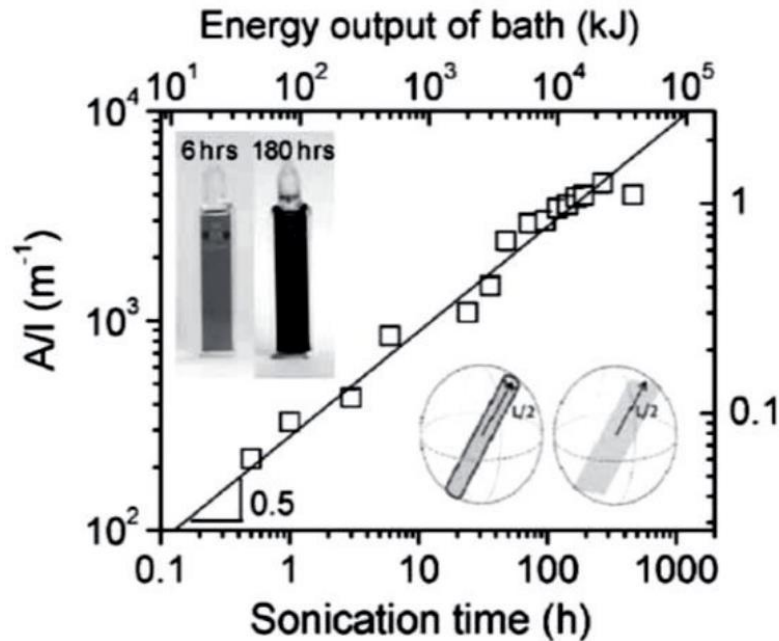


Fig 2.6 Graphene concentration against sonication duration [83].

The level of input transducer power can also be optimised to further improve yield and exfoliation efficiency. A larger input power generates a larger primary cavitation cloud produced under an ultrasonic horn. This in turn generally generates larger cavitation intensity (due to more transient cavitation and subsequent SW and liquid-jet generation). However, this is not always the case due to the acoustic/cavitation shielding effect [85]. As mentioned previously, when the population of bubbles becomes too large in a defined area, the acoustic emissions intensity is reduced. Effectively, the bubble collapses occurring under the horn tip interact with additional formed bubbles and therefore SW propagation is impeded, decreasing the overall cavitation intensity (at the cost of more energy used) [68], [86]. On the other hand, selecting a low input power reduces the cavitation cloud size, leading to fewer generated SWs and other acoustic emissions. This creates a negative effect on exfoliation and would require a longer sonication period to break apart the layered material. Therefore, a balance must be found when introducing cavitation into the system i.e. an appropriate input power for ULPE provides sufficient acoustic emissions whilst minimalizing acoustic shielding. It is also worth

noting that the input power effects the acoustic streaming within the liquid generating acoustic flow patterns that can re-circulate layered material particles back under the ultrasonic horn to expedite exfoliation. So by adjusting the input power you can regulate the acoustic streaming pattern and corresponding flows i.e. increasing input power above 50% for standard LF sonotrode ($\sim 200\text{-}500\text{ W}$) will drastically improve acoustic flow within a solution.

2.5.4 Effect of Temperature

One of the reasons temperature as a parameter for ULPE must be considered is its significance in effecting the physical properties of the liquid, and hence, the effect on exfoliating the layered material. As previously mentioned, properties such as surface tension have been of great importance during LPE as they effect the solution solubility i.e. Hansen's solubility parameter [78]. A similar surface tension between the liquid and bulk layered material facilitates exfoliation and aids to prevent re-agglomeration. Although surface tension does not vary drastically over small temperature changes, these differences can still alter exfoliation results and larger temperature changes bring about significant change to surface tension. For instance, over a range of temperatures from $0\text{-}100\text{ }^{\circ}\text{C}$ in water the surface tension drops from 76 to 59 mN m^{-1} [87]. Increases in solution temperature during ULPE are unavoidable due to the energy introduced into the liquid via the sonotrode or ultrasonic bath i.e. electrical energy converted into thermal energy. Additionally, increases in temperature can also affect the gas solubility and vapour pressure, which in turn can reduce the cavitation activity [88], [89], therefore reducing the exfoliation efficiency. Furthermore, high temperature solutions can also induce defects into the nanosheets as well as resulting in inconsistent exfoliation [90].

The aforementioned issues are generally overcome by employing a temperature control system during ULPE. Temperature moderation can be achieved by cooling fans, ice baths [12], [65], [91] or more precisely using a jacketed-beaker (dual-walled) connected to a cooling recirculator [92]–[94]. Generally, studies that include temperature moderation tend to aim to retain lower solution temperatures such as $20\text{ }^{\circ}\text{C}$ [95], under $30\text{ }^{\circ}\text{C}$ [91], [96] (not specified), $30\text{-}35\text{ }^{\circ}\text{C}$ [92], [93] and more. Specifically, temperature control using $40\text{ }^{\circ}\text{C}$ has proved some success for the efficacy of exfoliation. For example, the long-term stability of dispersed graphene has been reported using a $40\text{ }^{\circ}\text{C}$ liquid medium [97], citing that the elevated temperature introduced energy through the dissipation of sonic waves and remained stable up to 1 month in pure water (after sonication being stored at room temperature). Other

studies also noted an improved graphene quality sonicating at 40 °C [98], [99]. More recent studies have achieved greater yields and high-quality graphene in pure water; stating maintaining the same temperature at 40 ± 3 °C generated $\sim 1\text{--}3 \mu\text{m}^2$ and ~ 5 layers graphene in just 2 h [12]. Recent work also reported on an optimum balance of SWs and bubble clouds at 40 °C, producing efficient exfoliation in water as a liquid medium [38].

2.5.5 Effect of Frequency

The cavitation threshold is dependent on the driving frequency introduced into the liquid. As previously explained by the Minnaert equation, the acoustic frequency has an inversely proportional relationship with bubble resonance size. Therefore, this is an important consideration depending on the desired application of the acoustic cavitation. For ULPE, different cavitation sizes affect the interactions with the layered material and hence the exfoliation efficiency. Generally, ultrasonic horns have been used between 20-30 kHz for ULPE. This is partly due to the cavitation threshold intensity, which above 100 kHz rises significantly [100]. However, at low operating frequencies 20-30 kHz and in contrast to high frequencies above 100 kHz bubbles tend to acquire fairly large sizes i.e. in the range of few hundreds micrometers, hence, upon collapse powerful SWs and liquid jets are emitted that may have adverse effect of exfoliation quality damaging the produced flakes.

In the last decade more research has been conducted to investigate sonication frequency to improve exfoliation of layered materials. Telkhozhayeva et al. found using EtOH in bath sonication at 80 kHz produced thicknesses of three layers and less, with an average lateral size of 13 μm , for $\sim 77\%$ of the measured graphene flakes [91]. The results showed that using 80 kHz produced greater yields compared to a lower bath sonication frequency of 37 kHz (which did not produce any monolayer graphene), and a sonication probe using 20 kHz. It should be noted that for usually a probe sonication generates much larger acoustic emissions than sonication baths, hence, we may expect the probe to perform better (although it is worth noting this is over a more confined zone). However, EtOH as a liquid medium for ULPE generates less powerful SWs (produced by probe sonication) as the low surface tension impedes bubble collapse [101]. Additionally, the higher vapour pressure promotes bubble formation but also impedes bubble implosion [101]. Instead, the physical properties of EtOH greatly enhance bubble oscillation while under a HF influence (as later seen in Section 6). Other research comparing a probe sonicator (42 kHz, 240 W) and a bath sonicator (42 kHz, 160 W) at the same frequency noted that the probe required less time to exfoliate graphene oxide (GO) successfully, however, at the cost of inducing more structural defects

[102]. Similar results were also found whilst comparing a probe of 20 kHz against a cup horn reactor of 500 kHz, whereby the graphite was sonicated in water for 1 h at 20 kHz and 10 h at 500 kHz, demonstrating longer sonication periods required while not using probe sonication [103]. [104]. It has also been established in sonochemistry that mechanical applications such as dispersion, disruption and homogenization are performed better using a LF device, typically around 20 kHz, whereas radical production is more efficient while using a HF ultrasonic source (between 200-300 kHz) [105]–[107]. It is for these reasons why this thesis work chose to start the research (Chapters 3-5) using LF probe sonication.

As there are benefits and drawbacks to using different frequencies for ULPE, some studies have focused on the use of a DF experimental setup. These tend to consist of a LF source and a HF source working in conjunction during ULPE. This combination allows for a range of larger cavitation bubbles generated from the LF source and smaller size bubbles generated by the HF source. For a reference, bubbles using a LF source of ~ 20 kHz are ~ 138 μm , and a HF source of ~ 1 MHz produce bubbles of ~ 2 μm in size (which can be calculated using the Minnaert equation, that predicts the bubble linear resonance size [108]). In this scenario the larger sized bubbles work at initiating exfoliation and breaking up larger sized graphite flakes (due to larger bubbly clouds generating more powerful acoustic emissions from SWs and liquid jets), whereas the smaller bubbles are able to penetrate in-between the layered material layers, vigorously oscillating and shearing the layers apart [20]. Vinodgopal et al. back in 2012 investigated the combination of 211 kHz in a continuous mode and subsequently a 20 kHz ultrasonicator operated using a pulse mode i.e. 0.5 s on and 0.5 s off [92]. The use of pulsing ultrasound has previously been seen to replenish nuclei, generating a larger cavitation zone and also capable of increasing cavitation intensity with bursts of high powered acoustic emissions [37]. Employing a short, powerful ultrasonic burst has also been shown to be beneficial for a variety of applications such as preventing reactor clogging and reducing energy usage [109]. Reducing the energy output for ULPE is especially useful to help scale-up this method. Unfortunately, it may also be true that pulsing requires a longer overall sonication duration for higher yields of 2D materials to be produced. However, another positive of pulsing is that the short periods where the probe is off aids in temperature control of the solution, which as previously discussed is imperative for increasing the nanosheets yield, quality and overall reliability of the process. Brotchie et al. have investigated the performance of using variations of LF and HF setups, and found that using a LF source in pulse mode with a HF source in continuous mode produced a two fold increase in the

observed sonoluminescence. Additionally, they have also demonstrated the sonochemical efficiency of the reduction of gold (III) chloride using a DF system, which consisted of a HF source at 355 kHz in tandem with LF probe operating at 20 kHz pulses. The results showed that the rate of reduction of the Au (III) is considerably enhanced under these DF conditions more than the sum of the individual frequencies being used. The enhancement in cavitation activity was ascribed to a greater number of active bubbles due to inhibition of bubble coalescence in the DF system [110], [111]. Despite these points, ULPE using a pulsed probe may also affect the acoustic flow in the solution, being less efficient at re-circulating the layered material particulates back into the main cavitation zone under the probe tip (where high powered SWs are localised [37], [112]), which would also contribute to increasing the material processing duration. Furthermore, it is also worth noting that a multifrequency system of HF and LF sources both in continuous mode has also been shown to enhance cavitation activity, based on the increased subharmonic emissions (associated with inertial cavitation) and sonoluminescence intensities [113], [114]. Other benefits of using a DF system have also been documented. Dual acoustic sources have been reported to enhance metal leaching rates and the final recovery values of the metals [115], as well as enhancing sono-chemical degradation of pentachlorophenol [104]. The enhancement of the cavitation zone and cavitation intensity by using a DF system has also been demonstrated by various other previous works [20], [113], [116], [117], and hence, is potentially a beneficial process to improve ULPE of layered materials.

Recent research investigated a range of HFs (208, 378, 992 and 1174 kHz) in combination with LF sources in a venture for the best graphene exfoliation product [12]. The data showed that 1174 KHz in conjunction with the 20 kHz horn had the best performance to exfoliate graphite [20]. The use of the HF source for ULPE was also shown to produce a gentler exfoliation (a less intense cavitation regime that promoted exfoliation via vigorously oscillating bubbles in the vicinity [118] or in-between the flakes [37] imposing a layer fatigue exfoliation effect) than the LF source, which generated smaller yields with less quality nanosheets due to more induced defects into the surfaces and edges of the layers. This DF set up promotes bubbles' nucleation and greater acoustic pressures facilitating the exfoliation of graphite. Consequently, characterisation of the graphene nanosheets revealed sizes of up to 3 layers and cross-sectional areas of $1.5 \mu\text{m}^2$. This research was further improved by the addition of surfactants (SC) and using a DIW/EtOH solution which was shown to greatly

increase the stability of the exfoliated material. The enhanced cavitation zone generated by SC under the DF setup was able to produce an 11% yield [119].

2.5.6 Functionalisation of 2D materials

To end this chapter it seems appropriate to briefly discuss some industrial processes to functionalise 2D and nano materials after their exfoliation has taken place. Once the primary challenge to produce a high-throughput manufacturing of 2D materials is achieved, the remaining tasks are the functionalization and application of 2D materials that currently impose restrictions to reach the global markets with any emerging applications.

Depending on the desired application of the 2D materials, the exfoliation methods should be suitably considered. This is because the quality and yield of the nanosheets are often dependant on the process used for exfoliation. For instance, “bottom-up” methods such as CVD and ALD are limited by the high energy demand, cost and furnace size which reduces yield output due to scalability issues. However, as the method facilitates precise, single layer (SL) deposition on a substrate, pristine graphene or other 2D materials can be made [120]. The benefit of these materials is that their unique and extraordinary properties are not inhibited. This means applications that require significantly large electron mobility (such as semi-conductors) are an optimum choice for functionalisation. However, for mass-production to take place in an industry such as the mobile/smart phones to generate display screens, material processing times need to be greatly reduced.

On the other hand, ULPE cannot currently produce exactly the same yield and quality of exfoliated 2D materials every time due to the stochastic nature of ultrasonic cavitation and lack of precision bubble interactions with the bulk material. Complexities also arise from the rheology of the solution and localised cavitation zone ensuring the tendency that some layered material will be more exposed to high energy shearing forces than others. Although the output yield is greater than CVD, a controlled process is required to prevent variations in size, cross-sectional area of nanosheets, and generation of SL, few-layer (FL) and multi-layered graphene (MLG), with the likelihood of some induced layer defects within the overall yield. However, due to the abovementioned larger yields and cheaper production method of ULPE, appropriate applications are often flexible and ink-jet printed electronics, coating technology [121] or graphene quantum dots [122]. In the medical field, applications can include cell imaging, bio-sensing, tissue engineering, cellular interactions in neuroscience and eco-toxicological studies [38]. This wide variety of applications is another reason why

ULPE is considered a viable method to generate nano materials, and hence, was selected as the processing method for this thesis research.

Before this functionalisation occurs, a processing method of the graphene must be taken. Preparation of graphene samples starts once sonication is complete. A common procedure involves extracting the dark graphene poly-dispersions from the supernatant of the solution and placing them in a centrifugation device. This acts to sediment any un-exfoliated graphite particles/thick flakes. The resultant liquids are then placed onto suitable substrates and dried in a low heated furnace. Sophisticated ULPE processing includes a pump system which extracts exfoliated graphene from the solution after a set period, thereafter, replacing consumed liquid and source material to generate an industrial-style continuous process for ULPE. Utilising the materials can also involve surface modification to induce hydrophobicity, hydrophilicity, conductivity and corrosion resistance beneficial to enhancing the performance of the nanomaterials [123].

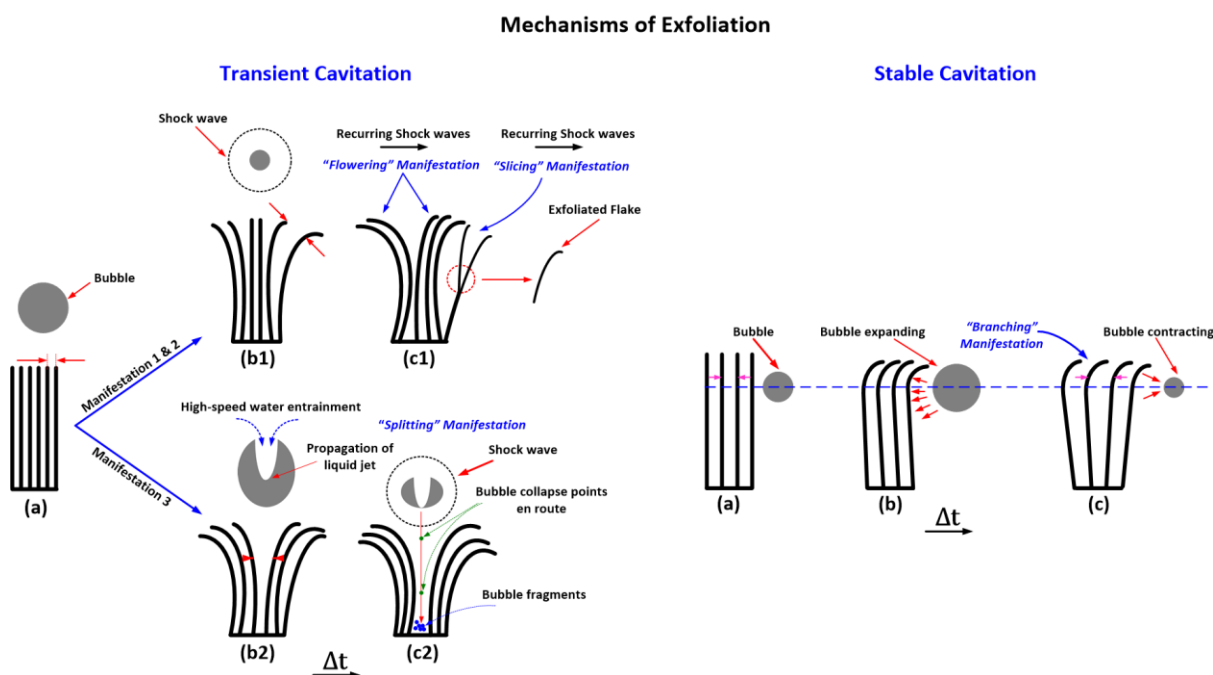
Despite these simple premises, protocols for efficient centrifugation are missing from the literature and vary from device to device. This means that an optimum protocol should be tailored to specific equipment and experiment setup. This specificity also extends to the ultrasonic parameters as well as the characterisation procedure. For instance, determining the yield or quality of the produced 2D materials can vary depending on which flakes are selected from the supernatant for analysis, which does not necessarily provide an accurate representation of the overall output nanomaterials. Due to this limitation, utilising a range of techniques provides more reliability and certainty when characterising nanomaterials. The following research in this thesis makes use of combining UV-Visible, Raman and TEM to ensure consistency (Chapters 5-6).

Following the literature review on the basic principles of acoustic cavitation and exfoliation mechanisms of 2D materials, we can now begin a detailed discussion into the experimental research which took place for this thesis (Chapters 3 to 7). Newly uncovered research and fundamentally important insights related to the identification of specific cavitation mechanisms that play a pivotal role for the development of ecologically friendly (as all experiments were performed in water) graphene sheets and other nanomaterials are delineated in this thesis. Furthermore, a robust, sustainable, eco-friendly procedure for ULPE of graphite is presented by systematically conducting tests to optimize and control the experimental parameters as shown in detail throughout chapters 4-7. However, a sensible

precondition to these experiments was first to understand how graphite flakes were interacting with acoustic cavitation by elucidating, for the first time, numerous manifestations that occur during sono-exfoliation. This work is presented in the next Chapter 3.

Chapter 3

Sono-exfoliation Mechanisms of Graphite



Graphical abstract: Sono-exfoliation mechanisms of graphite depicted for both transient and stable cavitation interactions.

Chapter Abstract

The application of ultrasound and acoustic cavitation in liquid exfoliation of bulk layered materials is a widely used method. However, despite extensive research, the fundamental mechanisms remain far from being fully understood. A number of theories have been proposed to interpret the interactions between cavitation and bulk layered materials and hence to explain the mechanisms of ultrasound assisted exfoliation. Unfortunately, most of the research reported to date is ambiguous or inconclusive due to lack of direct real-time experimental evidence. In this chapter, systematic work characterising cavitation emissions and observing the exfoliation of graphite in situ, in deionised water under the dynamic interaction with laser and ultrasound induced cavitation bubbles is reported. Using ultra-high-speed optical imaging, we were able to determine the dynamic sequence of graphite exfoliation events on a time scale never reported before. Four specific manifestations of “flowering”, “slicing”, “splitting” and “branching” driven by the two main mechanisms of transient and stable cavitation were identified and demonstrated to be essential contributing

factors to graphite exfoliation. Real-time observations also revealed that SWs with a pressure magnitude up to 5 Mpa and liquid-jets in the range of 80 ms^{-1} , from transient cavitation bubble implosions, were essential for the initiation and propagation of the exfoliation process. On the other hand, bubble oscillations associated with stable cavitation were beneficial for promoting a gentler delamination of graphite layers.

Published as J A. Morton, et al., Materials Today. Volume 49, Pages 10-22, October 2021- Reproduced after permission.

3.1 Introduction

The addition of ultrasound to assist exfoliation during LPE is a cost effective and energy efficient technique that uses the dynamics of cavitation bubbles to supply the necessary shear forces for exfoliation (sono-exfoliation). Cavitation bubbles were previously shown to be capable to generating high-speed liquid-jets exceeding 100 ms^{-1} [124], [125] and local hydrodynamic impact pressures up to 1 Gpa, which have been regarded sufficient to promote rapid exfoliation of bulk layered materials [1]. However, such exfoliation events have yet to be observed *in situ*, and sono-exfoliation mechanisms have only been suggested based on post-treatment analysis [126], [127]. Only very recently, experimental evidence from acoustic pressure measurements indirectly indicated that transient cavitation (associated with SW generation) is the main driving exfoliation mechanism in a sonicated environment [90]. On the other hand, a recent numerical approach revealed that the initiation of exfoliation is predicated on initial large shear forces from nano-jets (generated during bubble implosion), subsequently followed by tensile stresses from reflected SWs facilitating delamination of the surface layers, by overcoming the VdW forces [36]. These studies place emphasis on the contribution of SWs to sono-exfoliation, although the lack of *in situ* experimental evidence due to the inherent difficulties in capturing the real dynamic events in real-time, impose validation restrictions and limits our understanding, and consequently optimization and scale up of this promising process.

In this study we took the next step with advanced *in situ* observations of the sono-exfoliation process complemented by numerical modelling and *in situ* measurements of the acoustic pressure field. We thoroughly studied the exfoliation mechanisms of graphite flakes subjected to laser induced bubbles (LIB) (spatiotemporally controlled cavitation collapses) and acoustic

cavitation (multiple uncontrolled bubble collapses/sonicated environment). We investigated the role of different types of cavitation bubbles (transient and stable cavitation) in the exfoliation process, and elucidated their respective importance and contribution. Results of direct *in situ* experiments and camera observations made it apparent that there are multiple “manifestations” of exfoliation occurring, which have not previously been thought about. The next sections will analyse each of these newly identified manifestations in detail. Due to the benefits of developing a large scale environmentally friendly exfoliation process, all experiments were performed in deionised water as the prime liquid medium.

3.2 Methodology

3.2.1 Laser Induced Bubble Experimental Setup

The source material used was Sigma-Aldrich graphite flakes of approximately 149 μm in size (mesh 100). These were fixed vertically onto a metallic holder with a cyanoacrylate adhesive, which was then lowered and positioned into a custom-built chamber ($420 \times 438 \times 220 \text{ mm}^3$) on a translational stage filled with degassed and deionised water. The main components of the LIB set up included the pulsed laser, immersed parabolic mirrors, camera and synchronous illumination source as illustrated in Fig. 3.1(a). The full apparatus setup and schematic can be found elsewhere [128].

The water temperature was at ambient conditions ($25 \text{ }^\circ\text{C}$) and did not alter due to the generation and collapse of individual bubbles (because the duration of experiments was short). The design of the cavitation chamber allowed for precise image observation to capture the position of the LIB and the graphite flake.

A 6-8 ns laser-pulse was generated from 532 nm irradiation (Litron TRL 420-10 Q-switched frequency-doubled Nd:YAG), whereby the pulse was brought into focus through a curved mirror (Silver-Coated Concave Mirror, $f = 19.0$) and a macro-lens, which was used to provide imaging for the camera (Milvus 147 100 mm f/2M, Zeiss, Oberkochen, Germany). Laser power was between 10 and 88.8 mJ $\pm$ 10% (instrumental error) sufficient to generate elliptical plasma regions that rapidly expanded to form approximately spherical cavitation bubbles. The generated bubbles were within the range of ~ 0.8 -1.4 mm in radius at maximum inflation, experiencing between a ~ 0.18 and 0.3 ms lifecycle period before initial collapse. These bubbles generally underwent 3-4 rebound oscillation cycles.

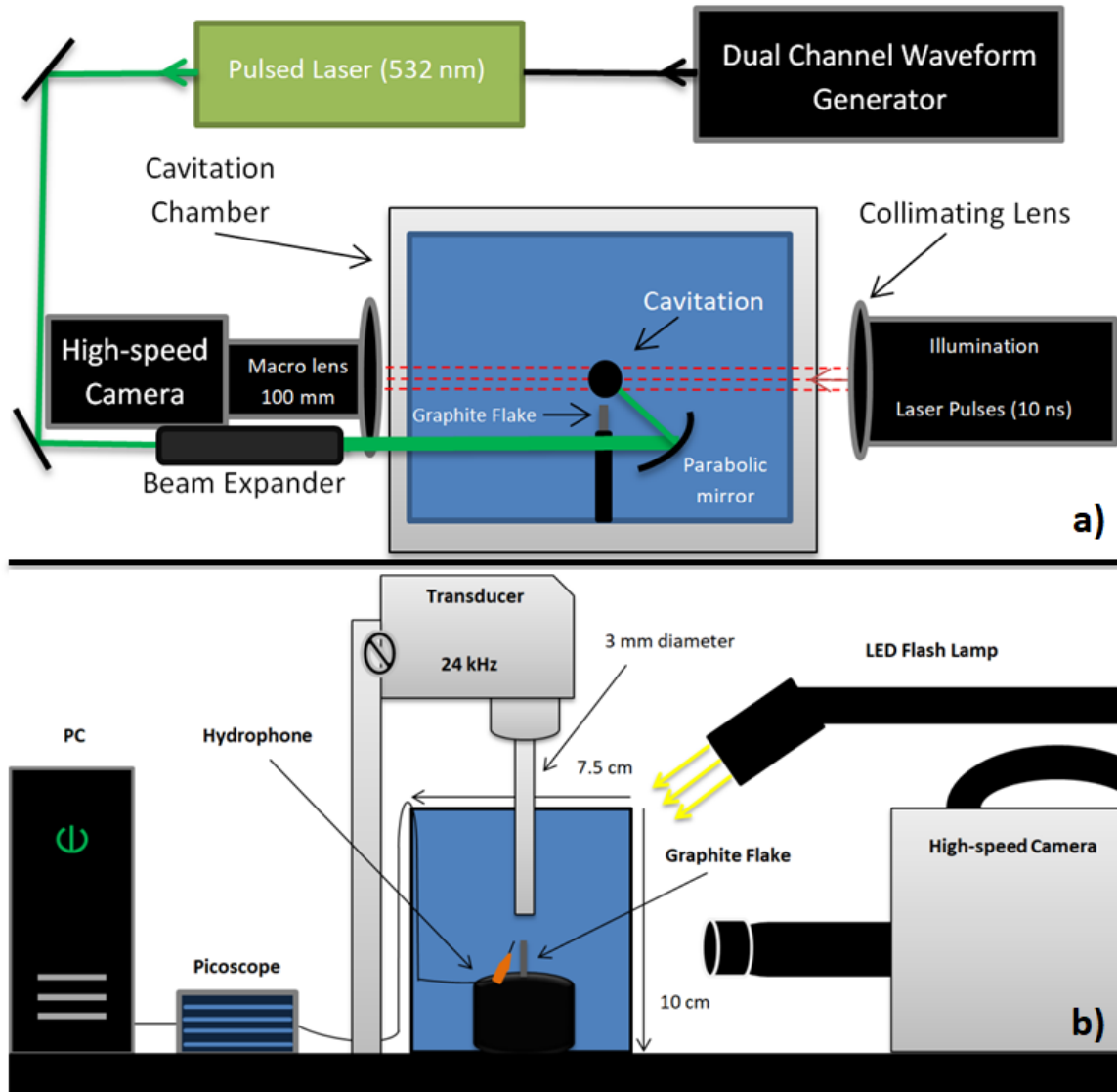


Figure 3.1. (a) Laser induced bubble (LIB) experimental setup. A 532 nm pulsed laser induces cavitation, illuminated by synchronous 10 ns laser pulses (640 nm) through a collimating lens, and recorded via high-speed imaging. **(b)** Schematic of the ultrasonic probe experimental setup including the sample, transducer, hydrophone, illumination, high-speed camera with oscilloscope and PC. The graphite flake is fixed to a substrate, with the sonotrode tip 1.2 and 2.5 mm distance over its centre (shown in Fig. 3.10 and Fig. 3.11). The fibre-optic hydrophone is positioned close to the graphite flake, with the same separation distance from the sonotrode.

Films were captured by high-speed shadowgraphic imaging using a Shimadzu (HPV X2) camera at a frame rate of 400,000 fps, with a resolution of 400×250 pixels, generating 256 frames for every recorded sequence. Synchronised 10 ns laser pulses through a collimating lens provided the illumination (CAVILUX Smart UHS system) and effective temporal resolution to observe the generated SWs.

3.2.2 Ultrasonic Probe Experimental Setup

Graphite source and sample setup was the same as mentioned above for the LIB experiment. This time a rectangular 7.5×10 cm glass chamber filled with deionised water (Hexeal chemicals) was used for measurements. The tank temperature remained ambient at 25 C° without the need of a temperature controller device due to using only short ultrasonic pulses (~250 ms) initiated from the sonotrode.

A Hielscher UP200S system with a 3 mm diameter titanium sonotrode and an operational frequency of 24 kHz was used to initiate cavitation. The peak-to-peak amplitude was set to 42 μm , corresponding to an operating power of 40 W, and used in a 25% pulse mode (~250 ms on/~750 ms off). The radiating surface of the vertically mounted sonotrode was immersed 55-57 mm below the liquid surface.

High-speed imaging was carried out using a Photron- SA-Z 2100K camera at a frame rate of 100,000 fps over 640×280 pixels, at a resolution of 12.7 $\mu\text{m}\text{pixel}^{-1}$ and a shutter speed of 8.39 μs . Illumination was provided by a powerful front light beam LED flash lamp (GS Vitec). Fig. 3.1(b) shows a schematic of the experimental setup.

Within the scope of our study, the size and shape of graphite flakes used did not affect the mechanisms observed with in situ observations (see Table 3.1).

3.2.3 Acoustic Pressure Measurements and Data Acquisition

A fibre-optic calibrated hydrophone system (Precision Acoustics Ltd) was used to measure the acoustic pressure emissions to which the graphite flakes were exposed, generated by cavitating bubbles and bubbly clouds via a sonotrode. The hydrophone was calibrated between 1 and 30 MHz thus only the pressure exerted from SWs could be captured and analysed as they lie within this frequency range [112]. The fibre-optic sensor was located at a distance of 1.2 and 2.5 mm from the tip of the sonotrode corresponding to the graphite flake position. These locations were chosen as they demonstrated a range where rapid exfoliation took place (up to 3 mm), including examples of both direct and indirect cavitation cloud interactions with the graphite flake, and being prime examples of the exfoliation mechanisms taking place. The pressure measurements were captured via a digital oscilloscope (Picoscope 3000 series) connected to the hydrophone and 60 waveforms of cavitating emission signals

were recorded and averaged. The corresponding readings were converted to spectra using fast Fourier transform over a 2-ms time period as previously shown elsewhere [85], [112]. The conversion process was used to calculate the maximum pressure ($P_{\max}$) values from the hydrophone output voltage, and also intrinsic background noise was removed during this stage, by means of subtraction from the initial voltage signal.

3.2.4 Multiphysics Modeling

The volume of fluid VOF method was used to track the bubble (primary phase) surface dynamics in water (secondary phase), assuming that the phases are not interpenetrating. The two phases are considered compressible. The continuum surface force (CSF) model was used to describe the effect of surface tension in the VOF model. The Reynolds averaging method (RANS) was used to handle turbulence in the flow field. The RANS method is based on the Navier-Stokes (N-S) equation, and introduces the Reynolds hypothesis to formulate the Reynolds-time N-S equation. Further details about these models can be found in the references elsewhere [129], [130].

Using bubble parameters (bubble diameter and distance from the graphite flake) from the single LIB experiments, simulations were developed to estimate SW impacts and bubble oscillation pressures. These simulations and estimates are to serve as an indication to the magnitude of forces emitted onto the graphite flake in each case of manifestation. I must declare that this contribution of experiments was conducted by Ling Qin of the University of Hull. Due to the relevance of the experimental analysis of this section this data is included.

3.3 Results & Discussion

3.3.1 Single Laser Induced Bubble Experiments

By focusing a laser beam, plasma is created within the liquid medium, which rapidly expands to form a growing cavity [128], [131], [132]. One of the benefits of producing cavitation through this method is that the position of the cavity can be easily determined and controlled, unlike the inherently stochastic nature of forming inertial bubbles from a sonotrode. In the latter case, bubble dynamics are difficult to discern due to the number of cavities formed. Moreover, by removing the uncertainties such as observing multibubble clouds, and knowing where and when a cavitation bubble will form, we could use a high-speed camera to capture high-definition and exceptionally high-frame-rate images capable of resolving these interactions and dynamics. For this study, individual bubble interactions including shock waves, liquid jets as well as oscillatory effects of stable bubbles with graphite flakes provided

a much more controlled observation and enabled the analysis of sono-exfoliation mechanisms occurring in response to acoustic cavitation.

Both types of cavitation bubbles; transient (rapidly changing bubble diameter with implosion) and stable (higher stability bubbles, pulsating for longer periods of time) were found to contribute to the exfoliation of the studied graphite flakes. In particular, the implosion of bubbles located just above the top of the graphite flake, aligning to the in-plane direction of the bonded inter-graphitic layers, was found to be effective. The orientation of the graphite flakes in this report were designed to promote scissions into the graphite layers and, hence, the samples were fixed vertically onto the metallic holder with adhesive. Evidently, this would not necessarily be the case in an uncontrolled or industrial scenario, however, the practicality of this report was to investigate and elucidate the fundamental mechanisms that promote and facilitate exfoliation, and propose optimised setups and sonication parameters leading to more efficient treatment.

3.3.1.1 Exfoliation via Transient Cavitation

Figure 3.2 demonstrates how the surface area of the graphite flake tip expanded (Fig. 3.2(d1)) from consecutive bubble implosions at the point of impact, which occurred at a distance between 0.8-1.25 mm above the graphite flake tip, ensuring contactless interaction, i.e. resulting in only SW interactions with the studied samples. Multiple SW fronts were recorded interacting with the graphite, promoting exfoliation in a manner resembling that of a flower blooming. This “flowering” manifestation appeared to constitute an initial stage of separation of layers at the graphite tip, hence widening the top of the graphite flake with force exerted by powerful SWs. Numerical modelling generated via the 2D VOF was used to provide estimates for LIB in situ measurements. These consisted of using specific bubble parameters for each experiment case. More information on these models can be found in the Method (Section 3.2) and the Appendix Section A. SW impacts based on parameters from Fig. 3.2 were estimated to emit pressures in a range of ~ 0.45 to 1.2 MPa depending on their initial distance away from the graphite sample. The temporal accumulations of these impacts were shown to drastically change the morphology of the graphite flake.

Initially, the thickness at the tip of the graphite flake was ~ 0.28 mm (Fig. 3.2(a1)), 30 LIBs later (Fig. 3.2(d1)) the graphite flake thickness at the tip increased to ~ 0.71 mm. Consequently, in Fig. 3.2(d5) the newly generated cavitation bubble imploded and SWs interacted with the already expanded graphite flake tip. At this point the weakened section of

~360 μm in length and ~120 μm in thickness separated from the flake, drifted away and sedimented in water. This cutting or “slicing” manifestation occurred when a crack or small pit was initiated due to the accumulative SW impacts, followed by a sharp scission straight through a section of the graphite flake in the direction parallel to the bonded inter-layers.

Figure 3.3 demonstrates an example of “slicing” whereby the propagation of graphite layer splitting is predominantly caused from SWs. Bubbles implode at a distance of ~0.7-1 mm behind the graphite flake tip and no liquid mass interacts with the graphite. Any liquid jet from implosions can be seen not to make contact with the graphite flake. The continuation of transient bubble collapses contributes a “slicing” manifestation as SWs exert forces directly above and at close distances, gradually exfoliating the graphite flake layers. After 15 cavitation bubble implosions (Fig. 3.3(b1)), the initiation of the split can be seen (Fig. 3.3(b2)), albeit subtly. As the depth of the split increases (Fig. 3.3(b2-d3)), the width at the tip of the graphite between the two splitting arms also increases. Fig. 3.3(f3) (at 28 LIB's) shows a small graphite section of size ~600 μm in length and ~80 μm in thickness delaminated from the bulk material. By observing the morphology changes from Fig. 3.3(g-i) two things are most apparent. Firstly, the visible appearance at the tip of the graphite is seen to create protrusions while also an increase in surface area is noticeable. However, due to the inherent flexible nature of graphite [133], the data can be misleading, as a shift in orientation can appear as demonstrable physical change. Therefore, a degree of caution is required when interpreting the camera footage; hence the provided images in this report were carefully selected to indicate surface area increase and widening of the fixed graphite flake. Secondly, a structural mechanism can be identified. After the exfoliated graphite flake in Fig. 3.3(f3) is detached, the split arm which was propagating the scission is significantly reduced in size. Nevertheless, this can be seen in Fig. 3.3(i) to have grown in length again with the continuation of SW impacts. Therefore, a reasonable assumption may be that after a split on the graphite arm has extended too far, graphite exfoliation occurs. Then with the continued exerted forces from cavitation bubbles, the arm will peel due to shearing forces until it reaches an unsustainable size for the bonds to keep the graphite arm attached, and delaminates again, hence, a repeating pressure cycle prompts layer material exfoliation.

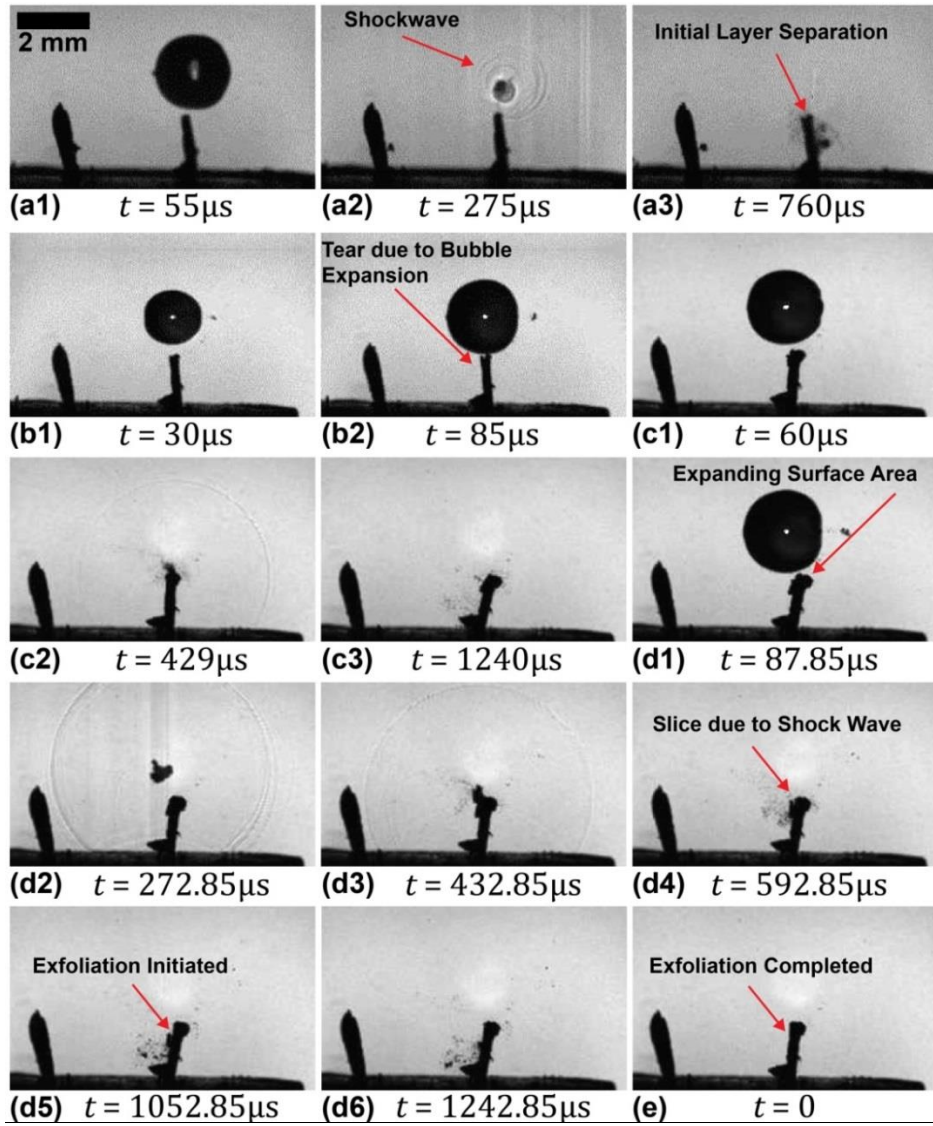


Figure 3.2. Representative frames selected from multiple high-speed sequences recording the interaction of repeated LIBs with a single graphite flake, depicting the “Flowering” manifestation. Each letter (from a-e) follows the time sequence respective to a specific LIB. **(a1-3)** An expanding LIB forms above the graphite flake (1). The bubble collapse generates a SW which interacts with the graphite flake tip (with a vertical reflected SW also seen on the right hand side) (2). A split is initiated due to the shear forces exerted by the SWs (3). **(b1-2)** An expanding LIB (1) pushes the graphite flake tip apart making the initiated split noticeably visible (2). **(c1-3)** After 16 more LIBs, the graphite flake tip surface area expands resembling a “flower” shape (1). A subsequent LIB collapses emitting SWs (2) which continue to widen the tip surface area. The graphite flake base is also seen to lift in position due to LIB interactions (3). **(d1-5)** Another LIB forms (1) and collapses propagating SWs towards the graphite flake (2). The post-collapse rebound generates a secondary SW closer to the graphite flake tip (3), which induces a small perceptible split to the graphite layers (4). Exfoliation takes place as the forces keeping the graphite layers in tact are superseded (5). The delaminated graphite flake sinks towards the substrate (5). **(e)** The final flake morphology. The supplementary video can be accessed with the published version of this chapter as Video 1 at <https://doi.org/10.1016/j.mattod.2021.05.005>.

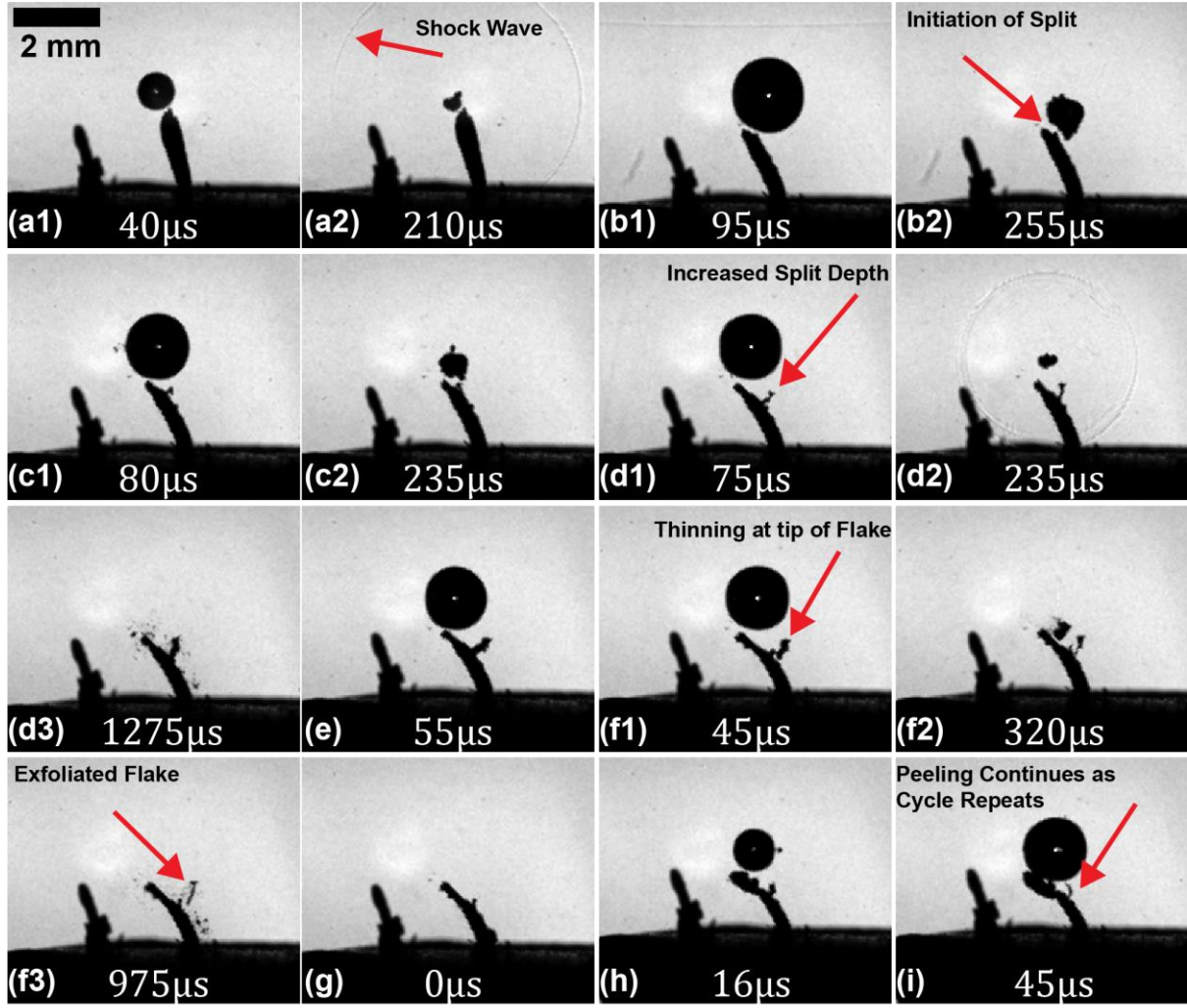


Figure 3.3 Representative frames selected from multiple high-speed sequences recording the interaction of repeated LIBs with a single graphite flake, depicting the “Slicing” manifestation. Each letter (from a-i) follows the time sequence respective to a specific LIB. **(a1-2)** An expanding LIB forms above the graphite flake (1), upon collapse a SW is generated which interacts with the graphite flake tip (2). **(b1-2)** An expanding LIB displaces the graphite flakes position. A slight notch starts to form at the tip (1), which transforms into a clear split after the collapse of the bubble (2). **(c1-2)** More collapses demonstrate the direction the split is propagating (1). During the 16th LIB collapse phase the split continues to widen (2). **(d1-3)** The split depth increases, while a LIB forms above (1). The bubble collapse emits a SW penetrating the graphite flakes surface (2), noticeably increasing the splitting arm size and thickness (3). **(e)** Continues the sequence demonstrating how the split propagates. **(f1-3)** A new LIB forms. The two splitting arms continue thinning, while the depth of the split is approximately half way through the graphite flake (1). The LIB collapses and emits SWs into the sample (these are cropped from the image for clarity) (2). The exerted forces are finally enough to exfoliate a thin section of graphite which is seen to drift away from the bulk material (3). **(g)** Shows the appearance directly after delamination and sedimentation of the graphite has taken place. **(h)** The graphite morphology begins to change again, with the tip widening in surface area. **(i)** The upper graphite flake surface area continues to expand. While this is happening, the new split is slowly growing with more cavitation collapses as the exfoliation cycle progresses.

Due to the predetermined position of the cavity, the distance between the graphite flake and bubble can be approximated. With the evidence of the SW present, and no visible direct cavitation bubble contact with the sample, it can be, therefore, concluded that the initiation of the split and propagation of exfoliation solely corresponds to SW interactions alongside weaker oscillating bubble forces (as discussed in Section 3.3).

From this series of observations it was apparent that the “flowering” manifestation opened up the tip of the graphite flake, essentially weakening the structure (breaking/relaxing the bonds) generally across the whole graphite tip followed by exfoliation of a section via the “slicing” manifestation, typically within 30 ms of accumulated LIB interaction time. In addition, although the graphite flake was seen to expand due to the separation of layers, in the microscopic level it is likely that micro-exfoliation was also occurring.

Figure 3.4(a-d) demonstrates an additional example of the “flowering” effect. SWs in this sequence of images are shown to not only widen the tip of the graphite flake and peel layers, but interestingly to also gradually thin the lower section. The initial thickness of the lower section was $\sim 234 \mu\text{m}$. Graphite flake thinning, which occurred over 17 LIB's, measured between Fig. 3.4(a) and Fig. 3.4(d) was $\sim 120 \mu\text{m}$. Considering the sample base was fastened and was observed to remain firmly fixed in place, as well as the fact that there were no direct interactions with the inertial cavitation bubbles, these observations provide clear evidence that SW impacts can induce micro-peeling, and hence the graphite thickness is seen to decrease with multiple SW interactions. This sequence with smaller generated cavities also presents evidence that multiple SWs are adequate in providing shear forces to initiate splitting and peeling of layers.

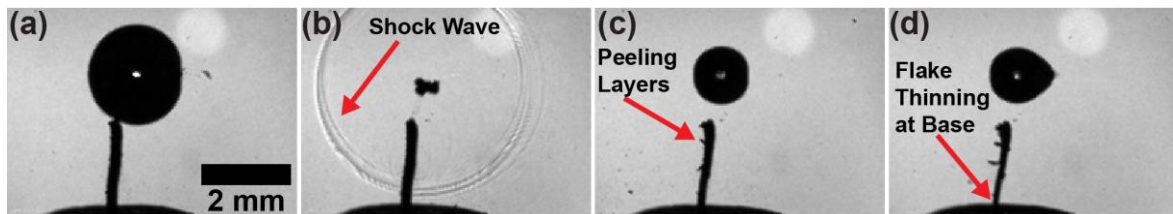


Figure 3.4. Timeline of inertial cavitation collapses displaying flaking of layers and an expanding top surface area. **(a)** Shows the initial morphology of the sample with a LIB forming behind. **(b)** The implosion produces a SW which propagates through the graphite flake. **(c)** Shows the graphite sample 20 LIB's later. Tiny layers are seen to peel from the bulk sample from SW impacts. **(d)** Shows the peeling layers growing in length; simultaneously the thickness at the base of the graphite is demonstrably thinner, while the tip is wider.

Apart from the SWs, liquid-micro jets were found to play an important role in promoting exfoliation of the graphite flakes. Figure 3.5 shows a LIB imploding at a distance between

0.72-1.38 mm from the fixed graphite flake which had already been half split intentionally by a previous cavitation interaction, in order to investigate the “wedge” effect phenomenologically described by Yi et al. [134]. During the bubble collapse phase a C-shape (or involution) cavitation vortex forms. Although micro-jetting cannot be resolved, the C-shape indicates the preliminary stage of the liquid-jet formation and has been reported on many occasions [1], [29], [135]. Water entrainment occurred from the back of the bubble, where liquid mass was pulled through and propelled towards the half-split section with high velocities approximately 80 ms^{-1} as calculated using the images from the high-speed camera in Figure 3.6.

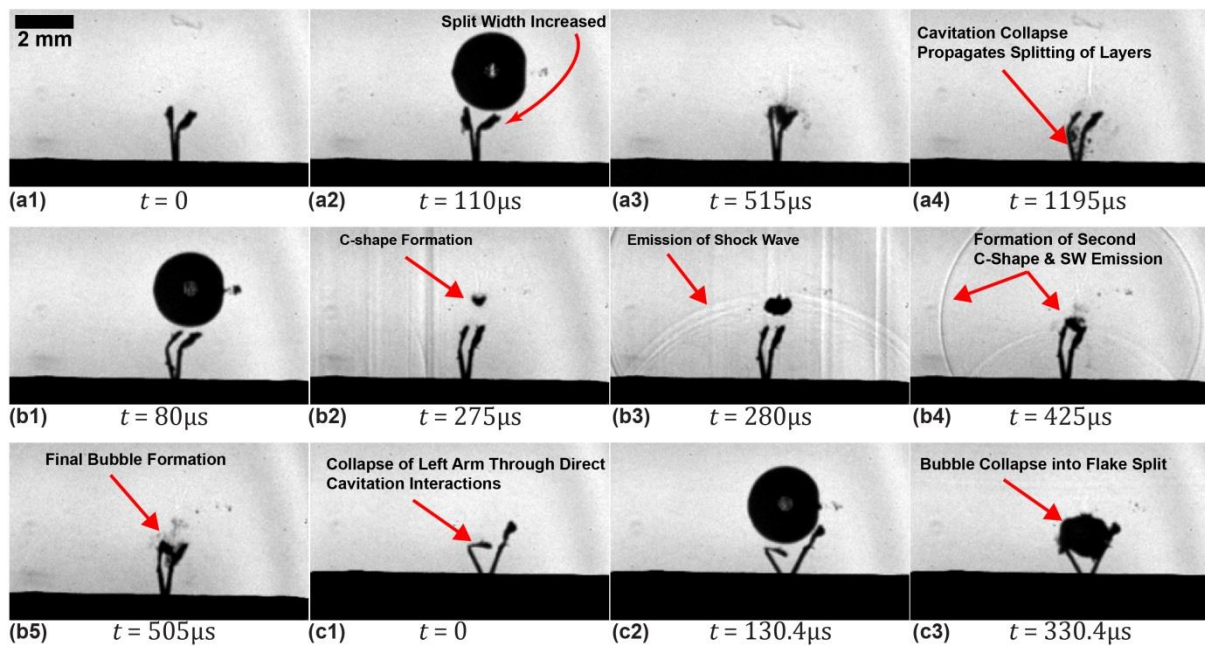


Figure 3.5. Representative frames selected from multiple high-speed sequences recording the interaction of repeated LIBs with a single graphite flake, depicting the “Splitting” manifestation. Each letter (from a-c) follows the time sequence respective to a specific LIB. **(a1-4)** A graphite flake, already split through previous interactions (1), displays further splitting as another LIB reaches maximum expansion (2). The bubble deflates and translates into the split, propagating it further (3). The post-collapse rebound completes the split along the length of the graphite flake (4) (The supplementary video can be accessed with the published version of this chapter as Video 2 at <https://doi.org/10.1016/j.mattod.2021.05.005>). **(b1-5)** A subsequent LIB at maximum expansion bends the open end of the split (1), deflates into a c-shape indicative of jetting (2) and generates a multi-fronted SW, reflecting from the substrate, on collapse (3). The rebounding bubble also deflates to form a c-shape and collapses to generate a secondary SW (4). The bubble collapses directly into the split (5). **(c1-3)** After 5 more LIBs the graphite flake component layers have thinned, one to the point of flexure (1), with further bubbles widening the split at maximum expansion (2), in addition to collapse and rebounds (3).

From analysing the high-speed camera footage used for the “splitting” manifestation in Fig. 3.4, we can estimate the average velocity of the liquid-jets before the collapsing bubbles

made contact with the graphite flake. For Fig. 3.6(a1-2), the distance the jet travelled was 0.435 mm. For Fig. 3.6(b1-2), the distance the jet travelled was 0.3627 mm. The time elapsed during this period was 5 μs for both. Calculating the jet velocity for a) and b) is then 87 ms^{-1} and 72.54 ms^{-1} respectively. Therefore, an estimate for the average jet velocity from the cavitation bubbles in Fig. 3.4 is 79.8 ms^{-1} .

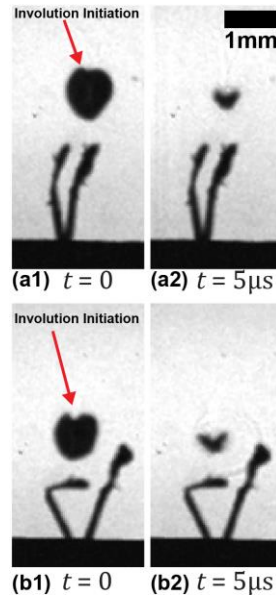


Figure 3.6. Two examples of liquid-jets from Fig. 2. **(a1)** Shows the initial formation of the involution. **(a2)** Shows the final position of the involution before the bubble collapse. **(b1)** Shows the initial formation of the involution. **(b2)** Shows the final position of the involution before the bubble collapse.

When this high momentum liquid mass interacted with the sample surface, large impact pressure forces in the Mpa range [1] were inflicted onto the layers promoting further splitting, hence our terminology for the “splitting” manifestation. Eventually, and after 9 consecutive bubble collapses (Fig. 3.5(a4)), the graphite flake was fully split down the centre with thinning becoming more prevalent. The final images (Fig. 3.5(c1-c2)) show that the accumulation of collapses was burgeoning the peeling of graphite layers. The graphite flake morphology was significantly altered with the split flake arms wedged further apart.

We observed that exfoliation via transient cavitation tends to manifest in three ways, “flowering”, “slicing” and “splitting”. Figure 3.7 displays a schematic representation of these manifestations. As previously mentioned, the graphite flake tip widens due to SW impacts (Fig. 3.7(b1)), followed by exfoliation (Fig. 3.7(c1)). Defects at the tip of the graphite flake, or weakened bonds at a specific point have the propensity to facilitate the “slicing” manifestation. Alternatively, liquid-jets propelled into the graphite flake surface (Fig. 3.7(b2)) can expedite exfoliation by rapidly tearing through layers (“splitting”) with bubble rebounds. After the cavity can no longer rebound being wedged between the two splitting

arms, bubble fragments remain and dissipate (Fig. 3.7(c2)). In a continuous sonicated environment, these bubble fragments can play the role of tiny nuclei that can be excited by the both the sonication and bubble-collapse SWs from the cavitation activity in the liquid. This could drive the intra-flake nuclei to further collapses and micro-jetting, or sustain a more stable regime with vigorous oscillations, with both cases further contributing to exfoliation [136].

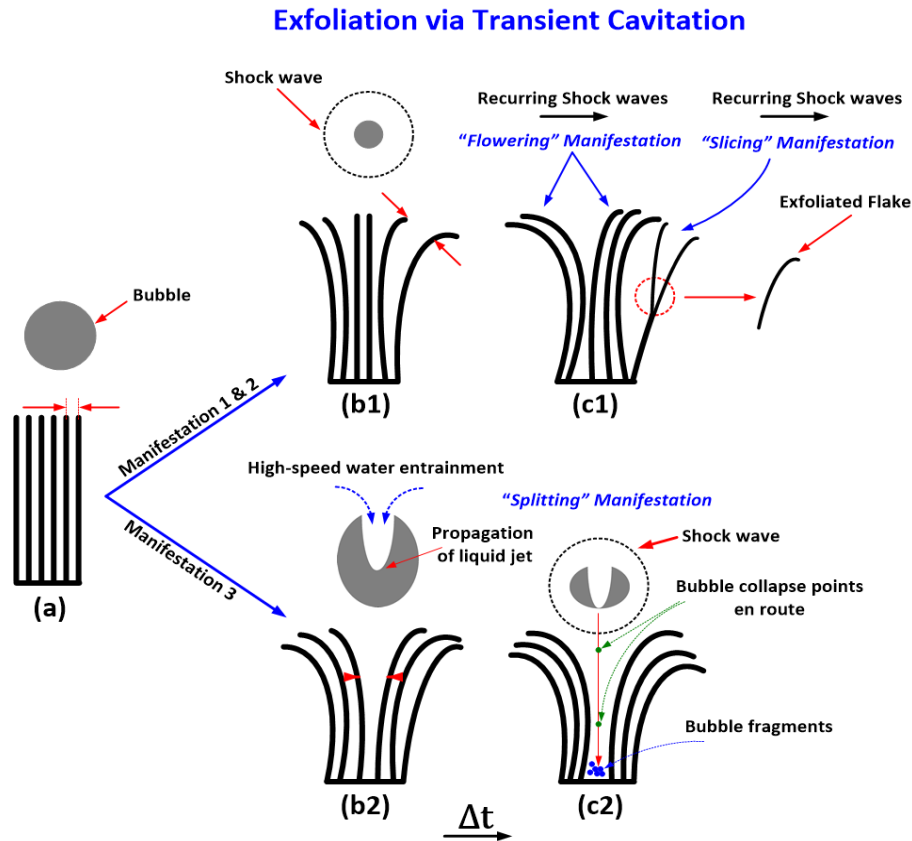


Figure 3.7. Schematic portraying a transient cavitation interaction with a graphite flake whereby three sono-exfoliation manifestations can take place (1 “flowering”, 2 “slicing”, 3 “splitting”). **(a)** Initially the layers are unaffected, bound by VdW’s forces and closely attached vertically (where each black pillar represents $\sim 50 \mu\text{m}$ thickness of graphite). **(b1)** Multiple SWs interact with the graphite flake tip pushing the layers apart and weakening their attractive force as a function of increased separation distance (demonstrated by the arrows on the graphite tip in (a) and (b1)). **(c1)** Layers overcoming their VdW’s electrostatic attraction break away from the bulk material, as indicated by the red dashed circle. **(b2)** The bubble entrains water in from the back as the depth of the involution increases. Preliminary displacement forces increase the width of the splitting layers, as demonstrated by the arrows on the graphite flake. **(c2)** The collapse after the C-shape also gives rise to a SW. As the bubble rebounds multiple C-shapes and SWs follow thereafter. The bubble collapse points in the diagram demonstrate this tendency, increasing layer separation distance. For clarity, the C-shape is portrayed larger. In reality, by the time the jetting water reaches the opposite side of the cavity wall, the bubble is entering the collapse phase [1], [2].

3.3.1.2 Exfoliation via Stable Cavitation

As opposed to the current views that stable cavitation is ineffective for the delamination of bulk layered materials, we show for the first time that bubble oscillation does indeed play a crucial role in the exfoliation process. In the situation where the LIBs were now located at either side of the graphite flake (Fig. 3.8 LIB generated between 0.77-1.5 mm from the sample), the largest exerting forces (SWs/liquid-jets) were less effective as they did not interact directly along with the stacked inter-graphitic layers (bubble location was normal to the plane surface of graphite) as opposed to the previous cases where bubbles were located along the axis of the graphite layers (Fig. 3.2 and 3.3). Instead, the cavitation mechanism observed here focuses on weaker expansion/contraction (oscillating) forces. Specifically, in this case after an initial split occurred at the top of the graphite flake (Fig. (3.8a), 497.5 μ s) from SW propagation, repetitive growth and collapse bubble phases pushed and pulled the surrounding medium like a pump, leading to layer tearing. Multiple “branches” were formed on the graphite flake that continued to grow in length as layer tearing propagated due to bubble oscillation. This manifestation is schematically depicted in Fig. 3.9. In general, the progression of a tear between sheared layers is only really observable during the collapse stage of the cavity as the inertia from the contraction stage pulls the layers apart. Similarly the same contraction/expansion mode can further facilitate the enlargement of the interlayer distance if the bubbles are located in-between the layers as shown in Fig. 3.5(c2).

Numerical modelling results using bubble parameters from Fig. 3.8 estimated the alternating compressive/tensile forces in the range -35 to $+80$ kPa (Appendix Section A), apparently adequate to facilitate further propagation of partial exfoliation leading to a “branching”-style formation. Stable cavitation mechanism in conjunction with the “branching” manifestation is likely to be the reason why smaller sized bubbles have recently been shown to be more effective in exfoliating graphite flakes [12] (the resonance radius of smaller sized bubbles is associated with high excitation frequencies in the MHz range making it difficult for the bubbles to catastrophically collapse with an incident low frequency source, and as such tend to vigorously pulsate in a stable cavitation manner promoting a “gentler” exfoliation). In addition, this hypothesis is in line with the observations in Section 3.3 (Fig. 3.11) where bubbles trapped between the graphite layers promoted a gentle and rapid multi-layered exfoliation of a bulk layered graphite flake under continuous sonication.

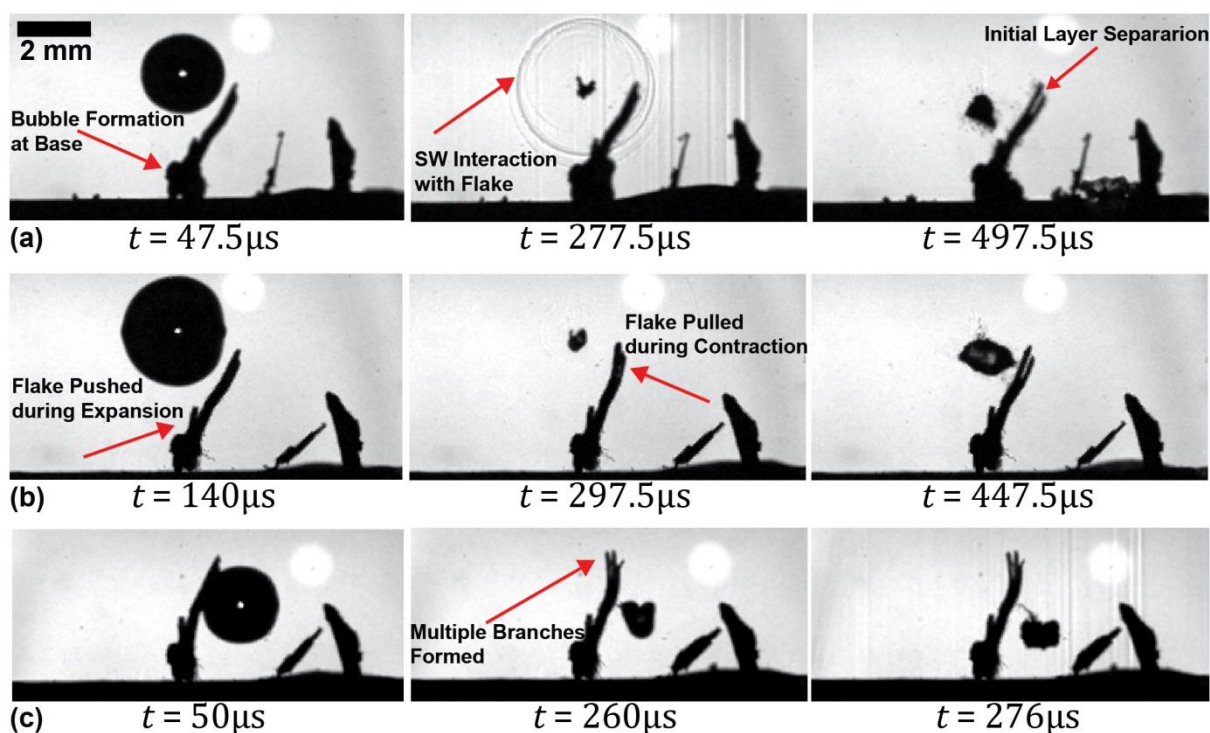


Figure 3.8 Representative frames selected from multiple high-speed sequences recording the interaction of repeated LIBs with a single graphite flake, depicting the “branching” manifestation. Each sequence for each row consists of bubble growth, contraction and collapse. **(a)** Shows the initiation of a split due to a SW interaction, with vertical SWs also present due to reflections off the curved mirror (The supplementary video can be accessed with the published version of this chapter as Video 3 at <https://doi.org/10.1016/j.mattod.2021.05.005>). **(b)** Displacement of the graphite flake occurs as it’s pushed away from the bubble during growth, pulled towards during contraction, and during collapse the split becomes evident. **(c)** The bubble implodes from the right hand side with the same phenomenon observable, which becomes more noticeable due to increased number of bubble collapses further propagating the split. The graphite flake is pushed during growth, pulled during contraction and after bubble collapse the full extent of the shearing process is apparent (The supplementary video can be accessed with the published version of this chapter as Video 4 at <https://doi.org/10.1016/j.mattod.2021.05.005>). The second image in (c) also displays the cavitation bubble beginning to jet toward the substrate. It is worth noting that the larger width seen at the lower half of the graphite in (a) is due to bubbles stuck at the base.

Exfoliation via Stable Cavitation

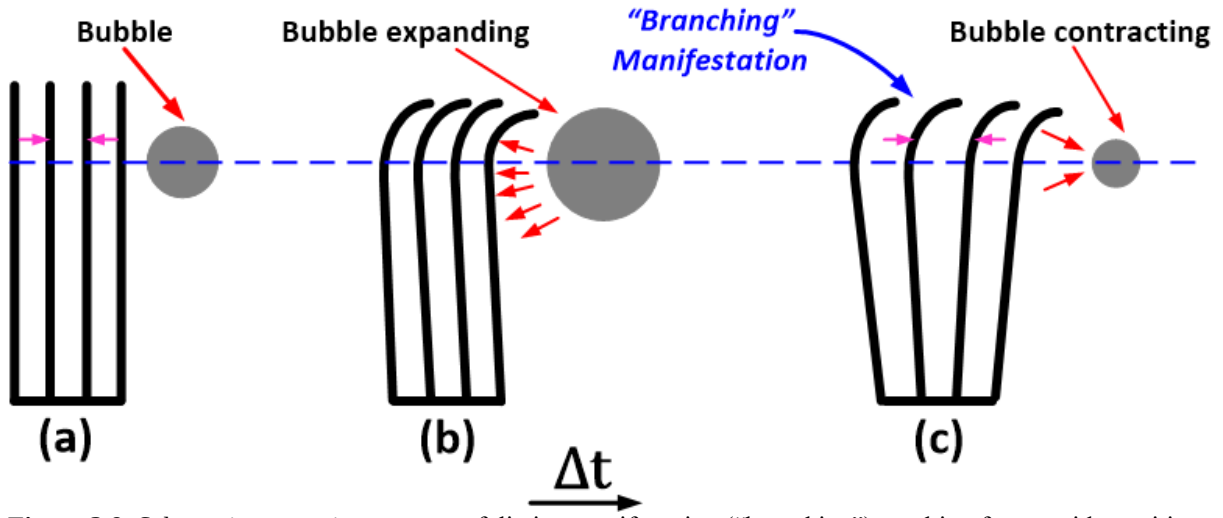


Figure 3.9. Schematic portraying a sono-exfoliation manifestation (“branching”) resulting from rapid transitions between bubble growth and contraction, where the output deflection pressures contribute to layered material shearing. **(a)** Shows the initial graphite flake with a forming bubble nearby the tip of the graphite (where each black pillar represents $\sim 50 \mu\text{m}$ in thickness of graphite). **(b)** Shows the cavitation bubble expanding. The expanding force pushes the closest graphite layers and shears the top layers. **(c)** Shows the bubble contracting. While pulling in the surrounding medium the closest graphite layers are pulled towards the bubble. During this, shearing at the tip of the graphite progresses and hence layer separation distance increases as demonstrated by the pink arrows on the graphite flakes.

3.3.2 Ultrasonic Bubble Cloud Experiments

Although the use of single bubbles shed light on the dynamics and the governing mechanisms of sono-exfoliation, it is not representative of the continuous dynamic events driven by acoustic cavitation and multiple bubble cloud collapses. Moreover, the fact that the LIBs are particularly large compared to those produced acoustically via ultrasonic excitation, means that a full picture of the underlying mechanisms cannot be assembled. Therefore, the second part of the experiments were performed using a sonotrode in conjunction with acoustic pressure measurements and high speed imaging at lower frame rates (up to 100,000 fps), in order to capture exfoliation under testing and processing conditions closer to those experienced in ultrasound-assisted LPE. To investigate sono-exfoliation mechanisms under the sonotrode, the experimental setup displayed in Fig. 3.1(b) was assembled, with the graphite fixed to the substrate at a distance of 1.2 mm or 2.5 mm from the sonotrode tip, in order to observe exfoliation inside and outside the cavitation zone, respectively.

3.3.2.1 Graphite Flake: Direct Cavitation Zone Interaction

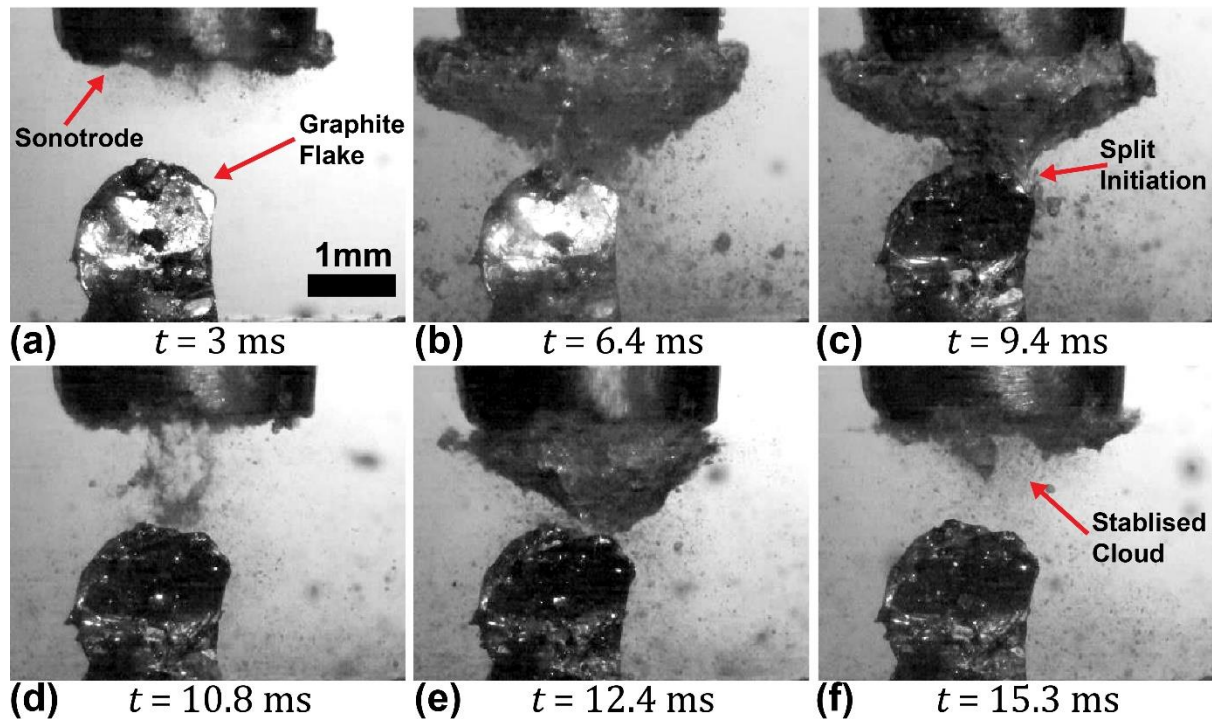


Figure 3.10. Sono-exfoliation via ultrasonic cavitation (single pulse, ~250 ms on/~750 ms off). Sequence displaying a cavitation cloud interaction with a graphite flake, splitting the bulk material layers in half. **(a)** Shows the initial morphology of the sample as the sonotrode is activated. **(b)** The cavitation cloud begins to make contact with the graphite flake as the sonotrode tip produces larger bubbly clouds. **(c)** Initiation of the graphite split occurs, with the tip of the cloud remaining in contact. **(d)** The progression of the exfoliating layers continues. The cloud pulse from the sonotrode alternates in size as it oscillates: here we witness weak and dispersed microbubble cloud interactions with the graphite flake. **(e)** Split progression is complete with the cavitation cloud beginning to stabilise, thin and decrease in size. **(f)** Shows no difference in split propagation to the graphite flake. The sonotrode has now normalised in operation, producing a stable and steady bubble cloud which no longer reaches the graphite flake tip, coinciding with the halt of rapid delamination of layers. The supplementary video can be accessed with the published version of this chapter as Video 5 at <https://doi.org/10.1016/j.mattod.2021.05.005>.

We can now analyse the acoustic cavitation effect of initiating exfoliation of a bulk layered graphite flake. Figure 3.10(a) shows that in the initial ~3 ms after the transducer was activated, no cloud is formed. However, after this, the cavitation zone developed to its maximum size for a period of ~ 10 ms (Fig. 3.10(b-e)). This was found to be a critical processing time as powerful pressure surges, most likely by a train of SWs directly exerted onto the graphite tip, severed the VdW's bonds after the first ~ 13 ms of processing. Thereafter a stabilised cavitation regime was achieved (Fig. 3.10(f)) with the active cavitation zone shrinking to a size about 2.5 times less in area (Fig. 3.10(f)) than the fully developed case (Fig. 3.10(c)), indicating reduced cavitation activity and thus a slower exfoliation

process. This tendency was also validated by acoustic pressure measurements as shown later in Section 3.3.3. As there was no direct contact with the graphite during the first few ms while the sonotrode was seen to oscillate it can be reasonably assumed that the governing exfoliation mechanism is the accumulation of powerful SWs generated from a fully developed cavitation zone interacting with the tip of the graphite flake (Fig. 3.10(b)).

3.3.2.2 Graphite Flake: Indirect Cavitation Zone Interaction

Figure 3.11 displays an ultrasonic experiment with twice the distance (~ 2.5 mm) between the sample and sonotrode to ensure that the cavitation zone would not interact with the graphite directly. The sample is viewed edge-on from a perspective orthogonal to that of Fig. 3.10, similar to the LIB observations of Figs. 3.2-8. The initial split induced (Fig. 3.11(b)) was similar to what was observed in Fig. 3.5, where the splitting occurred approximately down the graphite flake centre. Camera observations indicated that bubbles that did not implode could grow in size and sustain an oscillating motion, producing a translational force due to the acoustic pressure field inflicted upon them. Fig. 3.11(b-d) demonstrated this tendency, whereby smaller bubbles (in the range of 65-80 μm) in-between the split graphite flake layers oscillated rapidly to perpetuate layer shearing.

Although we cannot directly observe jetting from individual bubbles into the graphite clearly in Fig. 3.11 due to the multiple bubbles in the solution, we did witness an example of jetting which propelled the liquid mass towards the substrate upon implosion (as observed at 16 s during Video 6 <https://doi.org/10.1016/j.mattod.2021.05.005>). A larger bubble was seen to propagate towards the substrate with periodic implosions (Fig. 3.11 I), at which point a liquid-jet impelled into the base of the graphite, subsequently coalescing and triggering a mass implosion of the stable bubbles already oscillating at the base of the graphite (Fig. 3.11(f-g)). The bubble implosion along with the generated SWs and micro-jets appeared to coincide simultaneously with multilayer opening from the tip of the graphite (Fig. 3.11(h)), which occurred 7 periodic bubble collapses after the initial jet interaction with the bubbles at the base of the sample.

Interestingly, the graphite flake opened up in a fashion resembling flipping through pages of a book, prior to the interaction with satellite bubble clouds from the sonotrode. This can be clearly seen in Video 6 (<https://doi.org/10.1016/j.mattod.2021.05.005>), Fig. 3.11(f-h). To the best of our knowledge, this phenomenon was observed here for the first time demonstrating that graphite flake layers can separate and displace similar to book pages, with multiple

partially exfoliated graphite layers (still bound by VdW's bonds at the lower half of the sample) being able to move fluidly during the interaction with cavitating bubbles and corresponding acoustic emissions.

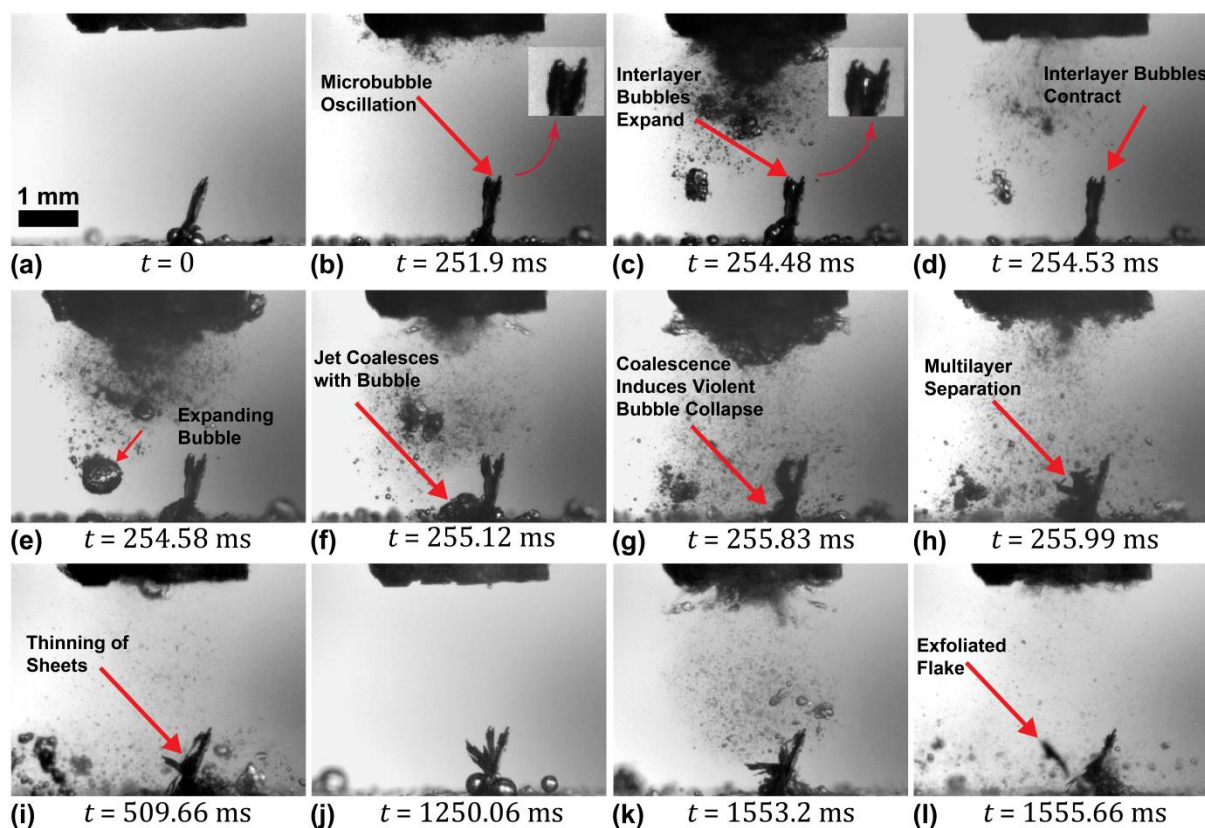


Figure 3.11. Sono-exfoliation via ultrasonic cavitation. The graphite flake was exposed to 7 ultrasonic pulses (~250 ms on/~750 ms off). The sequence consists of selected images highlighting the most interesting phenomena, and does not include every pulse. Images show active treatment, as well as an intermittent period absent of acoustic cavitation. **(a)** The initial morphology of the sample is shown. **(b)** Microbubbles oscillate between the split layers at the tip of the graphite (The supplementary video can be accessed with the published version of this chapter as Video 6). **(c)** Microbubbles expand within the split graphite layers. **(d)** Microbubbles contract within the split graphite layers. **(e)** A large bubble expands on the left side of the graphite flake. Meanwhile, the microbubbles in-between the graphite flake split no longer reform. **(f)** The bubble follows a pathway of continuous contraction and compression phases. A liquid-jet is formed, propelled and coalesces with the stable cavitation at the base of the graphite flake. **(g)** The coalescence induces a violent collapse separating the graphite layers. **(h)** Shows multilayer separation of the graphite. **(i)** Thinning of the graphite sheets becomes more noticeable. **(j)** Displays a still shot while the sonotrode has not yet produced acoustic cavitation. The larger exfoliating graphite sheets transform into smaller sub-sheets continuing to tear further towards the base of the graphite flake. **(k)** The multiple exfoliating layers are inflicted by inertial cavitation and acoustic streaming forces. **(l)** Exfoliation occurs. A small section is seen to fully sever from the bulk graphite and proceeds to flow around the solution (The supplementary video can be accessed with the published version of this chapter as Video 7 at <https://doi.org/10.1016/j.mattod.2021.05.005>).

It was recently shown that bubble implosions near a rigid solid boundary generate shear stresses in the range of up to 100 kPa [137] upon liquid-jet impact with corresponding SWs impact pressures in the range of 1-2 Mpa [27] (for a distance of about 200 μm , comparable to the studied bubble i.e. Fig. 3.11I, $\sim 300 \mu\text{m}$). Fig. 3.11(e-g) shows a visual representation of this phenomenon, whereby bubble implosions can be promoted by nearby solid boundaries. These values are in very good agreement with our measured and calculated pressure values given in Section 3.3.3. The most pertinent information from Section 3.2 is that the combination of the generated SWs, micro-jets and bubble oscillations each imposed shear stresses onto the graphite flake along with acoustic streaming, leading to “page-flipping” exfoliation. Thus, the next step was to map and resolve the pressure magnitude of these acoustic emissions in the sonicated environment and estimate the shear stresses responsible for the exfoliation. Fig. 3.11(i) demonstrates the thinning of separated graphite layers followed by an intermittent sonication period (Fig. 3.11(j)) where the graphite flake resembled the “flowering” manifestation, with an expanding tip surface area and separation distance. The subsequent ultrasonic pulse exfoliated a graphite flake section (Fig. 3.11(k-l)) of $\sim 650 \mu\text{m}$ in length, $\sim 520 \mu\text{m}$ width and $\sim 30 \mu\text{m}$ in thickness (Video 7 <https://doi.org/10.1016/j.mattod.2021.05.005>).

It was also observed in Fig. 3.11(b, c) that during the first $\sim 3 \text{ ms}$ after the transducer was activated, the graphite flake could be seen to vibrate in response to sonotrode tip vibration, in the absence of bubble collapse SWs. The next $\sim 10 \text{ ms}$ gave rise to a rapidly growing cavitation cloud with increasing aggressiveness, followed by shrinking to a stabilized cavitation zone, with rapid layer exfoliation no longer observed. This phenomenon was observed for both Fig. 3.10 using a single pulse, and Fig. 3.11 using seven pulses of ultrasound. Each pulse delivered to the graphite flake observed with the camera, demonstrated proliferation of layer delamination specifically during the $\sim 10 \text{ ms}$ cavitation cloud expansion, and hence provides visual evidence for the utility of short pulsed ultrasound for exfoliation.

Pulsed, as opposed to continuous ultrasound has been reported to reduce energy usage, ensure better temperature control and prevent reactor clogging [109]. It has been proposed that pulsed ultrasonic treatment facilitates and promotes the generation of cavitation by utilising the silent period during which the liquid medium is not treated [138], hence promoting nuclei replenishment. It was also hypothesised that generation of greater number of transient cavitation occurs due to increased nucleation sites [139]. However, these hypotheses have

never been experimentally confirmed before. In this research, photographic evidence along with acoustic pressure measurements (Fig. 3.12) revealed the foundation for the benefit of using pulsed ultrasound for treatment of graphite solutions.

3.3.3 Acoustic Pressure Measurements and Calculation of Cavitation induced Shear Stresses

In general, the collapse of a larger bubble cloud (many collapses of individual cavitating bubbles) produces larger force exerted due to increased acoustic emissions. Figure 3.12(a) presents additional evidence to the hypothesis made in Section 3.2 that a proliferation of layer tearing occurred during the initial sonication period (~ 13 ms). The cavitation intensity can be seen to increase until ~ 7 ms. Due to the fibre optic hydrophones flexibility to prevent breaking, the position of its tip displaced (increasing distance from the sonotrode) under the growing emissions from the cavitation cloud, and hence the recorded signal appeared to decrease. However, as observed from the camera recording in Figs. 3.10 and 3.11, this would most likely increase until ~ 13 ms. The fibre optic hydrophone synced to the high-speed camera (Fig. 3.12(a)) allows us to authenticate the supposition made in the previous section. The image at 6.35 ms showed a fully developed bubble cloud. At 6.5 ms the image showed the collapse of the cloud, which appeared to coincide precisely to the large peak in signal. The collapse of this large cloud was likely to have released multiple SWs due to transient bubble collapses which expedited the exfoliation of graphite layers. The latter half of the plot in Fig. 3.12(a) showed a stabilisation of the acoustic emissions, with much lower signals observed (about 3 times), reflecting a smaller cavitation zone.

The profile of acoustic pressure surges for a stabilised cavitation zone from SWs at the studied locations is given in Fig. 3.12(b) (the full pressure map of the active cavitation zone along with more detail can be found in Appendix Section A) using the methodology previously used by our group [112], [140]. Maximum pressure ($P_{\max}$) readings (averaged from 60 waveforms in Fig. 3.12(b3-4), corresponding to 120 ms) were measured as 1770 and 860 kPa for graphite sample positions in Figs. 3.10 and 3.11, respectively. However, SW pressure impacts at particular waveforms such as 28 and 35 (Fig. 3.12(c-d)) reached values up to 5 Mpa (at 1.2 mm) and 1.6 Mpa (at 2.5 mm), respectively. These local maxima correspond to the accumulated pressures peaks generated in Fig. 3.12(a), where the cavitation zone reaches maximum size. It is apparent that during the first 10 ms the accumulated pressure surges (Fig. 3.12(a) inset) facilitated exfoliation as also seen in Figs. 3.10 and 3.11.

Most other waveforms during a stabilised regime measured lower pressure values between 1-2 Mpa. These measured values are in good agreement with the calculated shear stress values required to separate graphite layers apart, as per discussion below in this Section and experimentally measured in macroscale experiments [141], however, they are much lower than those given in Table 3.1 and calculated using the double cantilever beam (DCB) formula shown below.

To estimate pressures needed to initiate the graphite flake split, the double cantilever beam (DCB) fracture mechanics formula can be implemented [142]:

$$P = \frac{3\delta E b h^3}{24a^3} \quad (1)$$

where P is the total force delivered to the subject sample tip, δ is the split length, E is the Young's modulus of graphite (which can be presented as a range from 3 to 30.8 Gpa, minimum to maximum [143]), a is the split depth, h is the height and b is the base of the graphite flake. The resultant calculated force is then divided by the material cross sectional area to determine the pressure (P_A). This data is given in Table 3.4, with calculations and parameter values presented below (Table 3.1-3.3). Deflection pressures inflicted onto the graphite flakes, as a consequence of cavitation expansion/contraction were also calculated. As mentioned previously, this weaker force helps expedite the process of delamination. In order to establish estimates for these shearing pressures (τ) displacing the graphite flakes position (for Fig. 2(a) and 6), deflection calculations can be obtained by treating the graphite flakes morphology as a simple rectangular cantilever [144]:

$$\tau = \frac{FQ}{Ib} \quad (2)$$

where F is the transverse shear force, calculated using maximum deflection (δ_{max}) of the cantilever and Young's modulus of graphite [143]. Q is the first moment of area, I is the moment of inertia, and b is the base of the graphite flake. Calculations are given in Table 3.1. Further detail on the calculation method can be found in our groups previous work [140].

Table 3.1. Graphite flake sample dimensions. Selected parameters were used for pressure calculations for Eq. 1 and Eq. 2.

	Flake dimensions- Length, Width, Thickness (mm)	Cross sectional Area (mm ²)
Figure 3.2-	1.73, 1.47, 0.39	7.63×10^{-6}
Figure 3.5-	1.85, 1.57, 0.31	7.93×10^{-6}
Figure 3.8-	3.43, 1.02, 0.32	9.8×10^{-6}
Figure 3.10-	1.81, 1.53, 0.23	7.04×10^{-6}
Figure 3.11-	1.2, 1.0, 0.15	3.1×10^{-6}

Table 3.2. Graphite flake parameters used for pressure calculations in Eq. 1.

	α (mm)	δ (mm)
Figure 3.5 Flake	0.98	0.55
Figure 3.10 Flake	0.89	0.64

Table 3.3. Displays the parameters used to calculate pressure induced deflections for Eq. 2. Min and Max correspond to the Young's modulus of graphite presented in the range of 3 (min), 30.8 (max) Gpa.

	Second Moment of Area (m ⁴)	Deflection (mm)	Shear Force Min (N)	Shear Force Max (N)	Shear Stress (min-max) (Mpa)
Figure 3.8(a)- “Branching” Expansion	2.66×10^{-15}	0.079	0.047	0.48	0.22-2.24
Figure 3.8(b)- “Branching” Expansion	2.66×10^{-15}	0.079	0.047	0.48	0.22-2.24
Figure 3.8(c)- “Branching” Expansion	2.66×10^{-15}	0.315	0.187	1.92	0.87-8.95
Figure 3.8(a)- “Branching” Contraction	2.66×10^{-15}	0.079	0.047	0.48	0.22-2.24
Figure 3.8(b)- “Branching” Contraction	2.66×10^{-15}	0.197	0.117	1.2	0.55-5.59
Figure 3.8(c)- “Branching” Contraction	2.66×10^{-15}	0.079	0.047	0.48	0.22-2.24
Figure 3.5(a2)- Expansion	3.97×10^{-15}	0.1182	0.667	6.85	2-21
Figure 3.5(a2)- Contraction	3.97×10^{-15}	0.039	0.22	0.48	0.68-6.90

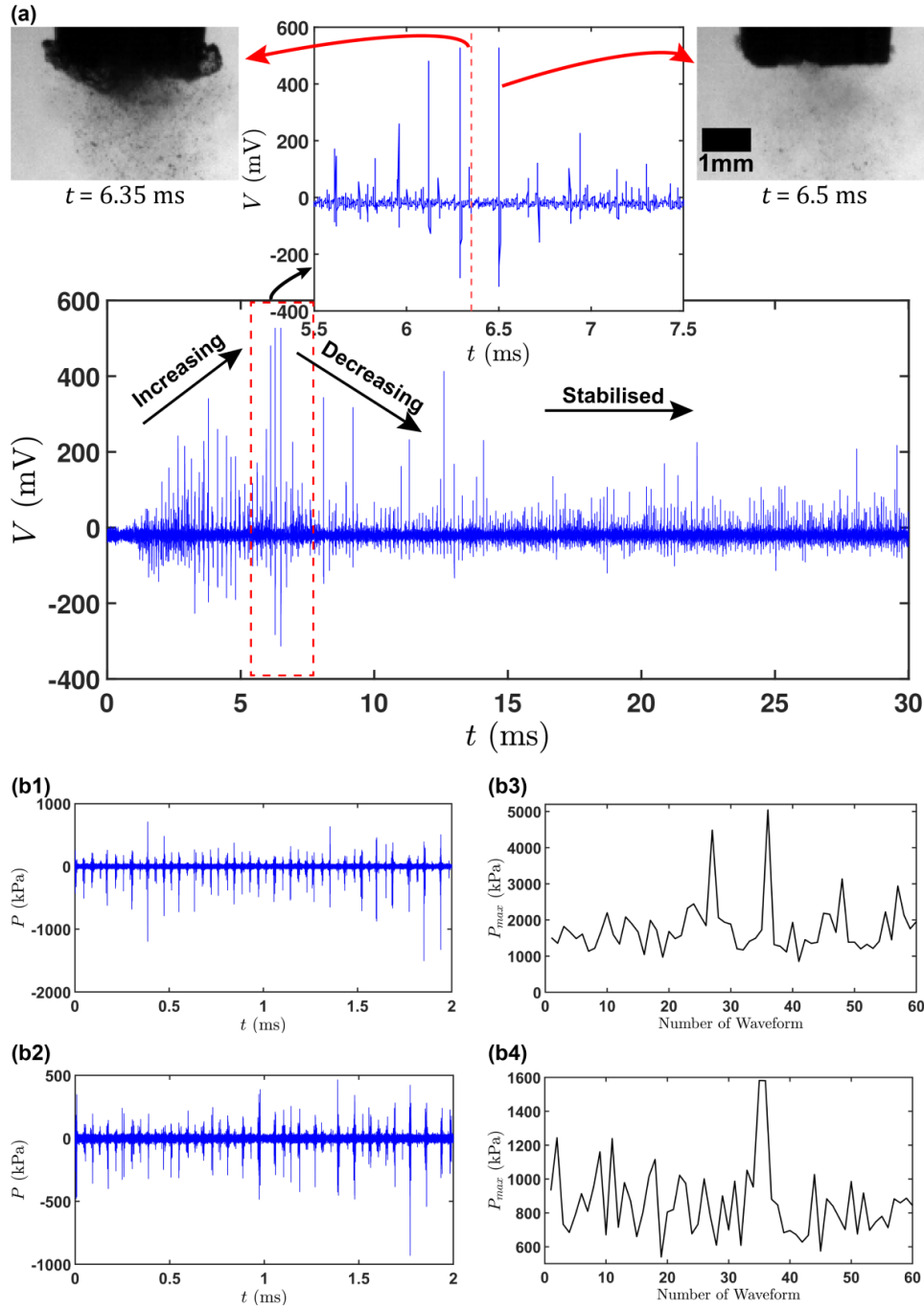


Figure 3.12. (a) Cavitation intensity plot for 2.5 mm distance from the sonotrode (as in Fig. 3.12). The zoomed dashed red box section highlights the initial sonication period where largest signal is detected by the fibre optical hydrophone. The image at 6.35 ms shows a fully developed bubble cloud. The image at 6.50 ms shows the collapse of this cloud, which corresponds to the large voltage peak. The black arrows on the main plot demonstrate the stabilisation of the trend/signal after ~ 13 ms as mentioned in section 2.2. **(b)** Temporal distribution of shock wave pressure: (b1) for sample in Fig. 6 and (b2) for sample in Fig. 3.12. These plots represent the first recorded waveform for each instance after bubble cloud stabilisation. The total pressures were averaged from 60 generated waveforms. (b3) and (b4) show the 60 recorded points against maximum pressure for corresponding cases (b1) and (b2) respectively.

Table 3.4. Pressure estimates for (a) graphite split, and (b) deflection. Flake parameters taken from Tables 3.1-3.3 with pressures calculated using Eq. 1 and Eq. 2.

(a) Double Cantilever Beam Impact Pressures (Mpa)	
(Calculated from Eq. 1)	
Figure 3.5	54 to 557
Figure 3.10	66 to 677
(b) Deflection Impact Pressures (Mpa)	
(Calculated from Eq. 2)	
Figure 3.5(a2)- Expansion	2–21
Figure 3.5(a2)- Contraction	0.7-7
Figure 3.8- “Branching” Expansion	0.2–9
Figure 3.8- “Branching” Contraction	0.2–6

The DCB formula estimates the total force delivered to the graphite flake tip from the collapsing bubbles. From the values in Table 3.4(a) it is apparent that shearing pressures for Figs. 3.5 (splitting induced from LIB jetting) and 3.10 (splitting induced from acoustic cavitation) are close in value.

To the best of our knowledge, quantifying sufficient shearing pressures to enact layer delamination brings about widely disputed and varying values, mostly due to the complexities of accurate measuring, variety of measurement techniques, and a multitude of parameters which are challenging to control. Therefore, a lack of reproducibility is often the case. One metrology which holds up as a reasonable estimate for exfoliation is the interlayer shear strength (ISS). Liu et al. pointed out the large discrepancies of calculated ISS values of graphite that were between 0.2 Mpa and 7 Gpa [141]. At the same time, they stated that much smaller ISS values in the range of 0.25 to 2.5 Mpa were attributed to the existence of many incommensurate contacts, which could significantly reduce the shear strength because of the superlubricity of non-pristine graphite.

Pressure estimates calculated via the DCB formula for graphite shearing (Table 3.4(a)) are greater than the reported SW pressures in the range of 4-11 Mpa (at a distance of 3 mm from the bubble centre) for LIB [145], as well as those measured with the fibre optic hydrophone in a sonicated environment. The calculated values of graphite shearing using DCB were, however, taken for samples with perfect integrity, without flaws/defects and cracks. Therefore, providing sufficient shearing would require a greater force as opposed to non-pristine graphite flakes. The fibre optic hydrophone measurements provided evidence that non-pristine graphite VdW's bonds can separate under much lower pressure impacts (we observed a range of $\sim 0.7\text{--}5$ Mpa for cases Fig. 3.12(b3-b4), with periodic pressure bursts from ~ 50 SWs in 2 ms from the sonotrode tip during sonication), which aligns with Liu's lower range of ISS measurements [141]. We can then hypothesise that graphite splitting and exfoliation mechanisms likely resemble a low cycle fatigue process by accumulating pressures, whereby the accumulation of SWs with pressure surges generally dismantle the VdW's bonds in due time (less than 13 ms for the studied samples positioned in plane with the VdW's bonds). Moreover, the contribution of micro-jets, acoustic streaming and cavitation expansion/contraction further provide the necessary shearing forces.

Deflection pressures calculated for the expansion cavitation bubble phase (Table 3.3) for the case shown in Fig. 3.5(a2) where the bubble imploded directly over the split were greater than those exerted onto the graphite flake in the case shown in Fig. 3.8 where the bubble oscillated on the side of the flake (Table 3.1). This difference was due to the bubble positioning which expedited the progression of inter-layer tearing as bubble expanding forces emitted were inflicted directly over the pre-split graphite flake in the case of Fig. 3.5. Due to this positioning, the expanding bubble appeared to promote efficacy of layer tearing, as it corresponded in plane to VdW's bonding. The contracting bubble in Fig. 3.5(a2) produced significantly reduced deflection pressures (about three times from Table 3.3), such that a contracting bubble in this location is less beneficial in terms of layer tearing. Bubble oscillating pressures from earlier research are shown to be between 0.1-0.5 Mpa [136], coinciding with the lower range of values in Table 3.4(b). By analysing the graphite flake in Fig. 3.8, the deflection pressures produced by bubble expansion were calculated in the range of 0.2–9 Mpa, while the deflection pressures for bubble contraction were in the range of 0.2–6 Mpa (Table 3.4(b); calculations above using Eq. 2). Therefore, no salient difference can be ascertained between the forces emitted as a consequence of either cavitation expansion or contraction. The larger values calculated for bubble expansion were attributed to larger

graphite flake deflection, which in turn produced greater impact pressures. However, the camera observation (Fig. 3.8(b-c)) indicated that bubble compression in this position mainly facilitated layer tearing, as pulling apart the layers helped to overcome their VdW's bonds via separation distance, as opposed to simply pushing layers together during rarefaction. However, this is not the case for bubbles that are already entrapped within the layers, whereby expansion seems to promote further opening of the graphite layers as observed in Fig. 3.11(b-d), and similar to Fig. 3.5(b) mentioned above (although that instance was a single bubble above the split) and explained in Fig. 3.5. Thus, we can certainly say that, depending on the position of the bubbles, an efficient synergetic mechanism based on the location of stable oscillating bubbles can be established. In our earlier research we suggested that the small-size bubbles excited by MHz frequencies can penetrate the thin layers of the graphite, grow in due time and increase the inter-layer spacing in a gentle fashion, while simultaneously, larger bubbles excited by kHz frequencies and located at the outer vicinity of the graphite can pull the layers further apart during their contraction [12]. This synergy can be instrumental in optimising and advancing the sono-exfoliation process. The following paragraphs present a proposed ultrasonic setup taking into account our experimental observations, acoustic pressure readings and guidelines on the technological implementation of the findings of this study.

The position of graphite flakes at distances larger than the size of the sonotrode tip (> 3 mm), seems to decelerate the exfoliation mechanism as the active cavitation zone is not sufficiently reaching the graphite flake surface and radiation forces as well as SWs emit lower energy. Thus, it can be deduced that effective treatment during continuous sonication in a cavitating field should be restricted within close proximity to the sonotrode surface and to the limits of the acoustic bubbly structures. As mentioned, all the acoustic cavitation clips presented in this thesis (as well as majority of the repeated experiments to ensure reproducibility of results) show that the 10 ms period of pulsed ultrasound treatment, where the cavitation zone grows in size, is when proliferation of layer delamination takes place, with lesser exfoliation also evident when the cavitation cloud shrinks and does not make direct contact with the subject graphite flakes. Therefore, one could assert a fair proposal that the transducer is most prevalent at shearing the VdW's bonds during this initial stage when cavitation cloud is at their most violent regime. These observations and evidence make the case that pulsed ultrasound can increase the productivity and efficiency of layer material exfoliation.

Since SWs have been identified as the driving mechanism to facilitate exfoliation of graphite for both LIB's and acoustic cavitation examples, we can propose a design model for a continuously sonicated environment to produce 2D materials. SW impact pressures rapidly decrease with distance as mentioned above (r^{-1}). For instance, Pishchalnikov et al.[27] measured a SW decay from the initial ~ 0.65 Gpa to ~ 150 Mpa over a $10\text{ }\mu\text{m}$ distance. Therefore, an effective cavitation zone must be established in order to efficiently utilise SW impacts for layered material breakup before their energy dissipates. Based on our hydrophone measurements coupled with exfoliation observations, pressure cycles of 0.7 to 1.6 Mpa (Fig. 3.12(b4)) at the separation distance of 2.5 mm between the sonotrode tip and the graphite flake are sufficient for exfoliation. We can suggest, therefore, that the effective cavitation zone is up to 3 mm for our case, or about 1D ratio: sonotrode diameter/effective cavitation zone.

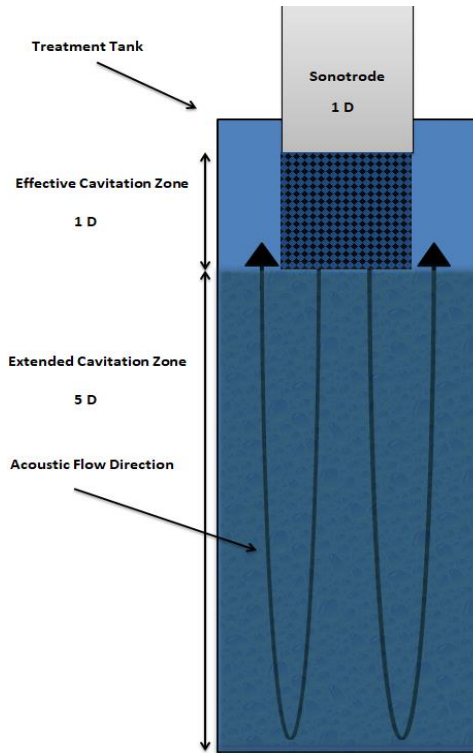


Figure 3.13. A proposed system to maximise ultrasonic exfoliation efficiency. The effective cavitation zone works to break up nearby graphite flakes, whereas the extended cavitation zone aids in layer separation, providing lesser shearing forces from stable cavitation, and the acoustic streaming recirculates larger graphite flakes back into the effective treatment zone.

Our observations also made it evident that acoustic streaming had utility for LPE assisted ultrasound, as harnessing the flow direction aided with separation, and could be employed to recirculate the layered material back under the effective cavitation zone. Based on previous work [54], we can estimate the depth of an extended cavitation zone to be 5-6 times the

sonotrode tip diameter. This way recirculation eddies/vortices still remain active, hence the treated solution volume is maximised and optimised. The vessel diameter also needs to be picked carefully under ultrasonic treatment. A size too large will leave untreated areas, whereas a size too small will not be efficiently optimizing the treatment zone. By varying the horn size using channels (which restrict the cavitation regime to a small volume) the bubble dynamics and cavitation intensity can be investigated. Previous research demonstrated that a ratio of $0.67D$ sonotrode tip to vessel diameter produced maximum cavitation intensity [146]. However, in our case this would not be sufficient due to the imperative to maximise and optimise the treating volume, while taking the acoustic streaming into account, as opposed to just maximising bubble cluster formation. To this end, we suggest a ratio of $\sim 0.5D$ sonotrode/vessel diameter. The model proposition presented in Fig. 3.13 enables us to exploit the range of SW powers so that both “lock-in” flakes, which require 0.14 GPa to delaminate [141], will have a high probability to be exposed to large cavitation pressures from SWs near to the sonotrode tip (> 1 mm), as well as “self-retracted” flakes, requiring 0.25 to 2.5 Mpa to exfoliate [141], which can be exposed to lesser SW pressures from 2-3 mm from the tip. Graphite flakes that fall out of the effective cavitation zone will get recirculated back in via acoustic streaming so they can again experience non decaying SWs to facilitate their breakup. In addition, recent studies demonstrated with numerical models that during the expansion stage of the cavitation bubble, and the beginning of the collapse stage, shear stress pressures of 1 kPa were generated onto the boundary wall, while after the jet impact this increased to around 100 kPa [137]. Therefore, the proposed model for containing the treatment zone to a confined area will produce more graphite surface/bubble interactions to benefit from microstreaming shear forces, whilst promoting liquid jet impacts. Hence, at this stage the source of graphite flakes seem beneficial for ULPE as the larger surface area complements these mechanisms, facilitating exfoliation of the graphite layers. However, the main drawback is that due to the size of these flakes, they often remain at the surface of the solution (as they are not fixed down as in this experiment), hence, interaction time in the cavitation zone may be limited.

Due to the atomic structure of layered materials which feature out-of-plane VdW's bonds and strong in-plane chemical bonds [7], one can infer the proclivity towards exfoliation to be through the axis of weakly held bonds. The orientation of the attached graphite flakes in this chapter's experiment promotes scissions into the graphite layers by fixing the graphite flakes vertically onto the substrates. Obviously in an uncontrolled or industrial scenario to

manufacture 2D materials such as graphene, these conditions would not be the case. For instance, LPE assisted via ultrasound creates a situation where layered material flakes are continually circulating around a solution while changing in orientation. Graphite flakes exposed to SWs and liquid-jets through varying orientation (not fixed vertically) would be subject to less efficient splitting and exfoliation as the plane of VdW's bonding would not be consistently under the acoustic source. In addition, graphite flakes horizontal to the acoustic source incur the possibility of structural damage as the chemical bonds in this plane may be broken. Moreover, other complexities arise due to the varying rheology of the solution. However, as mentioned in the introduction to the research chapters, the premise of this report is predicated on understanding the fundamentals of sono-exfoliation and optimizing sonication parameters for more efficient treatment. In addition to the important insights that identify specific cavitation mechanisms playing a pivotal role in the production of graphene sheets and other nanomaterials, a proposition of using pulse mode with the tip in close proximity to the bottom of the tank, i.e. extended ratio: sonotrode diameter/depth = 1/5, as well as promoting recirculation back into the primary exfoliation zone, effective ratio: sonotrode diameter/depth = 1, and sonotrode diameter/vessel diameter = $\frac{1}{2}$, can be confidently made. During the interactions between the LIB's and the samples, various mechanisms have been presented. Despite the numerous data, the most salient mechanisms and manifestations identified were SWs that induce expanding surface area and thinning, involution micro-jet assisted liquid mass interaction, expansion/contraction cavitation, inter-layer bubble pulsation, and microstreaming. The general factor which seems to determine whether the "slicing" or "flowering" mechanism occurs appears to be somewhat random, but mostly driven by the defects or flaws on the particular graphite flake (since they are not pristine in our case). For instance, a graphite flake with already partially separated or weakened layers down or close to the centre will have a propensity to enact the "slicing" manifestation. Whereas, a graphite flake with no, or equally weakened and partially separated layers across the tip has a higher probability to enact the "flowering" manifestation, as the SW impacts are evenly distributed across the graphite layers. For the "splitting" manifestation to take place the cavitation bubble must be positioned directly over the graphite flake (as opposed to adjacent or peripherally), or at a close enough distance (> 0.5 mm) for the generated liquid-jets to be impelled to accelerate onto the fake surface. The case of "branching" occurs due to close proximity oscillating bubbles, that further propagate partially exfoliated layers, which has the tendency to form multiple exfoliating arms or "branches". During acoustic cavitation our observations show that these manifestations do not tend to be

mutually exclusive. The diverse, multibubble interactions with the graphite often demonstrate these mechanisms and manifestations acting in conjunction with one other.

3.4 Conclusions

These experiments present the first ever recorded evidence of graphite exfoliation using cavitation bubbles. Phenomenological descriptions from the experiments uncovered various mechanisms and manifestations, which contribute to the exfoliation of graphite when subjected to laser induced single-bubble cavitation or acoustic cavitation. We demonstrated that the entire process of ultrasonic exfoliation of graphite is more complicated than previously thought.

Using high-speed imaging four specific manifestations of “flowering”, “slicing”, “splitting” and “branching” driven by the two main mechanisms of transient and stable cavitation were identified and demonstrated to be essential contributing factors to graphite exfoliation. Analysis of the high-speed imaging data proved that SW impacts alone are sufficient to initiate the exfoliation process as well as facilitate delamination of the graphite layers. The observations showed how cavitation bubble collapses can firstly increase the graphite flake surface area, followed by slicing and peeling. Moreover, micro-jets were seen to produce liquid mass entrainments that split layers effectively, while expanding and contracting forces emitted by oscillating (stable) cavitating bubbles also contributed to the exfoliation process.

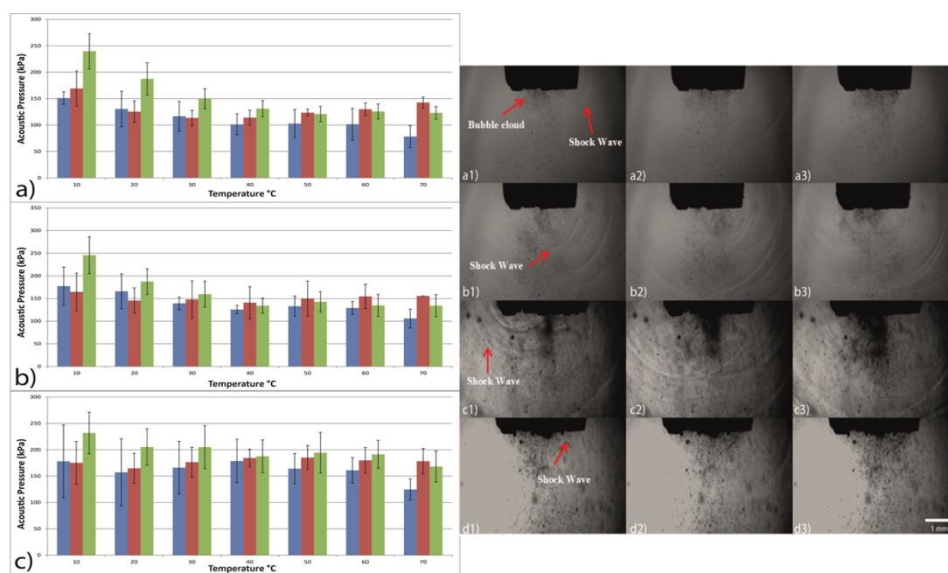
Accumulated SW pressures in the range of 0.7-5 Mpa are sufficient for exfoliation of the studied graphite flakes. In addition, acoustic streaming is seen to aid in the dispersion of LPE, as well as promoting bubble migration to the interlayers, and providing additional layer separating forces, where stable oscillating microbubbles nucleating between the split layers lead to “page-flipping” exfoliation. Finally, evidence for the utility of pulsed ultrasonic waves for exfoliation was presented. The short initial period of 10 ms (for our sonotrode) where the cavitation cloud grows was shown to proliferate layer tearing. It is worth noting that although these observations are well validated, variation in specific experiment conditions such as sonotrode diameter or peak-to-peak amplitude etc. would vary cavitation zone development and hence, values such as our calculated initial period of proliferated layer tearing.

The aforementioned sono-exfoliation mechanisms and manifestations provide direct and solid evidence of the fundamental proclivity of layer material exfoliation under cavitation. As a result, the reported data can be instrumental for developing a large scale, environmentally friendly ultrasound based liquid exfoliation process; and can be directly applied to the

validation and development of relevant sono-exfoliation numerical models that are required for optimisation and control of ultrasonic exfoliation processing.

Chapter 4

Optimizing Solution Temperature & Input Power for Graphite Exfoliation



Graphical Abstract: Acoustic pressure and high-speed imaging varying with input power.

Chapter Abstract

Ultrasound-assisted liquid-phase exfoliation is a promising method for manufacturing two-dimensional materials. Understanding the effect of ultrasonication parameters such as the temperature and input power on the developed pressure field is pivotal for optimization of the process. Limited research has been carried out to determine the optimal temperature for exfoliation, with some data generating disputed results. Simply maximizing the sonication power does not necessarily produce a higher yield because of shielding. In this study, a high-temperature calibrated cavitometer was used to measure the acoustic pressure generated in different graphite solutions in deionized water at various temperatures (from 10°C to 70°C) and input power conditions (from 20% to 100%). In addition, high-speed optical imaging provided insight on the SW generation from transient bubble collapses under different sonication conditions. The optimal sono-exfoliation parameters were determined to be 20% input power at 10°C for graphite flake solution, and 100% input power at 40°C to 50°C for graphite powder solution.

4.1 Introduction

In the previous Chapter the importance of SW and liquid jets by using high-speed imaging and identifying the 4 sono-exfoliation mechanisms at work were demonstrated [37]. In particular, SWs were shown as the driving mechanism of exfoliation, having sufficient force to initiate splitting of layers that led to delamination. In addition, stable cavitation bubbles trapped within graphite layers promoted high quality exfoliation with less defects on the final product by providing gentler shear forces through rapid oscillations [12], [37].

Despite the complementary shear forces, adverse effects deleterious to the LM's such as edge defects and holes can be produced due to prolonged ultrasonic treatment [147]. It has also been shown that temperature increase during sonication can result in inconsistent exfoliation [90]. Hence, implementation of a temperature control strategy is essential. Furthermore, ultrasonication enacted at higher amplitude is not necessarily beneficial due to the shielding effect, i.e. cushioning the acoustic emissions and SWs from the tip of the sonotrode [148], [149], which diminishes shearing of bulk material layers in the solution. Recent research has shown that by adjusting key parameters such as ultrasonic frequency and sonotrode geometry, high quality graphene flakes can be produced in a relatively short period of time [12].

In this Chapter, we focused on the effects that liquid temperature and input power had on the generation of cavitation to promote exfoliation based on the developed pressure field. A calibrated high-temperature cavitometer was used to measure acoustic pressure of solution temperatures between 10-70 °C during the inception of exfoliation (after ~5 min of sonication treatment). GP and GF were sonicated in DIW, which was previously identified as an ideal medium for exfoliation due to its low cost and non-toxic nature [12]. High-speed shadowgraphic imaging was also taken for different amplitudes to observe SW generation alongside the acoustic pressure measurements. Results showed that using specific combinations of solution temperature and acoustic power generates favourable conditions for LM exfoliation.

4.2 Methodology

4.2.1 Data Acquisition

Graphite solutions were made using GF (Sigma-Aldrich 100 mesh, maximum 149 μm) and GP (Alfa Aesar 300 mesh, maximum 56 μm). These sources were chosen as both are commonly used for exfoliation. Both types of graphite have a different structure and size, and as such, the effect of cavitation development will be different for each and warrants investigation.

In a 50 mm diameter glass beaker 0.06 g of graphite were mixed into 150 ml of DIW (Hexeal chemicals). About ~ 60 s of agitation was used to disperse the GP homogenously in the solution, whereas the GF's were pre-sonicated for two minutes for dispersion. Next the solutions were set to temperatures between 10-70 $^{\circ}\text{C}$ using either a chiller or heating plate (ARE Heating Magnetic Stirrer, Velp Scientifica) and verified with a thermocouple. When the set temperature was reached, the solution was sonicated for about a minute or two before a high-temperature cavitometer was introduced to capture the cavitation activity in the solution. The cavitometer consisted of a tungsten probe of 4 mm diameter, with a spatial resolution of 50 ± 10 mm, and calibrated in the National Physical Laboratory (UK) to frequencies between 15-50 kHz (able to resolve the fundamental frequency and the corresponding sub- and ultra- harmonics). It was submerged into the solution at an 80° angle, 80 mm below the water surface (see Fig. 4.1). The corresponding readings averaged from 60 individual readings of 2 ms each were converted to spectra using Fast Fourier transform as shown previously [85]. The conversion process was used to calculate the pressure values from the cavitometer output voltage. Further details and a description of the cavitometer can be found elsewhere [54], [150]. The data for all plots are presented as the root mean square (RMS) pressure for each combination of input power and temperature. These values provide an estimate for the average shearing forces the graphite sources would experience during ultrasonic treatment as reported previously [37], [140]. All pressure measurements were taken with respect to the ambient pressure, since the cavitometer had been calibrated at atmospheric pressure.

A (BS4d22) sonotrode with a 22 mm diameter titanium tip attached to a transducer (Hielscher UIP500hdT), with an operational frequency of 20 kHz was used for ultrasonic treatment. The peak-to-peak amplitude of the sonotrode was between 11.4 and 57 μm (corresponding to 20% and 100% input power, respectively), with a maximum operating power at 500 W. The sonotrode tip was lowered 10 mm below the solution surface and then activated. Experiments were repeated multiple times for each combination of parameters to ensure reproducibility of results.

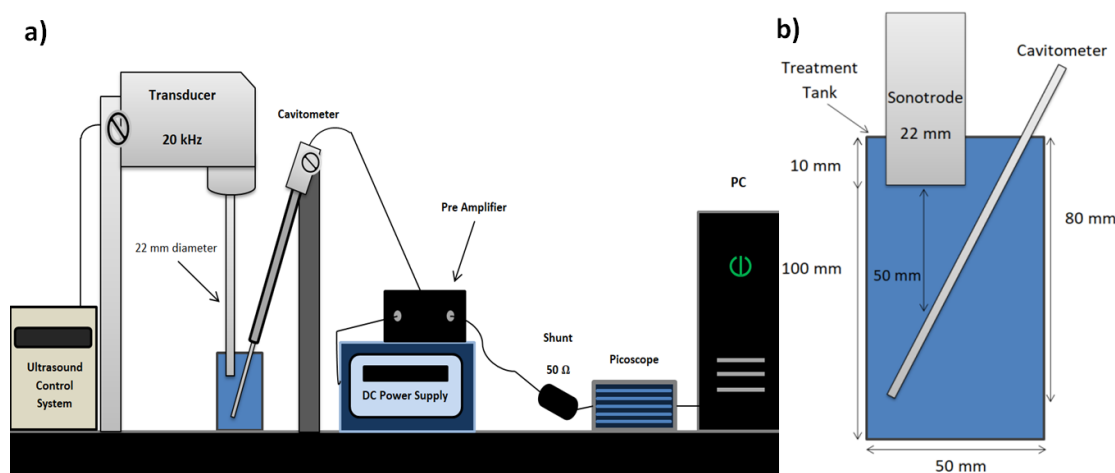


Figure 4.1. Ultrasonic setup. **(a)** Transducer is connected to the power control unit. The cavitometer is connected to a pre amplifier, power supply (Tektronix PWS2323), shunt, Picoscope and computer for running measurement software and data acquisition. **(b)** Enlarged schematic of the solution dimensions of the sonotrode, cavitometer and treatment tank.

4.2.2 High-speed Imaging Setup

High-speed shadowgraphic videos were captured using a Shimadzu (HPV X2) camera, at a frame rate of 1 million frames per second (Fig. 4.2). The camera generated 256 frames for every recorded sequence, producing shadowgraphic images with a resolution of 400×250 pixels as in chapter 3. Synchronised 10 ns laser pulses through a collimating lens provided the illumination (CAVILUX Smart UHS system) and effective temporal resolution to observe the generated SWs.

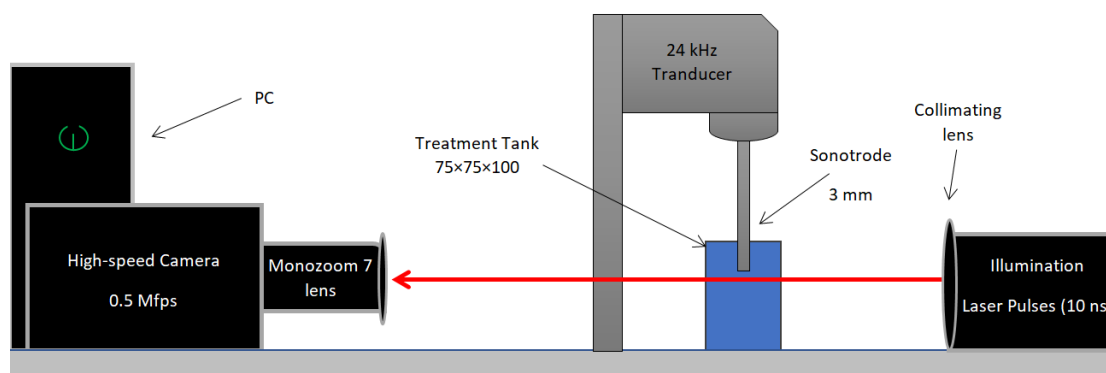


Figure 4.2. Schematic showing high-speed imaging setup, whereby the laser illumination passes through the treatment tank, whereby images are resolved by the camera and processed on the PC.

To produce high quality images using our camera and lens setup that would also show the entire sonotrode tip, a Hielscher UP200S with a 3-mm diameter titanium sonotrode and an

operational frequency of 24 kHz was used to observe cavitation and SW generation. The peak-to-peak amplitude was set to 42 μm and 210 μm , corresponding to an operating power of 40 W and 200 W (20 and 100%), respectively.

4.3 Results & Discussion

4.3.1 Temperature Effect on Acoustic Pressure

Figure 4.3(a) shows that the highest acoustic pressure (up to 250 kPa) is produced at 20% input power in the GF solution at 10 °C. Solutions for GP and DIW also gave rise to highest pressure readings at 10 °C, for their respective trends. Furthermore, the acoustic pressure for the GF solution and DIW gradually decreased with increasing temperature, while for the GP solution there was a slight increase in pressure above 40 °C.

At 50% power (Fig. 4.3(b)) all the studied solutions produced the highest acoustic pressures at 10 °C. After this, the acoustic pressure decreased with increasing temperature and remained approximately levelled from 30 °C onwards for the GF and 10 °C onwards for the GP. The DIW solution showed a slight downwards trend with temperature.

The GF solution at 100% input power (Fig. 4.3I) had a downward trend from 10 °C onwards, though not as pronounced as at lower powers. On the other hand, the GP trend showed less regularity with the largest pressures registered at 40-60 °C. Interestingly, the pressures for the GP solution were in the range of 165-185 kPa, while those for the GF solution had a much larger range between 170-270 kPa, however this pressure difference was smaller than that of GF solution at 50% and 20% input power (135-245 Mpa and 125-240 Mpa, respectively). The decrease in variation of acoustic pressure in such a small volume, as a consequence of increased input power was likely to be due to the shielding phenomenon [149]. Lower input powers produced less shielding, meaning the propagation of acoustic waves tended to be undisrupted (discussed in Figure 4.4).

The general decrease of acoustic pressure with temperature was likely due to the increase of the number of bubbles and vapour pressure (Laplace pressure) inside those bubbles, hence making them less likely to collapse. In addition, higher water temperature increased the tendency of bubble formation from gas nuclei, meaning pressure inside the bubble was higher than that of the vapour pressure at that corresponding temperature, and therefore a transient cavitation collapse was less likely. Furthermore, higher solution temperatures reduced the bubble surface tension, also decreasing the number of bubble implosions.

At low temperatures such as 10 °C, vapour cavitation bubbles had a higher tendency to nucleate as opposed to gas cavitation bubbles (though lower in numbers overall), and were usually more energetic, exhibiting more violent collapses. These generally featured shorter life-cycles (1-2 acoustic cycles) before catastrophic implosion, generating higher pressure emissions [101], [151]. Thus, a trade-off between the formation of vapour and gas bubbles with temperature rise regulated the pressure field in the solution.

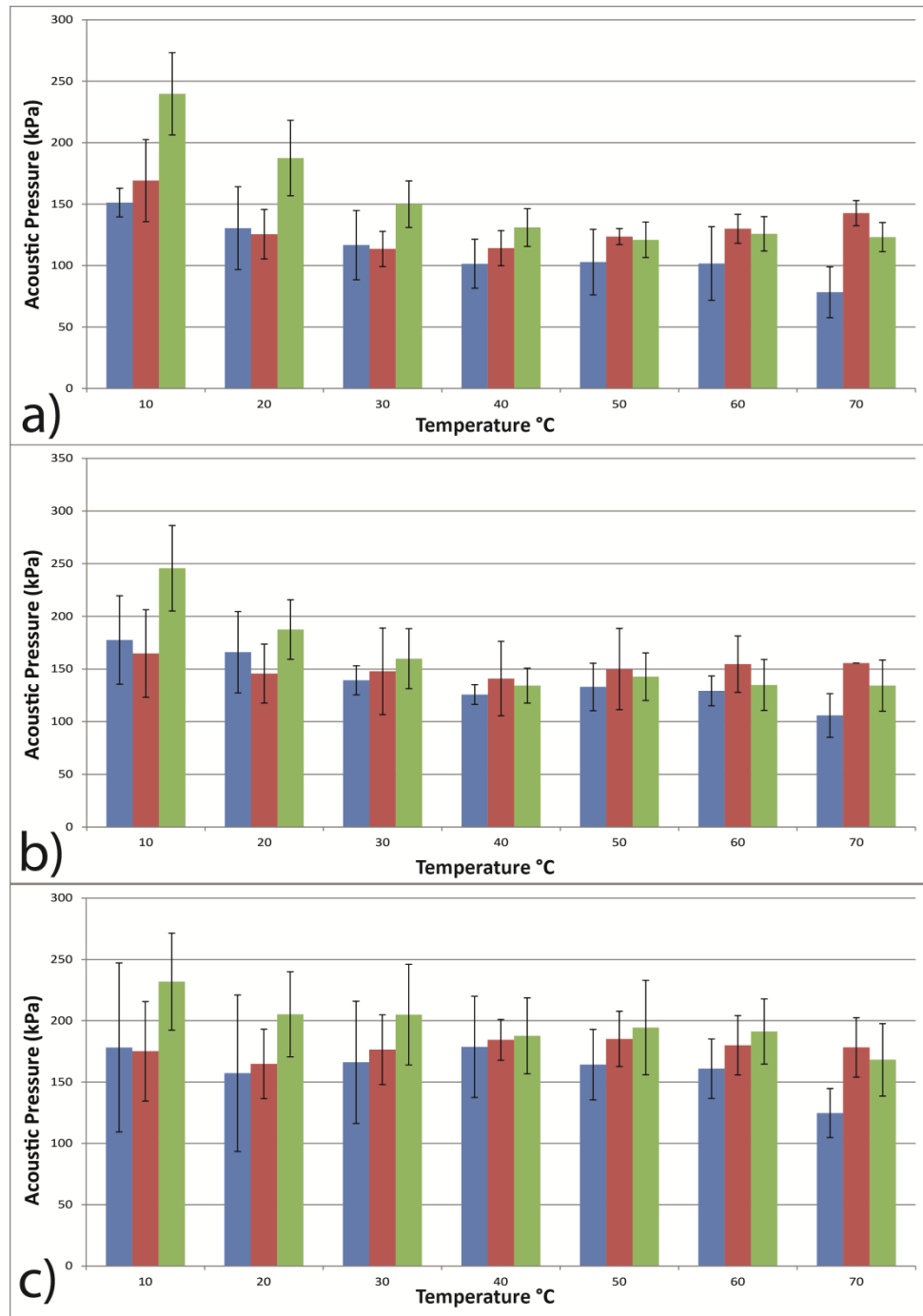


Figure 4.3. RMS acoustic pressure (averaged over 120 ms) comparison for three solution types: DI water (blue), GP (red) and GF (green), at a) 20%, b) 50% and c) 100% input power.

DIW solutions generally produced lower pressures, whereas the addition of GF or GP mostly increased the measured acoustic intensity. This was likely due to the addition of graphite particulates, which created more nucleation sites; in particular for the GF's which had a larger surface area compared to the much smaller GP particles. This observation also applies with the temperature change. We see the GF gave rise to a much larger range of pressures with temperature, as opposed to the GP source, where the small surface area was affected less by the number of nucleating bubbles varying with higher temperatures.

Although most of the acoustic pressure values for 100% input power were larger than those at lower input powers, a few selected parameters did demonstrate greater shearing pressures. For GP solutions the best candidates were 40 °C and 50 °C at 100% input power both giving rise to 185 kPa, which coincided with previously reported high yields at 40 °C [12], [99], [152] as well as with previous research, where under similar conditions it was numerically shown that the largest pressure corresponded to 35 °C [151]. However, using 10 °C at 20% input power and 10 °C at 50% input power gave rise to 169 kPa and 165 kPa, respectively. Therefore, from 20% to 100% input power we saw only a 9.5% increase in acoustic pressure (at the cost of 5 times more power).

However, for a solution to be kept at 10 °C throughout a prolonged sonication period, more energy would be needed due to the release of acoustic energy raising the solution temperature, whereas, maintaining a temperature around 40-50 °C should require less temperature control as a thermal balance in the solution may be reached naturally.

We can also hypothesize that, since the SWs are the governing mechanism of the exfoliation process [37], the stronger the pressure field, the more efficient the exfoliation should be. However, using 100% power (even with the presence of strong cavitation shielding) may cause excessive damage to the produced flakes, thus, lowering their quality, as well as decreasing the surface area due to more inertial bubble implosions. On the other hand, the low power at 20% generates a pressure regime slightly lower (by 16 kPa) to that of 100%, however, the extended cavitation zone is suppressed [101]. We have previously seen that the extent of the cavitation zone is of importance [140] as it regulates the efficiency of exfoliation [37]. Graphite particles closer to the tip of the sonotrode (where the majority of SWs are generated) exfoliate at a faster rate. Additionally, the flows induced by acoustic streaming at lower input power i.e. 20% are not powerful enough to generate a recirculating pattern that will continuously feed the cavitation zone with untreated graphite particles. This

can be ever more of an issue in the case of GF due to their large size and shape (as speculated at the end of chapter 3). It was previously shown that by doubling the power amplitude, the acoustic streaming and corresponding vortices may increase their velocity by 5 times promoting a higher throughput of the graphite particles from the energetic zone close to the sonotrode tip [54].

Thus, it can be deduced that an input power within these two extremes (20% and 100%) such as the 50% could be ideal as it combines a larger cavitation zone whilst avoiding damaging exfoliated nanosheets. Therefore, using a 40-50 °C at 50% power setting could also be a promising candidate for promoting exfoliation, using the powder source. For GF solutions, the highest pressures (approximately 240 kPa) were generated at 10 °C using all input powers. As the highest power setting generated slightly lower acoustic pressure, at the cost of 5 times more energy, we could conclude 20% power at 10 °C would be an ideal parameter for the GF source. However, the issue of temperature control and smaller cavitation zone, reducing the effective treatment area, would pose the same issue. If these considerations are taken into account then an optimal combination may emerge. To experimentally verify the pressure measurements the next Section presents high-speed shadowgraphic imaging.

4.3.2 Input Power Effect on Shock Wave Generation

When observing the production of cavitation clouds under a sonotrode we can see how using larger input powers creates a larger cavitation zone, with more acoustic emissions. However, as discussed in regard to Fig. 4.3, despite larger input powers creating more cavitation, this does not necessarily lead to greater acoustic pressures. Figure 4.4 shows shadowgraphic images under the tip of a sonotrode.

Figure 4.4a1) shows the initial release of SWs under the sonotrode tip at 20% power. In Figs. 4.4a2)-a3) these can be seen to propagate away from the tip. Figure 4.4b) displays the same phenomenon at 100% power, where each following image shows the propagation of the SW 1 μ s later. The obvious difference between the two input powers is the number of generated SW bands. From counting the number of released SWs between 20% and 100% power image sequences, we calculated ~33% more SWs for 100% power setting

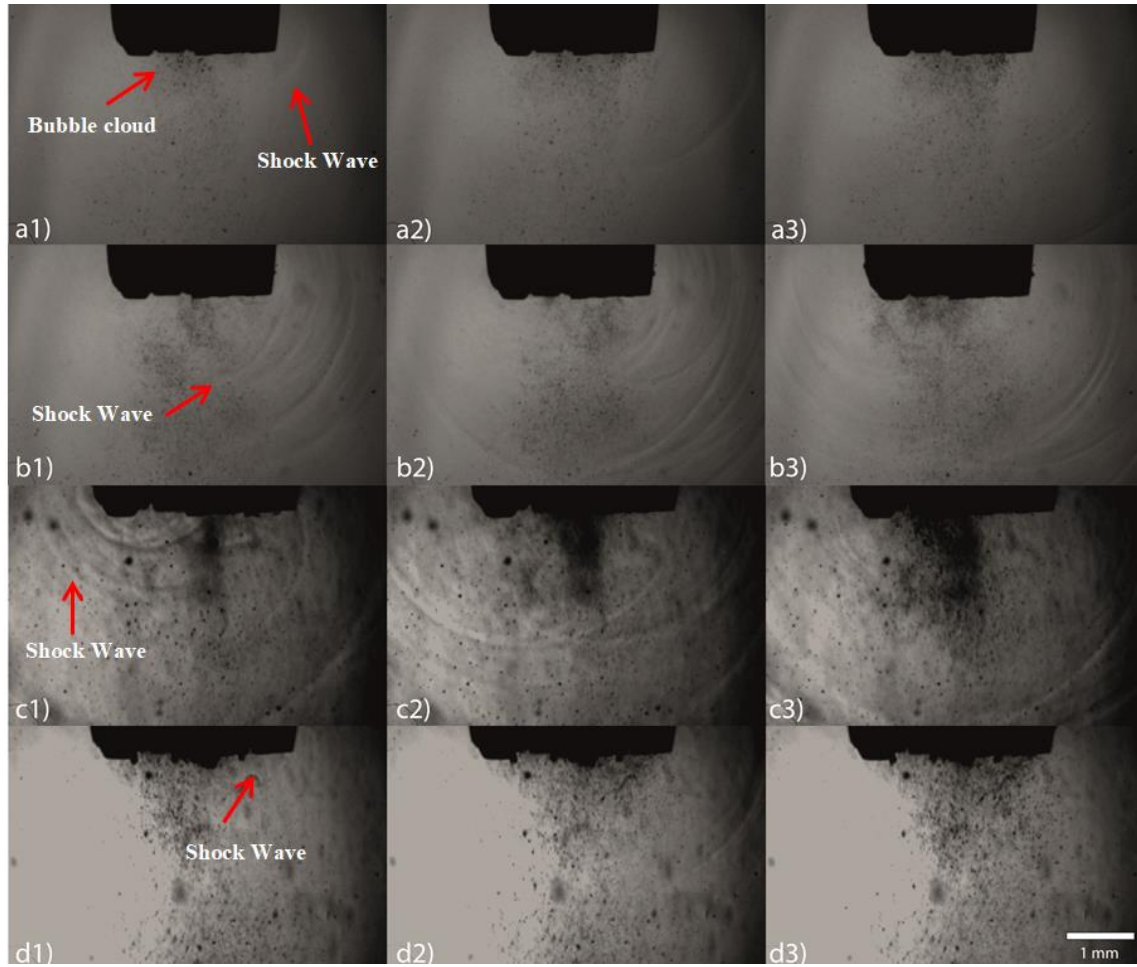


Figure 4.4. Representative shadowgraphic images showing SW generation for two different input powers; a) 20%, and b) 100% at 20 °C, and shock wave generation shown for two different temperatures; c) 10 °C and d) 70 °C, at 100% input power in DI water. Each image is 1 μ s from the preceding one.

Analysis was done for numerous images in order to get representative qualitative statistics. In order for the various measured acoustic pressures from Fig. 4.3 to be similar despite the larger input power (which has just been demonstrated to produce more SWs), we can deduce that these emissions were obstructed by the additional cluster of bubbles due to the higher input power. Therefore, following the discussion in Section 4.3.1, we would intend to choose an input power that produced the maximum number of SWs, whilst also limiting the size of the cavitation cloud such that the propagating SWs were not impeded and cushioned by the additional nucleated cavitating bubbles (i.e. shielding).

Figures 4.4c) and 4.4d) shows the release of SWs for 10 °C and 70 °C solutions in DIW, respectively. These selected images were chosen to highlight representative SW generation during the recorded clips. At 10 °C (Fig. 4.4c)) we see many more, and clearer bands of SWs propagating from the sonotrode tip, whereas, at 70 °C (Fig. 4.4d)) the number of SWs is

reduced (indicating a reduction of transient cavitation collapses, as discussed in Section 4.3.1). This may explain why acoustic pressure measurements for 10 °C are often greater than those in the higher temperature range (70 °C). However, despite these large pressures, one of the issues surrounding using a solution temperature at 10 °C for ULPE relates to chemical properties as opposed to physical. Exfoliation at 10 °C is likely difficult not only because of regulating the low temperature, but also due to an energy mismatch for graphite with surface tension and Hansen solubility parameters.

Before summarising the chapter findings, it is worth elaborating on the pressure discrepancies between Chapter 3 and the results in Fig. 4.3. Both sensors are calibrated at different frequencies and hence, primed for different uses. The FOH from Chapter 3 is specialised to detect SWs and pressure peaks in the MHz range (broadband noise), whereas the cavitometer is designed for detecting cavitation emissions near the incident source of 20-30 kHz. The difference in measured pressures also come from the much larger spatiotemporal resolution/sensitivity of the cavitometer compared to the FOH. Hence, the combination of these two sensors provides a full picture of the cavitation activity in the liquid.

Table 4.1 summarises the findings of this thesis, where the consequential effects of sonication parameters are listed. Taking these parameters into account, in conjunction with the discussion on beneficial input power and solution temperature, a trade off should be made beneficial for the exfoliation of graphite. The following chapters will focus on the combination of prolonged period experiments followed by characterization of the produced samples. To provide a balance of generating a large enough cavitation zone with minimal shielding and also satisfy surface tension and solubility parameters for the solution, ULPE experiments will be taken using GP at 40 °C.

Table 4.1. Summary of sonication parameters and effect on cavitation generation and behaviour.

Sonication Parameter	Effect on cavitation
Low input power	• Less shock waves • Less shielding • Smaller cavitation zone
High input power	• More shock waves • More shielding • Larger cavitation zone
Low temperature	• More transient/vapour bubbles • More shock waves
High temperature	• More gas bubbles (less prone to collapse) • Less shock waves

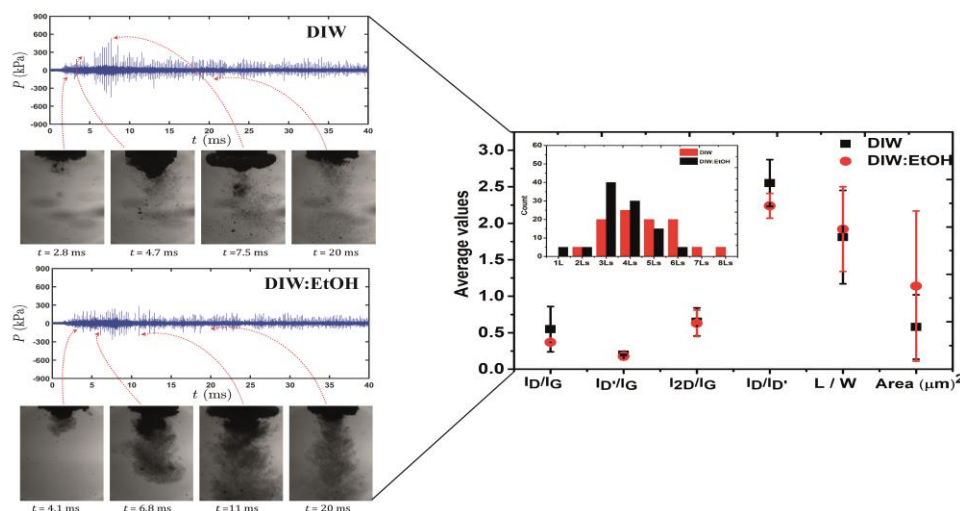
4.4 Conclusions

Based on the measured acoustic pressure field, the GF solution using 20% power at 10 °C was the optimal parameter setting for the magnitude of pressure. For the GP source 20% power at 10 °C also produced the highest pressure. This combination of low power and low temperature generated high acoustic pressures and was beneficial, as less bubbly clouds formed that may have suppressed the effect from multiple bubbles collapses. However, for a more practical exfoliation method, the use of 50% input power at 40 °C may provide a more appropriate treatment area and flow conditions, while minimizing damage to exfoliated nanosheets, and reducing energy input. These findings were further validated with high-speed images, confirming that using the highest input powers was often inefficient, and that despite the increased generation of SWs, the effect on potential shearing pressures for graphite could be lesser.

Taking this research to the next step will include *in situ* measuring acoustic pressures over long sonication periods (up to 2 h) to serve as a tool able to identify notable changes in acoustic pressure or spectra that will indicate the formation of graphene, verified via characterisation of the produced samples. This will be conducted in eco-friendly solvents, and is the objective of Chapter 5.

Chapter 5

Eco-friendly Solvent Selection of ULPE



Graphical abstract: Acoustic pressure and high-speed imaging with corresponding graphene yield and layer count.

Having identified the best/optimum ultrasonication parameters in Chapter 4 next step is to put them into practice for production of graphene. In this chapter four solvents; three green solvents (water, ethanol and water/ethanol) plus NMP for comparison, were sonicated and examined in terms of their bubble dynamics and acoustic emissions. Advanced fundamental analysis was conducted using high-speed imaging synchronised with acoustic pressure measurements complemented by shadowgraphic photography of the emitted SWs, in order to determine a suitable eco-friendly solvent medium from a cavitation bubbles dynamics perspective. Thereafter, ULPE of graphite in the optimum solvent took place for 2 h under controlled ultrasonication parameters of a 40 °C solution sonicated at 50% input power. The produced graphene samples were characterised by employing a series of techniques consisting of Ultraviolet–visible (UV-Vis) and Raman spectroscopy as well as transmission electron microscopy (TEM). A mixture of deionised water and ethanol was shown to produce a yield twice that of pure water, comprising of high quality few layer graphene (3-5 Ls) with an average area of $\sim 1.15 (\mu\text{m})^2$ and stability of $\sim 78 \%$ for the duration of six months. This combination is a promising eco-friendly substitute for future commercial manufacturing of graphene.

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5.1. Introduction

Recent development in the research of ULPE has led to high quality few-layer graphene (FLG) produced in relatively short periods of time (2 h) while using water as an environmentally friendly liquid medium [11, 13]. Despite these advances, graphene yield and nano material stabilisation (as a consequence of water's surface tension promoting re-agglomeration) still impose limitations for broad exploitation and upscaling. NMP is considered the optimum exfoliating agent for generating 2D materials via LPE [14, 15] due to its chemical properties facilitating the dismantling of the vdWs bonding holding the stacked layers together. However, in addition to its toxic nature and difficulty of removal of NMP from the final exfoliated product, the energy consumption due to long sonication periods also poses an issue. Previous research has been able to produce increasing yields of graphene, but at the cost of numerous hours of sonication, which also decreases the size of the graphene sheets (smaller than 1 μm) [84], [153].

One solution to overcome the drawbacks that NMP presents is to use eco-friendly solvents in combination with water that could exhibit appropriate cavitation behaviour while promoting high quality exfoliation and stability optimisation. Therefore, this chapter focused on investigating the effect of solvent selection and comparing eco-friendly solvents with NMP for ULPE. DIW, ethanol (EtOH), NMP and DIW:EtOH in a 50:50 (v/v) mixture were observed using high-speed imaging *in situ* for bubble dynamics and their respective cavitation zones generated under sonication with an ultrasonic horn. The rationale behind this specific choice of 50:50 DIW:EtOH ratio is due to its surface tension (23.91 mN/m) being close to the surface energy of graphite (23.93 mN/m), that promotes wettability and dispersibility as recently shown in [154] and hence provides more appropriate physical properties beneficial for high exfoliation efficiency of graphene than water or even NMP.

High-speed imaging observations were synchronised with real-time parallel acoustic pressure measurements using a calibrated (FOH). Additionally, shadowgraphic ultra-high-speed imaging was taken to analyse SW generation in the solvents under investigation, as SWs have previously been identified as the primary exfoliating mechanism upon ULPE [37]. The resulting data enabled us to define sonication parameters for a promising eco-friendly solvent to produce high-quality graphene. In light of the obtained acoustic pressure measurements and high-speed images, ULPE of graphene in DIW (as a reference liquid used in many previous studies [13, 15, 17–19]) and DIW:EtOH (found to be the most promising candidate)

was performed, followed by its in-depth spectroscopic and microscopic characterization to assess the quality of the final product. The experiments were conducted at 40 °C as this temperature was found to enhance ULPE results [38], [158].

This chapter presents the first in-depth analysis comparing fundamental physical properties and *in situ* observations of bubble dynamics for a range of solvents used for ULPE, including NMP (currently the most commonly used, and best performing solvent for exfoliation of graphene). This research consists of two main sections. The first section comprised data acquisition and *in situ* high-speed imaging for the investigated solvents. The second section demonstrated ULPE processing of graphene in the identified solvents, i.e. DIW and DIW:EtOH, and their characterizations together with a comprehensive comparison of dispersed graphene in terms of its degree of exfoliation, quality and stability in both solvents.

5.2. Methodology

5.2.1 Synchronised High-speed Imaging & Data Acquisition Experimental Setup

The solvents chosen to analyse for this study were DIW (Hexeal chemicals), EtOH (99.9%, Merck Life Sciences), NMP (Sigma-Aldrich), and a 1:1 ratio mix of DIW and EtOH. The mixture was investigated to establish an environmentally friendly replacement for NMP, a commonly used solvent for exfoliation of graphite. As such, the physical properties of DIW:EtOH were more alike to NMP (Table 5.1) i.e. a closer surface tension and viscosity, hypothesised to prevent re-agglomeration of exfoliated nano-sheets and reduce structural damage. A rectangular glass chamber (75×100 cm) was filled with 150 ml of the liquid medium under investigation.

A Hielscher UP200S with a 3-mm diameter titanium sonotrode and an operational frequency of 24 kHz was used for observation of generated bubble clouds and the cavitation zone. The peak-to-peak amplitude was set to 126 µm corresponding to an operating power of 120 W (60 %), respectively. A smaller diameter sonotrode was used than that of the larger 22-mm (Section 5.2.3) as the entire sonotrode tip/cavitation zone cannot be observed at suitable quality to resolve *in situ*, in-depth bubble dynamics using high-speed imaging. In addition, the 3-mm sonotrode prevents blocking of the camera field of view from the populated bubbly structures ensuring more clear and accurate data for analysis. As the fundamental frequency is the same for both transducers, qualitative information on the bubble dynamics was reliable.

The solvent temperature was set to 40±2 °C without the need for temperature control as only short ultrasonic pulses (~ 250 ms) were generated from the sonotrode. This temperature was

selected due to reasons mentioned in the previous chapter, and was found it to enhance ULPE results [158].

As in Chapter 3, the same calibrated FOH (Precision Acoustics Ltd) was used to measure acoustic pressures emitted from the cavitating bubbles and bubbly clouds. The calibration of the hydrophone was between 1 and 30 MHz, hence, within a frequency range ideal for detecting broadband SWs [112], which was previously demonstrated to be the driving exfoliation mechanism in Chapter 3 [37].

The FOH sensor was positioned and fixed 3 mm below the sonotrode tip (to detect high energy cavitation activity ideal for exfoliating graphite). A Peripheral Component Interconnect (PCI) card was installed into the PC, with the high-speed camera and FOH connected to enable synchronisation of the imaging and pressure measurements (Fig. 5.1).

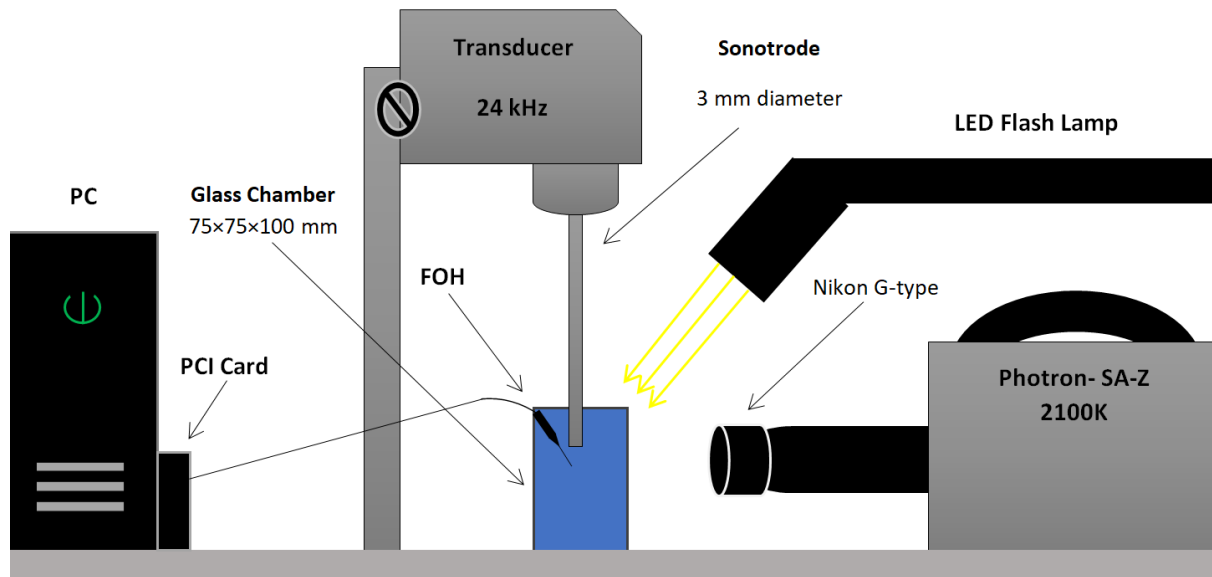


Figure 5.1. Schematic showing synchronised camera and acoustic pressure measurement setup. The high-speed camera records while the FOH measured acoustic emissions simultaneously.

Cavitation intensity was captured using a digital oscilloscope (Picoscope 3000 series) connected to the calibrated FOH device, where 60 waveforms of cavitating emission signals were recorded and averaged. A bandpass filter was applied to disregard everything outside the calibration range and below 1 MHz. The corresponding readings were then converted to acoustic pressures using fast Fourier transform over a 2-ms time period with sampling rate of 500×10^6 samples/s. Intrinsic background noise was removed, by means of subtraction from the initial voltage signal. Both the P_{RMS} and P_{max} were obtained and used to analyse the acoustic emissions. The P_{RMS} pressure measurements take into account all the associated

acoustic emissions, whereas P_{Max} measures the maximum acoustic pressure from each waveform, then averages over the total number of waveforms. As the FOH is primed to detect SWs (which generally responsible for generating the largest acoustic emissions) the P_{Max} plots are indicative of the inertial cavitation contribution. A step by step procedure on the calibration, signal processing and pressure conversion can be found elsewhere [85], [112].

High-speed imaging was carried out by the Photron- SA-Z 2100K camera (as used in Chapter 3) in conjunction with the measured pressures, using a frame rate of 50,000 fps over 512×712 pixels with a shutter time of 16.25 μs . A powerful front light beam LED flash lamp (GS Vitec) was used to provide illumination.

In order to measure acoustic pressures emitted from the sonotrode ideal for ULPE (Section 5.2.3), a Hielscher UP400St with a 22-mm diameter titanium sonotrode and an operational frequency of 24 kHz was used. The peak-to-peak amplitude was set to 9.2, 23 and 46 μm , corresponding to an operating power of 40, 200 and 400 W (20, 50 and 100%). In this instance the FOH was positioned 22 mm below the sonotrode tip, with both P_{RMS} and P_{Max} calculated. Temperature conditions were set to $40 \pm 2\text{ }^{\circ}\text{C}$ for the solvents under investigation.

5.2.2 Shadowgraphic High-speed Imaging Experimental Setup

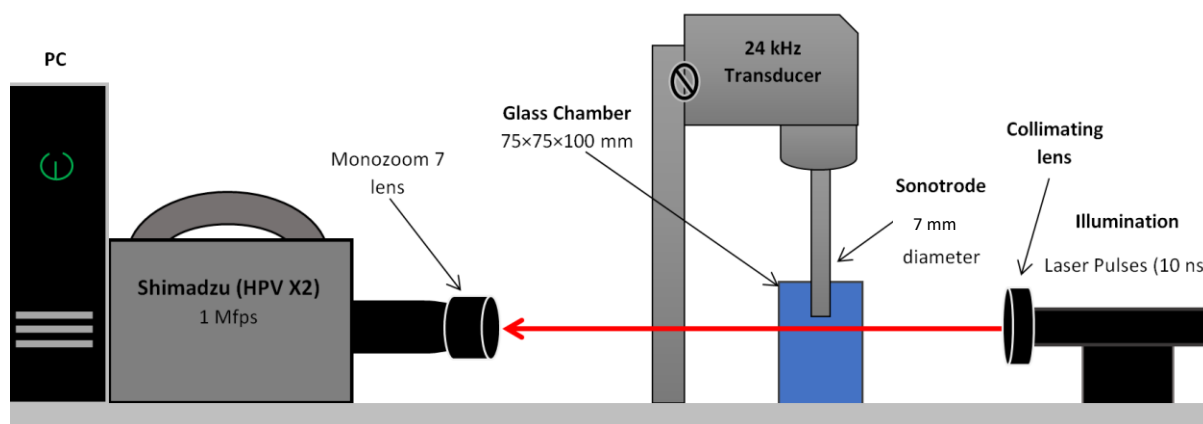


Figure 5.2. Schematic showing high-speed camera and transducer setup. Laser illumination passes through the selected liquid medium in the glass chamber, where images are then resolved by the camera and processed on the PC.

The same solvents and chamber dimensions specified in Section 5.2.1 were used for shadowgraphic imaging.

To observe cavitation and SW generation for the solvents we opted for using the Hielscher UP200S (described in Section 5.2.1), this time with a 7-mm diameter titanium sonotrode attachment. This allowed for the best combination of observing cavitation activity in

conjunction with the widest field of view available for imaging (measurements were taken at input powers of 20, 60 and 100% equivalent to peak-to peak amplitudes of 35, 105 and 175 μm respectively). High-speed shadowgraphic videos were taken using a Shimadzu (HPV X2) camera with the same setup parameters as described in the Chapter 4 Method.

5.2.3 Ultrasonic Exfoliation of Graphite & Its Characterisation

GP (Alfa Aesar 300 mesh, maximum 56 μm) was used as the exfoliating material. The solvents used for exfoliation are listed in 5.2.1.

To start with, 150 ml of DIW was filled in a double walled borosilicate glass beaker (Cole Parmer, 250 ml, 50 mm-diameter). The beaker was integrated to a recirculating cooler (Cole Parmer Stuart SRC5) through hose pipes allowing for temperature control. An input power of 50% at 40 °C was used as the best suitable combination parameter (as discussed in chapter 4). For DIW:EtOH, 75 ml of DIW was homogeneously mixed with 75 ml of EtOH to make 50:50 v/v mixture. First, ultra-sonication was performed in DIW with a Heilscher UP400St (as described in Section 2.1) at 50% input power for 5–10 min with the cooler on, to achieve the constant solution temperature of 40 ± 0.1 °C. The probe tip was kept 10 mm below the liquid surface throughout the duration of the experiments. After attaining a constant solvent temperature of 40 ± 0.1 °C (verified with RS 52 Digital Thermometer), 60 mg of GP was added to the DIW and stirred with a glass stirrer until well mixed, followed by its ultra-sonication for an uninterrupted 2 h duration. This experiment was further executed with the solvent DIW:EtOH mixture under the same experimental parameters. After sonication, dark graphene poly-dispersions of 10 ml were pipetted from the upper part of the solution and near the tip of the sonotrode. Dispersions were then centrifuged at 1500 g RCF for 30 min using SciSpin One Benchtop centrifuge to sediment un-exfoliated graphite particles/thick flakes to obtain supernatants. After centrifugation, the top two-thirds of the supernatants were decanted via careful pipetting and retained as a final product for further characterizations, and labelled as DIW and DIW:EtOH samples. Firstly, UV–Vis absorption spectra of the obtained supernatants were recorded in the wavelength range of 200–800 nm with Cary-60 spectrophotometer (Agilent Technologies) using quartz cuvettes (volume 3.5 ml, Agilent Technologies) with an optical path length of 10 mm. Dual-beam mode and baseline correction were used throughout the measurements to scan the samples. The spectra were recorded immediately after collecting supernatants to circumvent the agglomeration of flakes and scans were repeated a minimum of five times to obtain consistency in results. After

getting reasonable findings from preliminary UV–Vis measurements, the examined supernatants were drop-casted onto a cleaned silicon substrate and dried in a vacuum oven prior to Raman investigations. Furthermore, micro-Raman analyses of the drop casted samples were performed with InVia spectrometer (Renishaw) at an excitation wavelength of 514 nm laser (2.33 eV). The laser power was kept below 1 mW in order to prevent sample damage and peak shift induced by the laser. Data collection was performed with 50 × magnification and acquisition time was adjusted accordingly to have a coherent signal/noise ratio. To obtain reliable results, Raman spectra of at least 20–30 random flakes were recorded for each sample in the range from 1200 to 3100 cm⁻¹. Simultaneously, 2–3 drops were put onto holey carbon coated copper grid placed on a filter paper to wick away excess solvent and dried completely for TEM investigations. TEM analyses (both low magnification and high resolution) were performed to interrogate the individual flakes using a JEOL 2100F Field Emission Gun operating at 200 kV. Additionally, image processing was performed with ImageJ software to evaluate the quality and dimensional analyses of registered flakes to generate meaningful statistical data.

5.3. Results & Discussion

5.3.1 High-speed Imaging Synchronised with Acoustic Measurements

The use of the FOH synchronised with high-speed imaging allowed for precision acoustic pressure measurements mapped to cavitation activity. Figure 5.3 shows this synchronisation technique for the various solvents under investigation, whereby the cavitation intensity has been converted into acoustic pressure. We can see from observing the ultrasonication in DIW (Fig. 5.3(a)) that once the sonotrode was activated the first batch of acoustic emissions were detected from the FOH (video 1, accessed with the published version of this chapter <https://doi.org/10.1016/j.carbon.2022.12.070>). During the first 2 ms after the activation, low cavitation intensity (represented by only a few spikes in the time domain signal) was measured, with no visible cavitation bubbles (Fig. 5.3(a)). However, after ~ 2.5 ms bubble nucleation occurred and coincided with the rise in cavitation intensity (represented by prominent spikes in the time domain signal) on the graph (Fig. 5.3(a)). During the next ~ 5 ms the camera footage showed an increase in size of the primary cavitation cloud, which again occurred in accordance with the increase in the measured cavitation intensity (as indicated by the red arrow). We have previously reported this phenomenon, noting that upon sonotrode activation, a higher intensity is recorded until a stabilised period is reached where the cavitation under the sonotrode tip remains stable, after which little variation in size occurs

[37]. This rise in acoustic pressure can be seen for all plots in Fig. 5.3, where thereafter, a stable period was observed with generally lower acoustic pressures. Interestingly, the EtOH solution took longer to generate observable cavitation bubbles (~ 6 ms, Fig. 5.3(b)), in addition to giving rise to the smallest pressure peaks than the other solvents under investigation. For DIW:EtOH, we observed more pressure peaks than EtOH, with larger intensities (Fig. 5.3(c)). NMP produced a pressure-time plot alike to DIW, with higher intensity peaks than EtOH and DIW:EtOH and also gave rise to the largest measured peak for all the solvents (Fig. 5.3(d), ~ 7.5 ms).

The recorded collapse of a bubble cloud under the sonotrode tip can be seen to produce a pressure spike on the graph. For instance, the highest measured acoustic pressure of EtOH (Fig. 5.3(b), next to the red arrow) at ~ 7.5 ms (generating ~ 300 kPa) coincided with the cavitation zone just after collapse. Images in Figure 5.3 display four representative moments of developing bubble dynamics (specified in the caption). At ~ 7.5 ms for EtOH the image captures the large primary cloud formed under the sonotrode tip just before this collapse. After the cavitation cloud collapsed, multiple SWs were generated and detected by the FOH (indicated by the large pressure spikes, Fig. 5.3(b)). Often, a larger bubble cloud collapse will trigger transient bubble collapses sporadically from the secondary clouds and, hence, a higher measured intensity is registered via the FOH. However, this is not always the case due to acoustic shielding [101], as well as the position of the FOH under the sonotrode which influences the recorded pressure [112].

The visual observation of a large bubble cloud collapse in conjunction with a large spike can be seen for each tested solvent in Fig. 5.3 (the third image in the sequence). For each solvent the maximum area of the developed cavitation zone was measured using the high-speed imaging. Salient observations from the DIW cavitation activity showed a localised primary cavitation cloud at the tip of the sonotrode, measured to be $\sim 1.13 \text{ mm}^2$ in cross-section (Table 5.2) at 20% sonication power. The satellite bubbles underneath were small in size (65-250 μm maximum diameters) and vigorously oscillated mostly in stable cavitation modes. In contrast, EtOH, DIW:EtOH and NMP all generated much larger cavitation zones. The cross-sections of the primary cavitation cloud formed under the sonotrode tip for EtOH, DIW:EtOH and NMP were measured to be ~ 3.19 , 3.17 and 2.33 mm^2 , respectively. As DIW has a significantly higher surface tension compared to the other solvents (Table 5.1), it is less likely to nucleate bubbles at such a low input power (20%); therefore, the primary cavitation cloud was expected to be smaller in size [21, 23]. Table 5.1 and 5.2 shows this trend in solvents

with a decreasing surface tension producing a larger cavitation cloud. Additionally, the viscosity of the liquid medium influences the cavitation zone size. A larger viscosity can contribute to increasing the cavitation zone [159], hence, producing a larger cavitation zone formed under the sonotrode tip.

Table 5.1. Physical properties of the solvents under investigation at ~ 40 °C.

Solvent Type	Surface Tension (mN.m ⁻¹)	Density (kg.m ⁻³)	Vapour Pressure (kPa)	Viscosity (mPa.s)	References
DIW	69.6	992.2	7.38	0.653	[87], [160]–[162]
EtOH	21.58	772	17.98	0.866	[163], [164]
DIW:EtOH	23.91	842	NA	1.275	[163], [165], [166]
NMP	40.27	1015	1.319	1.29	[167]–[170]

Table 5.2. Representative bubble statistics for each solvent, calculated by analysing high-speed imaging sequences.

Solvent Type	Sonication Power (%)	Primary Cavitation Cross-sectional Area (mm ²)	Flow of Secondary Cavitation (ms ⁻¹)	Diameter Range of Secondary Cavitation Bubbles (mm)
DIW	20	1.13	0.52	0.065-0.25
	60	3.65	1.23	0.08-0.48
	100	4.16	1.25	0.05-0.26
EtOH	20	3.19	0.91	0.15-0.45
	60	4.03	0.94	0.13-0.8
	100	4.63	1.36	0.13-0.7
DIW:EtOH	20	3.17	1.08	0.13
	60	4.1	1.27	0.01-0.21
	100	5.3	1.35	0.11-0.14
NMP	20	2.33	0.53	0.08-0.4
	60	3.55	1.28	0.13-0.42
	100	4.24	1.55	0.16-0.43

These tendencies were also observed for the secondary cavitation clouds produced by each solvent, with more satellite bubbles extending the overall cavitation spatial distribution. For instance, satellite bubbles generated in EtOH were measured to have diameters approximately twice the size of those in DIW at the same input power (Table 5.2). The larger primary and secondary cavitation zone formed under the sonotrode for NMP (coinciding with the proclivity for bubble collapse demonstrated by the large pressure spikes in Fig. 5.3(d)) is likely a contributing factor for its exfoliation efficiency. We have previously demonstrated

using synchrotron X-ray phase-contrast imaging that the bubble density under the sonotrode for NMP was nearly twice that of DIW [118]. The synchronised imaging and pressure measurements provide additional evidence that the bubbles produced in NMP are more effective in terms of delamination of layered materials such as graphite.

It is important to note that despite producing a larger cavitation zone, or more bubbly clouds, larger acoustic pressures are not necessarily generated. Increased intensity of cavitation activity is determined by the level of detectable prominent peaks and SWs within the emission signal [26, 27]. We can observe from Fig. 5.1 that during the initial period upon the sonotrode activation (<15 ms) ultrasound produced higher acoustic pressures than afterwards, when the primary cloud reached its stable size (the fourth image in the sequence). This short ultrasonic period giving rise to higher pressures makes a case for using pulsed ultrasound. The higher measured pressure amplitudes could be due to the phenomenon that pulsed ultrasound can promote nuclei replenishment, hence generating more cavitation and transient cavitation collapses detectable via the FOH [28, 29]. Employing a short, powerful ultrasonic burst may be beneficial for a variety of applications such as preventing reactor clogging and reducing energy usage [109]. However, for ULPE, further testing would need to be conducted. The “pause” during deactivation of the sonotrode may decrease the time that flakes require to sufficiently exfoliate, as well as affecting sustained acoustic flow and recirculation.

The appearance of the cavitation activity for DIW was very different due to the reduced nucleated bubbly clouds. EtOH and NMP were similar (Video 2 & 3; accessed with the published version of this chapter <https://doi.org/10.1016/j.carbon.2022.12.070>), producing darker clouds demonstrating the larger area occupied by the bubbles. Interestingly, the addition of EtOH to the DIW significantly changed the appearance and bubble dynamics. Activation of the sonotrode was seen to generate “mist” of cavitation bubbles, producing an extended, very dark cavitation cloud (observed in Fig. 5.3c and Video 4; accessed with the published version of this chapter <https://doi.org/10.1016/j.carbon.2022.12.070>). Due to the largely dispersive nature of the bubbles (where clouds appeared to be comprised of tiny cavitation bubbles spread out homogeneously, which made it difficult to distinguish between primary and secondary cavitation clouds), measuring the secondary cavitation cloud posed a problem. We can, however, suggest that this type of bubble dynamics may be more useful for exfoliating layered material by in-layer penetration, producing a gentler exfoliation as reported previously [37].

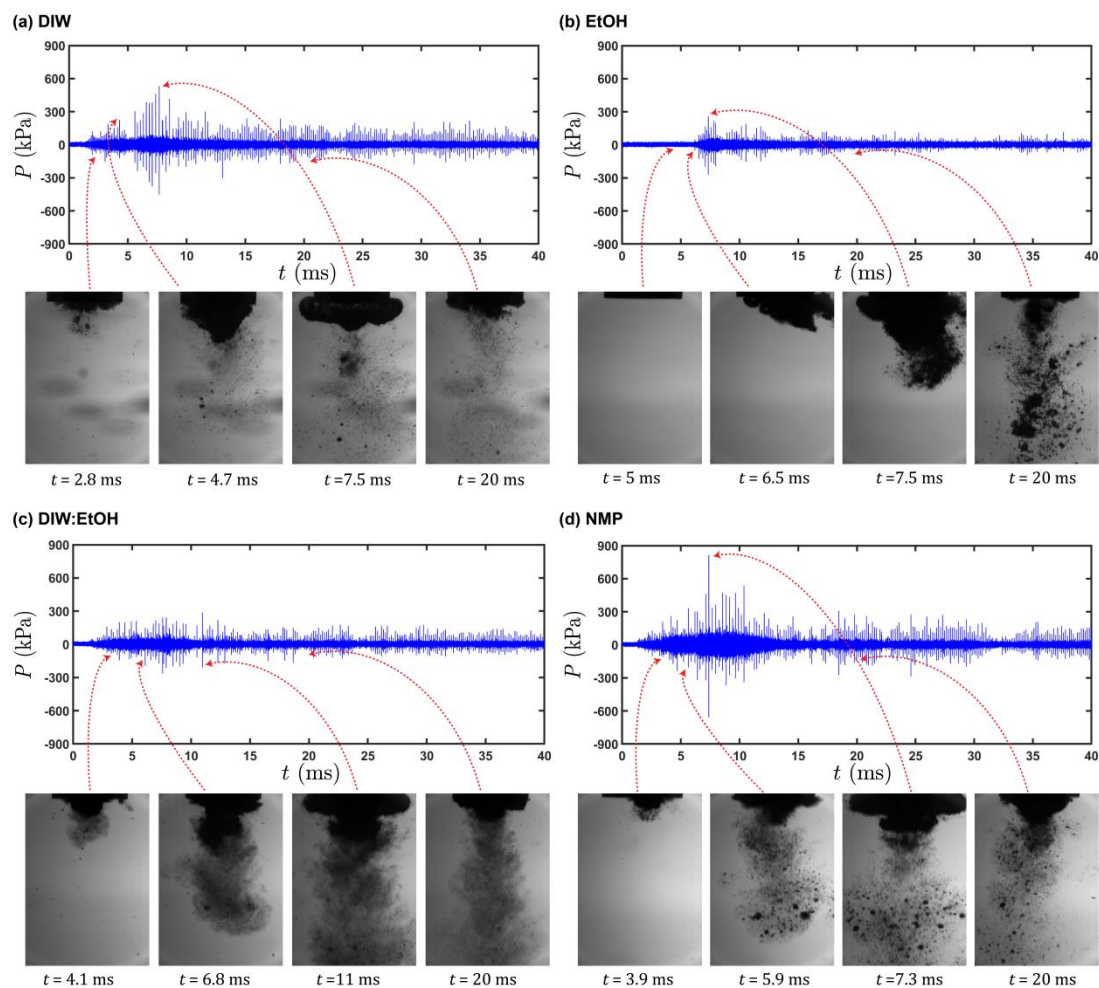


Figure 5.3. Synchronised high-speed images (insets) with acoustic pressure plots from 0-40 ms for each solvent; **(a)** DIW, **(b)** EtOH, **(c)** DIW:EtOH & **(d)** NMP. The insets display four representative moments (indicated via the red arrows) of the developing bubble dynamics for each solvent; (1) initial activation of the sonotrode, (2) cavitation cloud development, (3) maximum cavitation cloud before collapse (thereafter, a large corresponding pressure spike is induced), (4) stabilised cavitation period. Imaging was taken at 50 kfps, with intensity measured via a FOH and converted to acoustic pressure. The transducer input power was set to 60% with the solution temperature at 40 °C.

General observations from the data in Table 5.2 demonstrated that an increase in sonication power for each solvent generated a larger primary cavitation cloud. We observed DIW to show the greatest percentage increase in primary cavitation area, of $\sim 270\%$, when changing sonication power (equivalent to the generator power) from 20 to 100%. Interestingly, the increase in acoustic power was less effective at generating a larger primary cavitation cloud for solvents with lower surface tensions (the increase measured as 82, 67, 45% for NMP, DIW:EtOH and EtOH, respectively).

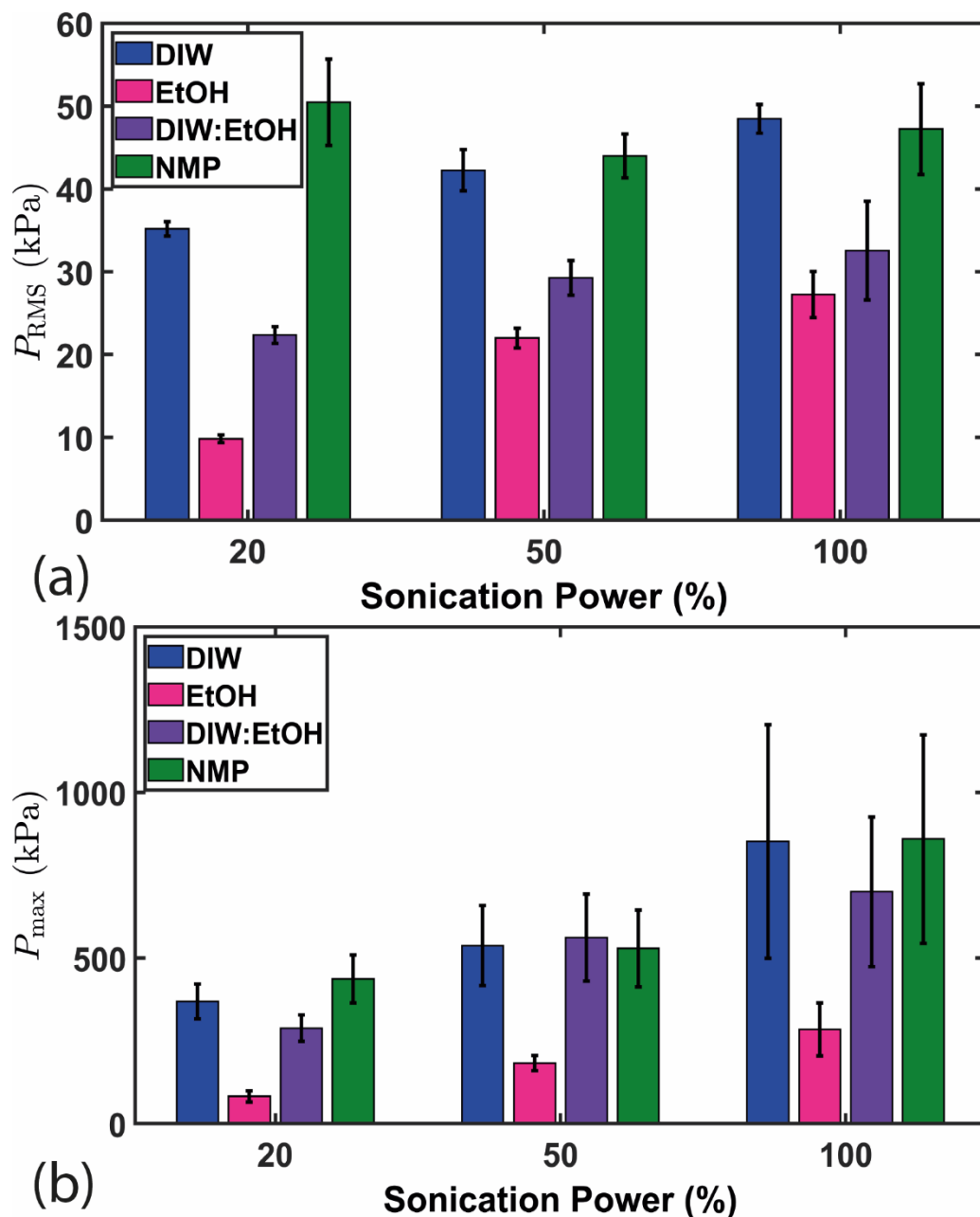


Figure 5.4. Pressure measurements taken with the FOH for solvents under investigation; (a) P_{RMS} ; (b) P_{max} . The acoustic intensity ($\times 10^{-4}$ W/m²) corresponding to the sonication input powers are as follows: DIW; 9 (20%), 13 (50%), 37 (100%); EtOH; 3 (20%), 10 (50%), 30 (100%); DIW:EtOH; 3 (20%), 17 (50%), 34 (100%); NMP; 8 (20%), 20 (50%), 40 (100%) (calculations in Appendix Section B Table B2). Data was recorded from 60 waveforms of cavitating emission signals using a 2-ms time period, and averaged for each case (Section 5.2.1). The temperatures of the solvents were maintained at 40 °C.

Figure 5.4 presents the measured acoustic pressures for each solvent using a larger sonotrode (Section 5.2.1) ideal for ULPE at scale, which was used for prolonged experiments in Section 5.3.2. A stabilised cavitation regime for the solvents revealed the same trend (as seen in Fig. 5.3). The highest recorded P_{RMS} pressures arose from NMP and DIW, followed by the DIW:EtOH mixture and EtOH (Fig. 5.4(a)). This observation once again confirms the effect

of physical properties. NMP has a significantly lower vapour pressure than all the solvents under investigation (Table 5.1, ideal for more bubble collapse). This may explain the high acoustic pressures measured. However, the significantly higher surface tension of DIW (Table 5.1) promotes more powerful bubble implosions, hence, producing a larger number of SWs interacting with the FOH tip than in NMP. EtOH producing the lowest acoustic pressures can also be explained by the physical properties [101]. The cavitation strength is directly affected by the surface tension at the liquid-gas interface, as well as the initial bubble radius, therefore, we can also expect the large pressure difference between DIW and EtOH (having the highest and lowest surface tension, respectively). Due to the ability of EtOH to reduce cavitation bubble impact [172], we can hypothesise that a bulk-layered material exposed to repeated SWs (of smaller acoustic pressure, Fig. 5.4) would suffer lesser deleterious effects such as structural defects. EtOH has a significantly higher vapour pressure that promotes bubble formation but also impedes bubble implosion (Table 5.1) [101]. The mixture of DIW and EtOH was, in-part, proposed to balance generating sufficient SW impacts to exfoliate layered materials, as well as ensuring minimal surface damage. It has been previously reported that DIW as a liquid medium can induce defects due to the greater impact of SW interactions [20]. Lowering defects promotes production of pristine graphene, and would increase applicatory uses of the exfoliated nano-sheets. This defect reduction is also later confirmed in Section 5.3.2.

Before optimizing our experimental setup for ULPE at 40 °C, preliminary testing was also conducted at 20 °C. The acoustic pressure plots demonstrate the same trend for most of the solvents, albeit higher measured pressures at 40 °C (Fig. 5.4). Interestingly, NMP pressure measurements at 20 °C (Appendix Section B Fig. B2) were significantly lower than those at 40 °C, and also in comparison to the temperature change in the other solvents. Some previous research has opted to use NMP at 40 °C during ULPE, without presenting specific, fundamental justification [173]. It is possible that from a physical perspective, increased cavitation activity facilitates of exfoliation at this temperature. A higher temperature solution can often increase the production of cavitation bubbles [174]. Non-dimensional analysis of NMP at both 20 °C and 40 °C revealed an increase in the Reynolds number (Appendix Section B Table B1), indicating the temperature rise enhanced inertial forces leading to bubble collapses [101].

To our knowledge, this is the first time NMP has ever been investigated quantitatively in terms of acoustic pressure in conjunction with cavitation dynamics under ultrasound. The

analysis of the data implies that NMP can produce strong cavitation that varies distinctly with temperature (Fig. 5.4). NMP needs lesser agitation to break apart layered materials than other solvents, largely a consequence of its chemical properties (i.e. Hansen's solubility parameter) [78]. This chapter's research indicates the proclivity to exfoliate so effectively is a combination of chemical and physical properties, whereby cavitation bubbles play a larger role than previously thought. The higher temperature increases the number of these bubbles, hence, increasing the SW generation and aligns with our previous camera observations and measurements of the large cavitation zone for NMP at 40 °C. The introduction of ultrasound increases the exfoliation efficiency, in addition to assisting in the dispersion of material within the liquid medium (Section 5.3.2). Despite these benefits, due to the large acoustic pressures measured, the ultrasonic cavitation in this case may increase the chance for deleterious effects on the nano-sheets. It is also noteworthy to recall the hazardous and contaminating nature of NMP.

As SWs appear to be the primary mechanism to facilitate exfoliation of layered materials in DIW [37], we must also consider the $P_{\max}$ pressure (Fig. 5.4(b)). The calibration of the FOH (1-30 MHz) is primed to detect SWs, and the data on the maximum acoustic pressure assists our analysis to detect the role of SWs generated in each solvent (i.e. SWs generally induce the highest cavitation intensity). We observed that NMP, DIW and DIW:EtOH behave similarly, despite some variation due to sonication power. From Chapter 4, we have identified a moderate generator power (50%) to provide appropriate acoustic flow [54] in conjunction with the necessary cavitation intensity to promote exfoliation of graphite [38], [158]. Interestingly, conditions set at 40 °C and at 50% input power demonstrated very similar acoustic pressure for NMP and DIW:EtOH in the range of 0.5 Mpa (Fig. 5.4b)). We could hypothesise from this data that these conditions may ensure exfoliation in DIW:EtOH through similar bubble dynamics and SW interactions as in NMP.

Another positive aspect of using DIW:EtOH may arise from an increased wettability. For the case of DIW (with the highest surface tension), a poor wettability with the source graphite leads to floating particles on the liquid surface (even when acoustic energy is introduced), therefore, promoting an inefficient use of the material. Additionally, a higher wettability for DIW:EtOH aids to disperse the layered material into the solvent, facilitating exfoliation as graphite particles can be re-circulated into the primary cavitation zone under an acoustic flow.

These data, along with the high-speed imaging are indicative that the combination of DIW:EtOH would be a promising candidate for ULPE. As previously mentioned in Chapter 2, the surface tension of DIW is not ideal for stabilisation of exfoliated nano-sheets, therefore, re-agglomeration occurs over short periods. Due to the DIW:EtOH mix decreasing the surface tension disparity between DIW and NMP (considered to have close to optimum surface tension for exfoliating graphene) we can hypothesize that the exfoliated material suspension would remain stable, and in turn increase the yield (as later demonstrated in Section 5.3.2 Fig. 5.6(i) and (d)). Furthermore, we suggest that due to the increase in size of the cavitation zone (Fig. 5.3), the localisation of cavitation would pose less of an issue, and lead to increased layered material exfoliation throughout the liquid medium due to extended shearing forces introduced via larger and more distributed satellite bubbles and cavitation bubble “mist”. Finally, due to the size of cavitation “mist” bubbles induced within the DIW:EtOH mix, a gentler exfoliation may be promoted (similar to the high-frequency (~ 1.2 MHz) exfoliation mechanism [20]) with these cavitation bubbles fitting in-between inner flake layers, hence, reducing structural defects whilst expediting layer delamination.

Therefore, the use of the high-speed camera that proved to be a beneficial tool for this Chapter revealed the behaviour of bubbles in the studied liquids with different properties. For example, it is shown that bubbles in EtOH with low surface tension coalesce and generate large bubbly structures with less tendency to collapse (also indicated by the pressure waveform in Fig. 5.3). However, bubbles in DIW:EtOH with a surface tension closer to NMP and higher viscosity produce a stable “mist” of bubbles that has been previously identified in [172] as a potential mechanism to enhance exfoliation via the interaction with partially exfoliated graphene flakes as predicted in [37]. High quality exfoliation using DIW:EtOH was later confirmed by the outcomes of this study (Section 5.3.2).

5.3.2 Shadowgraphic Ultra-high-speed Imaging

Although the analysis on the bubble dynamics in conjunction with synchronised acoustic pressure measurements gave us some indication as to the mechanisms through which sonication in different solvents may affect exfoliation, more specific features of this exfoliation can be analysed through detailed observation of SW generation and propagation for each solvent. Previous research has demonstrated SW analysis from the perspective of acoustic spectra [112], [172], however, to gain a better insight shadowgraphic photography was utilised to evaluate the evolution and propagation of SWs in real-time. This was taken as a pre-condition experiment before we undertook ULPE for extended durations (Section

5.3.2). Figure 5.5 shows representative, *in situ* image sequences of SW generation with varying input power for each tested solvent.

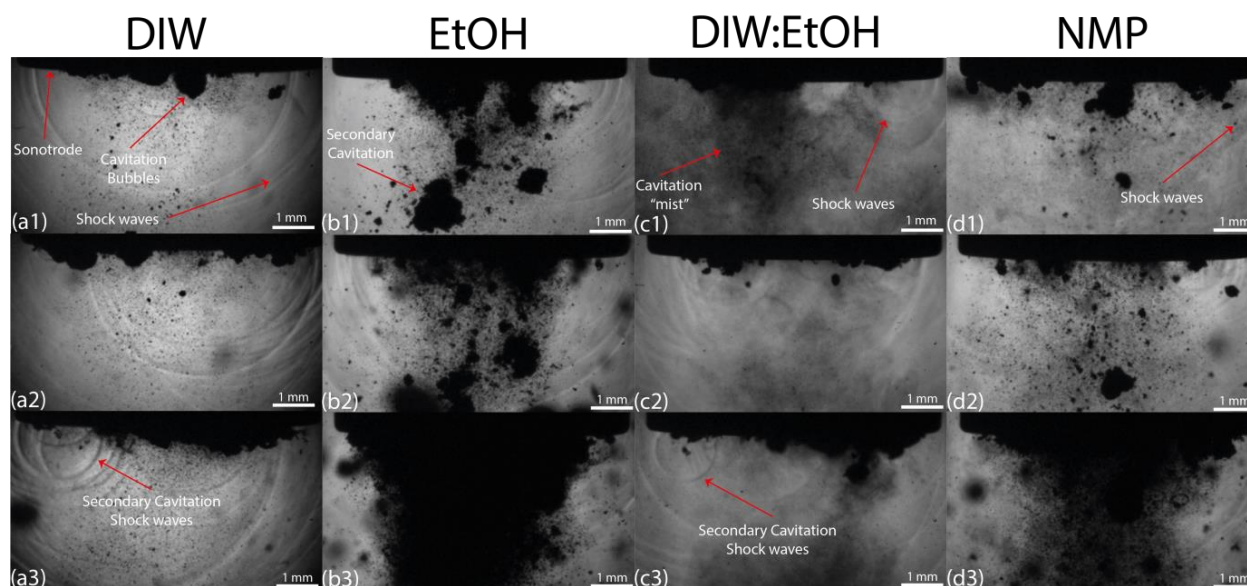


Figure 5.5. Shadowgraphic images showing representative frames of SW generation for solvents; **(a)** DIW, **(b)** EtOH, **(c)** DIW:EtOH and **(d)** NMP. Sequences 1-3 show an increasing generator power of 20, 60 and 100 %, respectively.

In the duration of 255 μ s of sonication (corresponding to ~ 6 acoustic cycles) we registered the solvents to produce six “bursts” of SWs, i.e. multiple SWs generated upon collapse of the primary cavitation cloud. These bursts were fairly periodic and hence, bubble clouds were collapsing harmonically consequently to the sonotrode operational frequency (24 kHz). Despite the number of these bursts remaining constant irrespective of the liquid medium, the duration of the release of SWs, as well as the approximate number of generated SWs varied with the sonication power and solvent. We observed that an increase in sonication power generally produced more SWs. Figure 5.5 displays this tendency with the number of visible SWs increasing from images 1 through 3. We observed additional SW generation particularly for DIW (Fig. 5.5(a)) with increasing the power to 100%. However, it was also evident from the imaging that using 100% power could heavily suppress some SW bursts due to the larger induced primary cavitation cloud (i.e. shielding effect) [35]. This was especially evident for EtOH (Fig. 5.5(b3)) where the large extended cavitation cloud failed to collapse entirely, and hence, SW propagation was impeded by subsequent portions of the cavitation cloud which did not collapse. Although DIW:EtOH also produced an expanded cavitation cloud compared to pure DIW, the proclivity of the cavitation bubbles to collapse was greater than EtOH. The smaller “mist” cavitation enabled the propagation of SWs more freely (Fig. 5.5(c3)), similar

to DIW. This appears consequentially of the dark and opaque large aggregated bubble clouds observed in EtOH, as opposed to the light and transparent nature of the “mist”, with tiny dispersed bubbles in DIW:EtOH.

Calculating SW velocities for each solvent using the high-speed image sequences revealed no change with sonication power as expected [112]. All the solvent SW velocities were in the range of 1400-1550 ms⁻¹ with the exception of EtOH, generating lower velocities between 1100-1200 ms⁻¹. This correlates to the known speeds of sounds for these liquids (e.g EtOH is ~ 1100 ms⁻¹ [163], [175], [176]. These weaker generated SWs are likely a contributing factor as to the lower recorded acoustic pressures for EtOH (Fig. 5.4).

Recent research has previously investigated the frequency spectra related to SW generation for DIW [112] and EtOH and DIW:EtOH [172]. The findings for DIW revealed a characteristic pressure peak at ~ 3.3 MHz predominantly generated via SWs. Interestingly, further results identified this peak for DIW:EtOH. Our analysis revealed that NMP also produced this inherent SW peak (Appendix Section B Fig. B2), additionally confirming that transient cavitation is a prominent feature in NMP that aids exfoliation (consistent with generating large SW-induced peaks in Fig. 5.3d and large P_{max} pressures in Fig. 5.4(b)), in addition to its chemical properties. However, for EtOH, this SW-induced pressure peak was only generated at higher sonication powers indicating suppressed transient bubble collapses, whereby shielding decayed the SW impact before its interaction with the FOH (aligning with EtOH’s physical properties). The data also corresponds with the lower measured acoustic pressure for EtOH (Fig. 5.4), along with the lower propagation speed of SWs throughout the medium.

All solvents were seen to produce SWs close to the sonotrode tip. Despite a larger number of secondary cavitation bubbles formed by EtOH, they demonstrated fewer transient collapses, in addition to having oscillations of reduced amplitude. For the case of DIW, secondary cavitation collapses appeared to occur more frequently (Fig. 5.5(a3)), demonstrating the solvent capability to generate higher acoustic pressures. This property was also noticeable for DIW:EtOH (Fig. 5.5(c3)). It is possible that due to the heightened ability to produce secondary cavitation (adopted through the addition of the EtOH) in a “mist” cloud formation (as discussed in 5.3.1.1), DIW:EtOH may work as a more efficient exfoliator, able to shear layers of flakes at further distances from the sonotrode tip. This hypothesis was tested in the next section 5.3.3.

5.3.3 Ultrasonic Exfoliation of Graphite & Its Characterisation

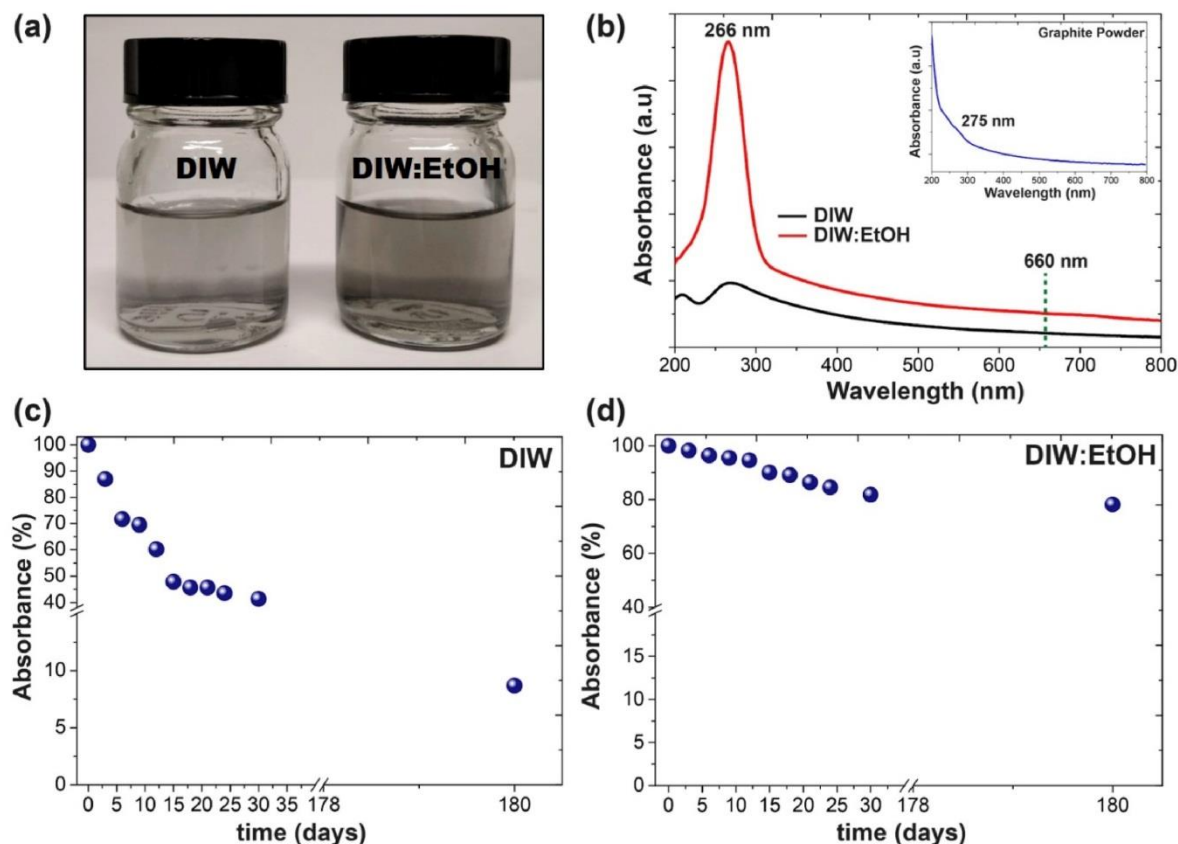


Fig. 5.6. (a) Photograph of obtained supernatants in DIW and DIW:EtOH post sonication-centrifugation process. (b) UV–Vis spectra of obtained supernatants. The inset displays a UV–Vis spectrum of the starting material GP. (c) & (d) sedimentation plots of graphene suspension in DIW and DIW:EtOH, respectively.

Following the investigation of cavitation activity and bubble dynamics for each solvent, analysis could now be carried out to determine the benefits of using DIW:EtOH as an eco-friendly liquid medium for ULPE. The experiments were conducted using the optimized ultrasonication parameters based on previous research; a sonication power of 50% and solution [20], [38], [158] temperature of 40 °C over a 2 h sonication period. The following experiments characterized the graphene samples using UV-Visible, Raman Spectroscopy and TEM.

UV-Visible characterisation revealed that the stability of DIW:EtOH was far superior to that of DIW. The term “Stability” can be defined as the amount of retained graphene in the supernatant over a period of time, which has also been considered as a relative measure of the ability of the solvent to stabilize the graphene suspension. This amount was estimated by recording the absorbance of the suspension at a wavelength of 660 nm (as per Lambert–

Beer's law), followed by its normalization and conversion to percentage [177]. The remaining graphene for DIW:EtOH after a 6 month period was measured to be 78% as opposed to only 8% for DIW (Fig. 5.6). This was reflected in the spectra whereby the characteristic graphene peak (at ~ 266 nm) is only visible for the DIW:EtOH sample.

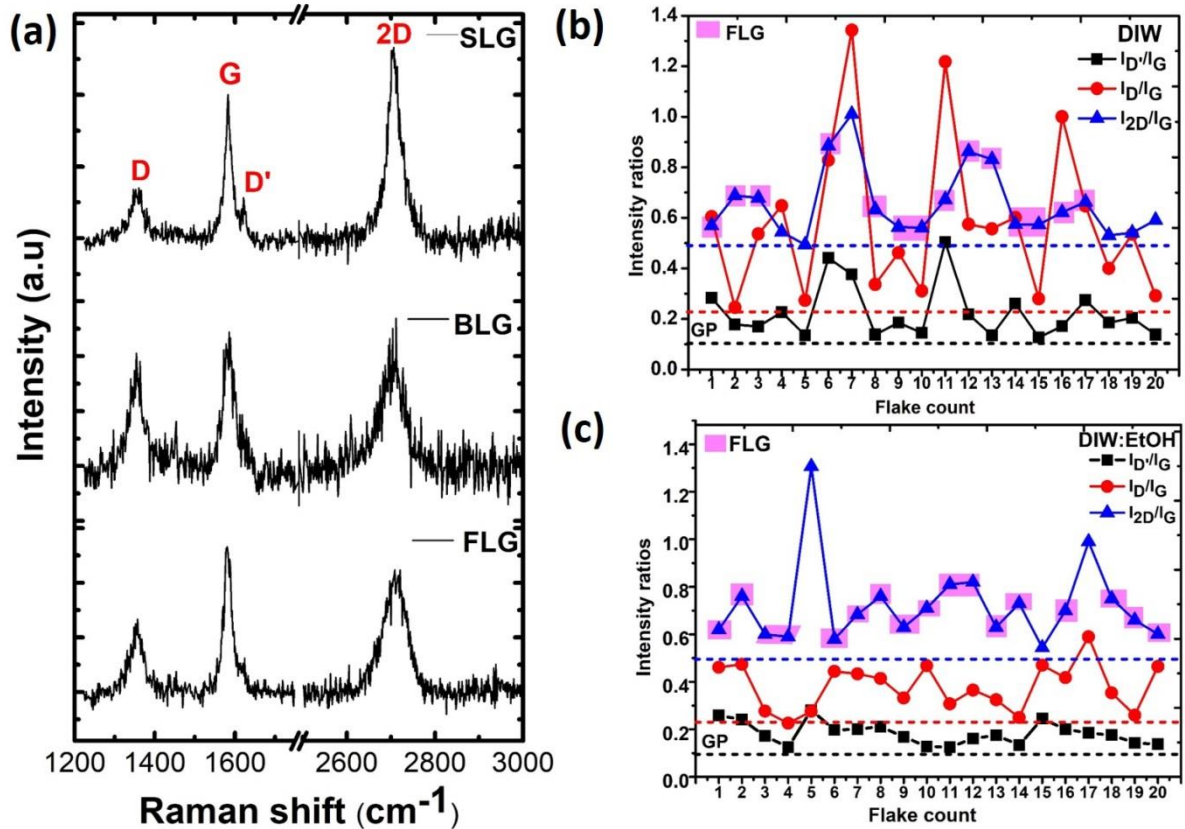


Figure 5.7 (a) Representative Raman spectra (normalized to the G-band intensity) of SLG, BLG and FLG found in DIW and DIW:EtOH featuring the characteristic signals of graphene: D, G and 2D bands. The spectra are labelled SLG, BLG and FLG in accordance with I_{2D}/I_G intensity ratios (note SLG was only found in the DIW:EtOH samples). (b) and (c) highlight intensity ratios ($I_{D'}/I_G$ (black squares), I_D/I_G (red spheres) and I_{2D}/I_G (blue triangles) of graphene related peaks found in DIW and DIW:EtOH, respectively. Each point corresponds to parameters extracted from an individual spectrum of a registered flake. Intensity ratios for the original GP are shown by the dashed lines of the same colour as data for intensity ratios.

Raman spectroscopy provides information on a variety of sample properties ranging from defect density, layer-count and evidence of exfoliation [178]. Figure 5.7 (a) depicts the Raman spectra of representative graphene flakes found in DIW and DIW:EtOH, establishing characteristic signatures of graphene, i.e. D, G, D' and 2D bands. The spectra are labelled as single-layer graphene (SLG), bi-layer graphene (BLG) and FLG in accordance with their intensity ratios (I_{2D}/I_G) which is discussed comprehensively below. The D and D' bands centred on ~ 1350 cm^{-1} and 1620 cm^{-1} respectively manifest the structural defects in sheets

arising due to disruption in regular aromatic sp^2 networks that are so called non- sp^2 or sp^3 defects [178]. The G peak at $\sim 1580\text{ cm}^{-1}$ governs in-plane motion of sp^2 bonded carbon atoms together with its upshift towards higher wavenumbers indicating both disorder in regular structure and increasing sheet thickness [178]. Finally, the 2D peak around $\sim 2720\text{ cm}^{-1}$ features a second-order overtone of in-plane vibration of the D band [179]. Principally, the variations in line-shape, intensity, peak-position and width of the 2D band reveal information related to the number of graphene layers [178], [179]. The defect ratio, i.e. ratio of the intensity of the D band to G band (I_D/I_G) is a quantitative index and can also be analysed to gauge the degree of disorder in carbon based materials. Plots 5.7 (b-c) demonstrate graphene sheets in the DIW:EtOH sample were constantly falling within the low defect regime ($I_D/I_G \sim 0.23$ - 0.58), as opposed to the DIW sample which demonstrated a more erratic behaviour ($I_D/I_G \sim 0.24$ - 1.34). In addition, I_D/I_G ratios for graphene in DIW posed a rather wider range of ~ 0.12 - 0.51 in contrast to DIW:EtOH with a narrower range of ~ 0.13 - 0.25 , indicating less defective exfoliated sheets in DIW:EtOH.

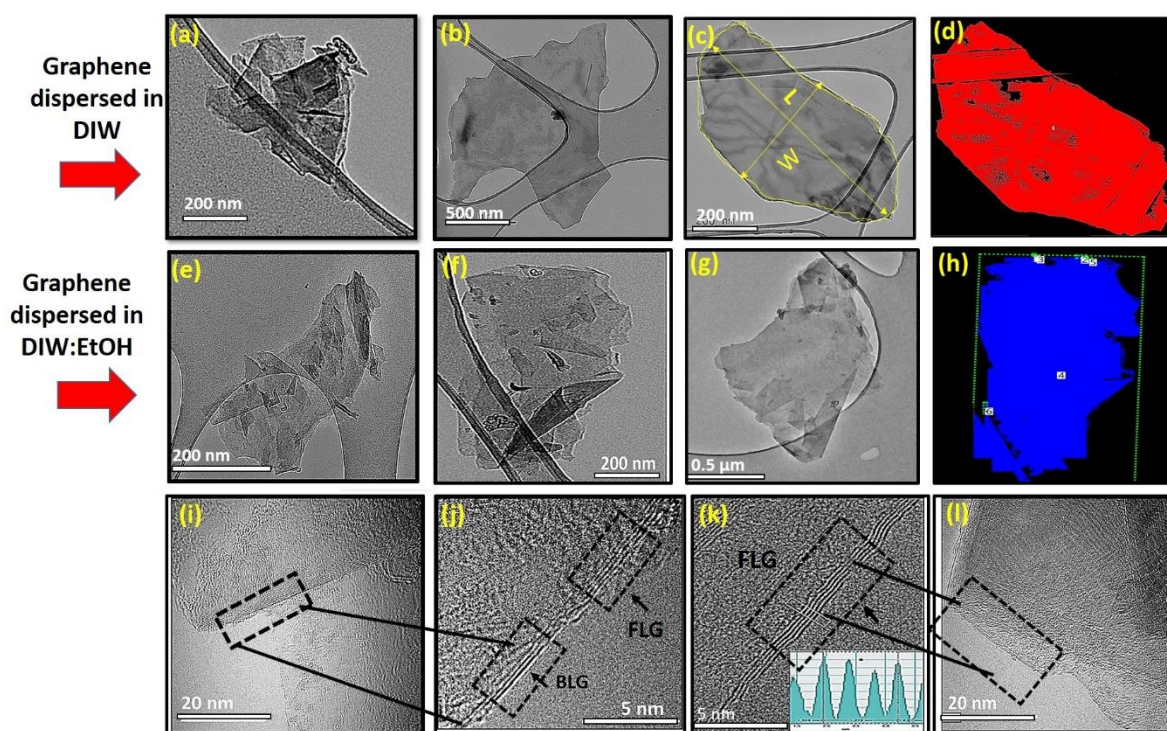


Figure 5.8 (a-c) Representative TEM images of graphene sheets exfoliated in DIW, indicating measurement of average length ($\langle L \rangle$) and width ($\langle W \rangle$). (d) & (h) Illustrative measured area of investigated flakes designated with coloured regions. (e)-(g) Representative TEM images of graphene flakes exfoliated in DIW:EtOH. (i)-(l) HR-TEM images of examined FLG flakes (highlighted with black dotted rectangles). The inset of (k) displays a plot-profile of the highlighted portion, indicative of interlayer distances and layer-count performed using *ImageJ* software.

Figure 5.8(a-c) gives representative TEM images of graphene sheets exfoliated in DIW with Fig. 5.8I indicating measurements of length, $\langle L \rangle$ and width $\langle W \rangle$. It should be noted here that flakes that have a visible outline have been considered for dimensional analyses. Some of the recorded images exhibit folded and wrinkled regions which can be assumed as the intrinsic nature of graphene sheets after ULPE [180]. Fig. 5.8(e-g) feature representative TEM images of graphene sheets dispersed in DIW:EtOH. For measurement accuracy the area of each flake had been exemplified in Fig. 5.8(d, h). High-resolution TEM (HR-TEM) images were recorded to estimate the layer-count by means of the edge counting method [181] as clarified in Fig. 5.8(i-l). Correspondingly, layer-count has been confirmed from respective plot profile diagrams (using *ImageJ software*) given in the inset of Fig. 5.8(k).

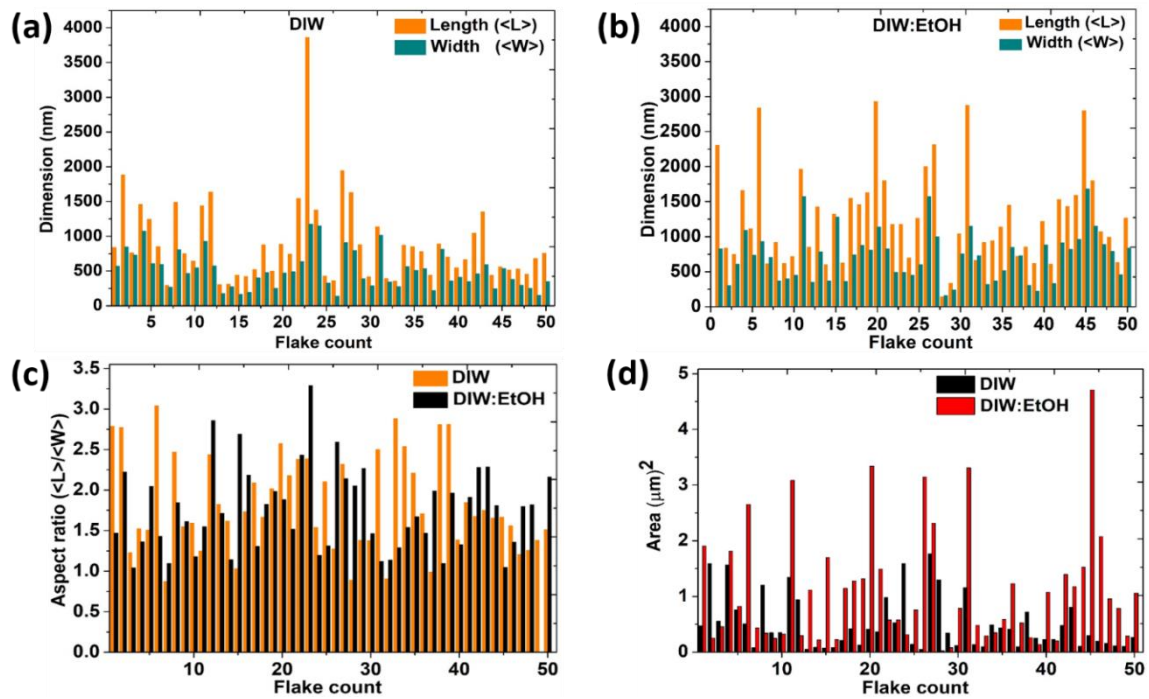


Figure 5.9 (a), (b) Statistical histograms for dimensional analyses of observed 50 graphene flakes found in DIW and DIW:EtOH, respectively. (c) Statistical histogram showing mean aspect ratios ($\langle L \rangle / \langle W \rangle$) of the investigated flakes. (d) Statistical histogram of observed flakes for area measurements.

Statistical data from the recorded set of TEM images of the exfoliated graphene nanosheets was generated (Fig. 5.9). Fig. 5.9(a) and (b) demonstrate statistical analysis for the average values of length ($\langle L \rangle$) and width ($\langle W \rangle$) for the investigated graphene sheets found in DIW and DIW:EtOH, respectively. These data reveal the formation of FLGs several microns in cross-section and several μm^2 in area after ULPE in DIW:EtOH. Fig. 5.9(c) features the estimations of the mean aspect ratios ($\langle L \rangle / \langle W \rangle$) of flakes which are found to be in the ranges of 1.04-2.85 and 1.03-3.28 for DIW and DIW:EtOH, respectively. Fig. 5.9(d)

advocates the occurrence of large sized graphene sheets in DIW:EtOH (area ~ 0.02 - 4.70 (μm)²) as compared to DIW (area ~ 0.07 - 1.76 (μm)²).

Fig. 5.10 features the average values of parameters I_D/I_G , $I_{D'}/I_G$, I_{2D}/I_G , $I_D/I_{D'}$, L/W and Area (μm)² identified from Raman and TEM measurements for interrogated graphene flakes found in DIW and DIW:EtOH. From the statistical information related to the lateral sizes of graphene sheets recorded by TEM, we can deduce that the population of large sized graphene sheets, i.e. for the range of 500-1000 nm in DIW:EtOH is $\sim 66\%$ higher in comparison to DIW.

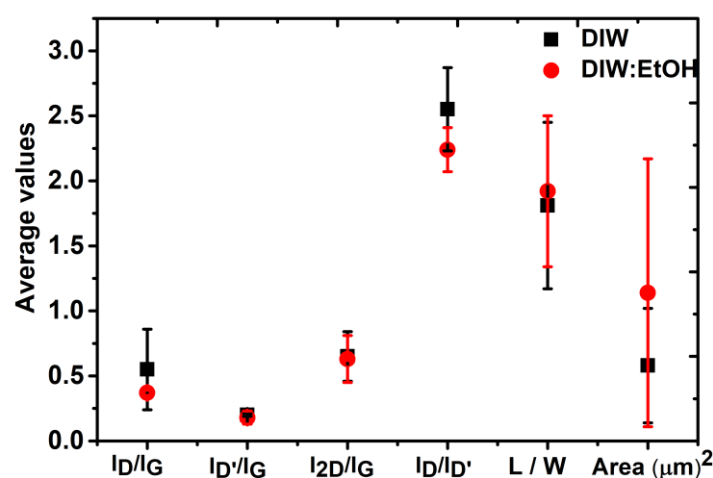


Figure 5.10. The average values of I_D/I_G , $I_{D'}/I_G$, I_{2D}/I_G , $I_D/I_{D'}$, L/W and Area (with error margins) identified from Raman and TEM studies for the interrogated graphene flakes observed in both DIW and DIW:EtOH.

As these experiments were in part contributed by fellow co-author Dr. Kaur and Dr. Tyurnina, the full Section relating to characterisation can be found at the published version of this Chapter; <https://doi.org/10.1016/j.carbon.2022.12.070>.

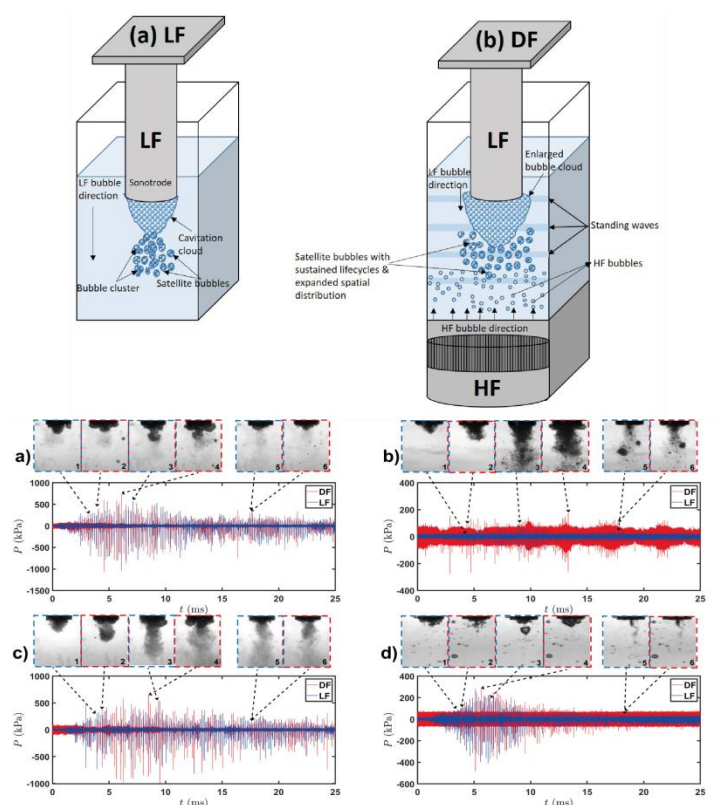
5.4 Conclusions

This chapter presented the first in-depth analysis comparing fundamental physical properties and *in situ* observations of bubble dynamics for a range of solvents used for ULPE, including NMP (currently most commonly used efficient solvent for exfoliation of graphene). Through the combination of high-speed imaging synchronised with acoustic pressure measurements recorded via a FOH, in conjunction with high-speed shadowgraphic imaging elucidating SW generation, a promising eco-friendly substitute (DIW:EtOH) was identified. ULPE for 2 h was carried out at various input powers for DIW and DIW:EtOH with resultant flakes

analysed using a range of characterisation techniques. The mixture of DIW and EtOH was shown to produce higher quality few layer (3-5) graphene with a yield twice that of DIW, average flake area ($\sim 1.15 \mu\text{m}^2$) and reaching a stability of $\sim 78\%$ for the duration of six months. The following chapter will include further optimisation of experimental parameters and upscaling of the ULPE process. This will include the investigation of a DF setup along with the optimised ULPE parameters currently used.

Chapter 6

Dual-frequency Acoustic Cavitation for ULPE



Graphical abstract: Dual frequency setup, bubble dynamics and acoustic pressure measurements.

Up to now we have investigated various parameters that effect acoustic cavitation and the exfoliation of 2D materials. First Chapter 3 identified the mechanisms of exfoliation. Chapter 4 then optimised ultrasonication parameters and Chapter 5 determined a suitable green solvent for exfoliation. Typically, for ultrasonic cavitation processes and applications, a single frequency source is used to produce the desired effects. However, optimisation of the efficiency of ultrasound reactors is necessary to improve cavitation activity in specific applications such as for the exfoliation of two dimensional (2D) materials. This ending thesis chapter takes the final step to investigate the effect of a dual frequency (DF) transducer system on the bubble dynamics, cavitation zone, pressure fields, acoustic spectra and induced SWs for four liquids with a range of physical properties. Using ultra-high-speed imaging and synchronised acoustic pressure measurements, the effect of ultrasonic dual frequencies on bubble dynamics was investigated. The addition of a high frequency transducer (HF) (1174 kHz) showed that the bubble fragments and satellite bubbles induced from a low frequency

(LF) transducer (24 kHz) were able to extend their lifecycle, increase spatial distribution, thus, extending the boundaries of the cavitation zone. Furthermore, this combination of ultrasonic frequencies generated higher acoustic pressures (up to 180%) and enhanced the characteristic SW peak, indicating more bubble collapses and the generation of additional SWs. The DF system also enlarged the cavitation cloud size under the sonotrode. Final analysis involved undertaking ULPE experiments utilizing a DF system and green solvents. These observations specifically delineated the enhancement of cavitation activity using a DF system pivotal for optimisation of ULPE and existing cavitation-based processing technologies.

Published as J A. Morton, et al., Physics of Fluids. Volume 35, January 2023 – Reproduced after permission.

6.1 Introduction

We have covered that optimising and controlling acoustic cavitation is necessary for developing a wide variety of industrial applications such as sonochemistry [101], [182]–[184], medical therapy [185]–[187], cleaning [188], [189], fragmentation [140] and the exfoliation of 2D nanomaterials [10], [12], [90]. In particular, the control of liquid jets and SWs greatly aid in developing these technologies [190].

The formation and characterisation of these SWs are also of importance. For instance, the optimisation of SW generation can be used to understand and prevent fatigue and fragmentation of metallic compounds [140], or of more importance to this thesis can facilitate exfoliation of layered materials [37]. Analysis of these acoustic emissions is often recorded using acoustic sensors such as a hydrophone where cavitation intensity is resolved and acoustic pressures are measured as discussed in Chapter 2 [72], [101], [128]. Additionally, SWs from bubble implosions have been shown to generate a specific peak (~ 3.3 MHz) on the acoustic spectrum [112] which can be used to resolve and map the spatiotemporal evolution of SW events. This has the potential to control and monitor any ultrasonic cavitation process. For example, during UPLE, acoustic spectra capture the SW peak development in real-time, indicating graphene generation (i.e. the sharpening of the peak being indicative of graphite exfoliation) [20]. Furthermore, the addition of another ultrasound source an order of frequency different has been shown to greatly benefit the exfoliation process, generating tiny bubbles (a few microns in size) that have the potential to promote a gentler exfoliation (a less intense cavitation regime that promotes exfoliation via vigorously

oscillating bubbles in the vicinity [118] or in-between the flakes [37] imposing a layer fatigue exfoliation effect, also shown in Chapter 3) improving the quality, size and yield of the produced graphene flakes [20].

However, the addition of multiple frequency sources increases the complexity of cavitation bubble dynamics hampering their optimization. Understanding the multiple-frequency sound field and corresponding acoustic pressures is pivotal for advancing existing cavitation reactors tailored to specific applications. In accordance to this challenge, there are only a few studies using a DF source that has been seen to enhance acoustic cavitation based on the increased subharmonic emissions (associated with inertial cavitation) and sonoluminescence intensities [113], [114]. Dual acoustic sources have also been shown to enhance metal leaching rates and the final recovery values the metals [115], as well as enhancing sonochemical degradation of pentachlorophenol [104], demonstrating additional uses to sonochemistry applications.

In line with these studies, other work has previously reported that the combination of a 20 kHz and a 1174 kHz source significantly enhances the production of high-quality nanomaterials [20]. Hence, this chapter, and in conjunction with the results in [20] intends to understand the effect the DF processing has on the cavitation dynamics in the same three liquids from Chapter 5 (DIW, EtOH, DIW:EtOH), and an additional liquid (glycerol), and elucidate the governing cavitation mechanisms. The choice of these liquids was made based on previous fundamental research [172] and on the fact that their physical properties largely vary (Table 6.1), whilst also previously seen to be suitable for exfoliation of graphene [154], [191]. It is well documented that improving exfoliation efficiency and quality depends on further analysis of solvent selection and cavitation behaviour, which changes with the characteristic properties of liquids [192]–[194]. Previous research [2], [101], [154], [172], [191] provides the foundation to expect that cavitation dynamics and SW propagation may vary distinctly due to significantly different density, surface tension, viscosity, vapour pressure and speed of sound in the studied liquids. The results of this chapter can be applied to a wider range of DF sono-processes where different properties are required such as emulsification [195], sonochemical synthesis [196], [197], in clinical practise [198] and most notably the exfoliation of 2D nanomaterials [154]. Experiments were conducted for two frequency setups; a LF sonotrode (24 kHz) and a DF system consisting of both the LF sonotrode and a HF transducer membrane (1174 kHz) i.e. 24 kHz + 1174 kHz. Bubble dynamics and the cavitation zone were investigated for each case using ultra-high-speed

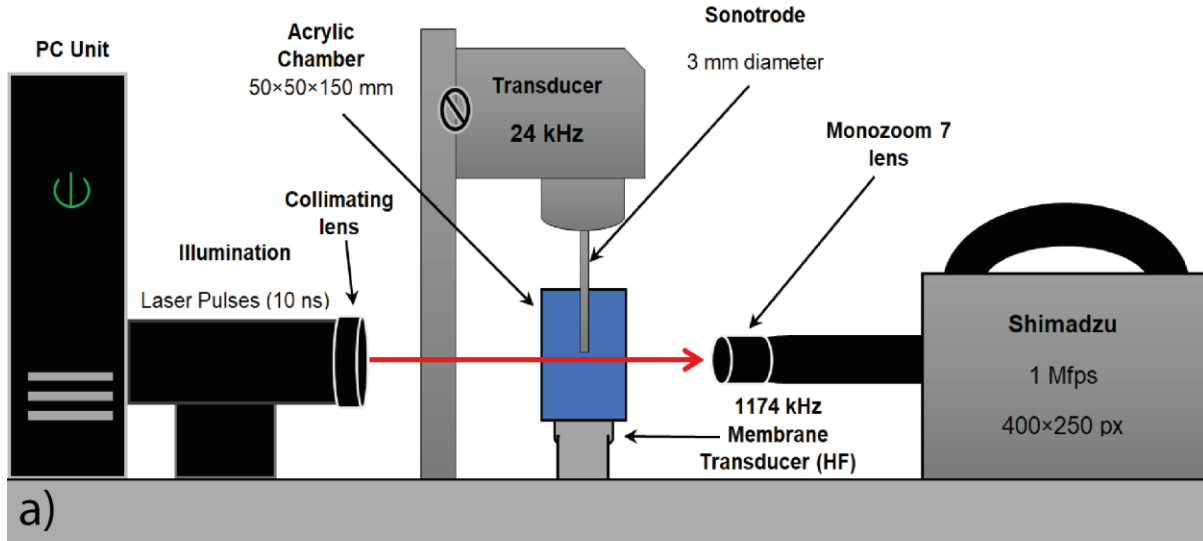
shadowgraphic camera footage, followed by synchronised high-speed camera imaging in conjunction with acoustic data acquisition measurements recorded using a FOH. These experiments captured *in situ* high-speed imaging and acoustic pressure/spectra to produce a full picture of the cavitation activity. The results revealed that using the DF system cavitation is enhanced, increasing the cavitation zone and density of bubbles for all liquids. Additionally, DF setups produced larger acoustic pressures. The DF setup was then used for ULPE with a selection of green solvents, demonstrating the benefits of using DF sources for exfoliation. The findings of this chapter may lead to optimizing DF applications, in addition to further understanding the mechanics involved in multifrequency cavitation bubble interactions.

6.2. Methodology

6.2.1 Synchronised high-speed imaging & data acquisition experimental setup

A multifrequency membrane transducer (Meinhardt Ultrasonics) with a 50 mm Titanium diaphragm was used as a HF (operational frequency of 1174 kHz) source for this chapter. It should be noted here that this particular frequency was found to be the most suitable in a combi-mode for exfoliation of nanomaterials [20]. A custom-made attachment was used converting the 50 mm circular diameter base into an acrylic rectangular chamber ($5 \times 5 \times 15$ cm) for high-speed camera observations during sonication (i.e. to prevent refraction of light invalidating video recordings) (Fig. 6.1a). The chamber was filled with either 200 ml of DIW, EtOH, DIW:EtOH (1:1), or glycerol (99.9%, Merck Life Sciences). Next, a Hielscher UP200S transducer (operational frequency of 24 kHz) with a 3 mm diameter (to allow clear observations and fit within the camera field of view) titanium sonotrode was lowered into the chamber ~8 cm above from the HF membrane. Experiments were conducted for two scenarios; the LF sonotrode exclusively and the HF membrane combined with the LF sonotrode to form a DF setup (note that HF setup as a scenario is excluded as using only the transducer membrane generates a weak cavitation development as well as being insufficient for exfoliation).

Detection of Shockwaves and Standing Waves



Elucidate Acoustic Emissions and Bubble Dynamics

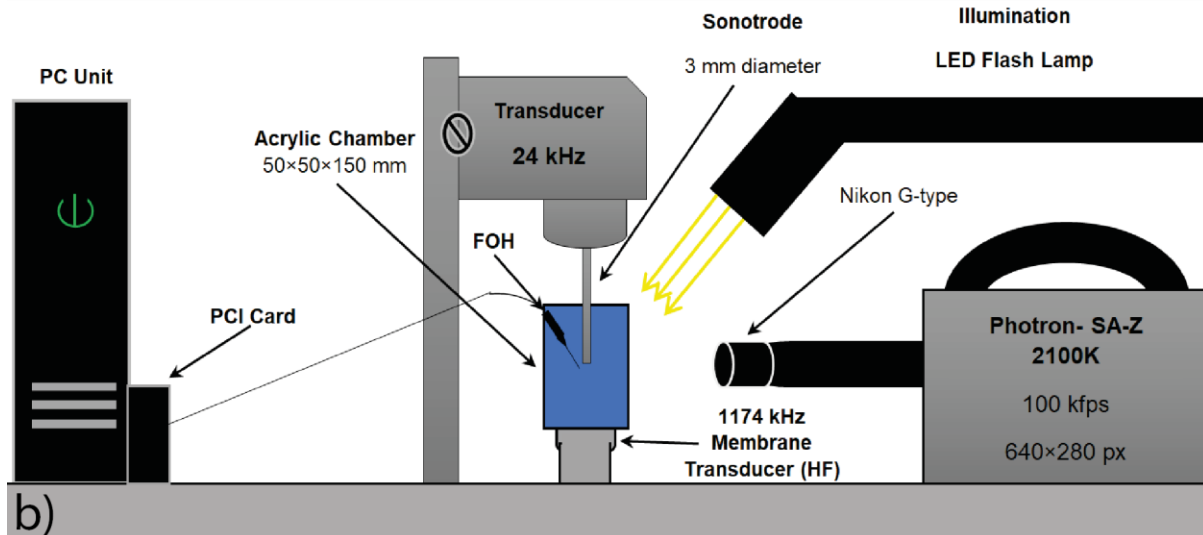


Figure 6.1. a) Schematic of the chamber dimensions, transducer membrane, sonotrode and high-speed imaging setup. The laser illumination passed through the chamber walls and into the camera lens where the image was then resolved and processed on the PC unit. **b)** The same schematic using a Photron camera instead for high-speed imaging, and illumination provided by a powerful LED flash lamp. A FOH connected to a PCI card collected acoustic measurements, synchronised with high-speed imaging.

Acoustic pressure measurements were taken for each case of LF and the DF setup, for each liquid. The LF source was set to input powers of 20, 60 and 100% (peak-to-peak amplitude 42, 126 and 210 μm , respectively) in order to introduce a range of acoustic emissions into the liquids. It is worth to note that each of the transducer input powers are measured in percentage of the maximum power and reflects a certain level of amplitude that is maintained by the transducer. This provided a range of cavitation development and SW generation variation. This variation of acoustic intensity (shown in the Figure 6.2 caption for each

respective liquid and also calculated in Appendix Section C Table C1) is also an important factor for exfoliation of layered materials and helps to optimize the facilitation of nanosheets production. DF measurements used the same input powers with the HF source set at 50% input power. The sensor was positioned ~5 mm away from the sonotrode tip and ~75 mm above the membrane (Fig. 6.1b). The same FOH used in chapters 3 and 5 was deployed to capture pressure (a sensitivity plot can be found in the Appendix Section C Fig. C1). As in Chapter 5, Fast Fourier transform was used to deconvolute and convert the hydrophone output voltage to spectra, where the P_{RMS} and P_{max} were calculated.

Table 6.1. Physical properties of solvents under investigation at 20 °C.

Physical Properties	DIW	EtOH	DIW:EtOH	Glycerol
Density, ρ (kg/m ³)	1000	785	859	1260
Surface Tension, σ (N/m)	0.079	0.022	0.026	0.064
Viscosity, μ (Pa.s)	1×10^{-3}	1.1×10^{-3}	2.37×10^{-3}	0.95
Speed of Sound, V (m/s)	1480	1150	1540	2000
Vapour Pressure (Pa)	2.2×10^3	5.3×10^3	3×10^3	Negligible

High-speed shadowgraphic imaging was performed using a Shimadzu (HPV X2) camera capturing at 1 million fps (Fig. 6.1a). The combination of using laser illumination with this large frame rate elucidates high resolution images able to capture the formation of standing waves and SW propagation (as previously demonstrated in [37]). The other camera parameters were set the same as in Chapter 5 Methodology.

Finally, the PCI card was installed into the PC to conduct synchronisation of the high-speed imaging and acoustic pressure measurements (Fig. 6.1b) [191]. For this experiment setup, the Photron- SA-Z 2100K camera was used at a frame rate of 100,000 fps over 640×280 pixels. This setup provided the capability to capture longer duration recordings of cavitation events occurring in the liquids. The camera resolution was 12.7 μ m per pixel with a shutter speed of 8.39 μ s. The same illumination as the previous Chapters was used (3 and 5).

6.2.2 Ultrasonic Exfoliation of Graphite & Its Characterisation

The procedure used for ULPE in this chapter was mostly the same as laid out in Chapter 5. The experiments were again performed in a 50-mm diameter double walled beaker filled with 150 ml of DIW, DIW:EtOH (50:50) (75 ml DIW, 75 ml EtOH) and this time including DIW:IPA (50:50) (75 ml DIW, 75 ml IPA). The top LF sonotrode used was the same as in Chapter 5 (22-mm diameter titanium horn (H) sonotrode) which was immersed into 10 mm deep from the liquid surface. It is to be noted that ULPE experiments were also performed with bell-shaped (B) sonotrode of diameter 40 mm with a same LF transducer (designated as Lf-B). This choice was made to investigate how a larger diameter sonotrode would effect sono-exfoliation under a DF system. The HF transducer settings were the same as section 6.1.

Both transducers were used at 50% of their maximum input power. This means the LF transducer was set at 200 ± 2 W with a peak-to-peak amplitude $23 \mu\text{m}$ for the horn, and a peak-to-peak amplitude of $9 \mu\text{m}$ for the bell sonotrode. The HF transducer operated at 160 ± 5 W.

The remaining ULPE procedure, preparation and characterisation of the samples can be found back in Chapter 5 section 5.2.3. The obtained supernatants were then labelled as Hf & Lf-DIW (H), Hf & Lf-DIW (B), Hf & Lf-DIW:EtOH (H), Hf & Lf-DIW:EtOH (B), Hf & Lf-DIW:IPA(H) and Hf & Lf-DIW:IPA(B) which represent samples processed in DIW, DIW:EtOH and DIW:IPA, respectively, in DF (Hf & Lf) configuration using the horn (H) and bell (B) sonotrode.

6.3. Results & Discussion

6.3.1. Acoustic Pressure Measurements & Spectra

Acoustic pressure plots of LF and DF setups are shown in Fig. 6.2. It is apparent that the addition of the HF membrane (in DF) increased the cavitation intensity (measured in the range of 1-30 MHz) in each liquid for the majority of the power settings. This was expected with the introduction of the HF acoustic source at 1.174 MHz giving rise to fundamental and harmonic signatures (as seen by Fig. 6.3 a-c). Interestingly, glycerol demonstrated the greatest increase in acoustic pressure (P_{RMS}) under the DF setup for 20% and 60% input power (Fig. 6.2d, 180% and 97% increase, respectively). For DIW, EtOH and DIW:EtOH the pressure percentage increases from a LF to DF setup for the P_{RMS} were measured to be 36, 54, 44% (at 20% input power) and 27, 19, 11% (at 60% input power), respectively (Table 6.2). The combination of the two frequencies is likely to increase acoustic pressure by promoting additional bubble activity, hence, greater intensity detected by the FOH. This

enhancement of cavitation activity under a multifrequency source has been previously reported in [20], [113]. For the case of solely using the HF source, sufficient cavitation is not generated at low input powers to be of use in many sono-processes, as noted for the exfoliation of graphite in [12] (also refer to Fig. 6.1 & 2 and Table 6.3). However, acoustic pressures are in the same range of those generated by the LF source due to the calibration sensitivity of the FOH being in the MHz range (1-30 MHz) with contributions mainly from the fundamental frequency of the HF source at 1.174 MHz and the corresponding harmonics. The generated spectrum has no evidence of transient cavitation activity being present. Hence, we decided to present only the cases of LF and DF where cavitation is developed as captured by the high-speed camera and the corresponding spectra.

Table 6.2. Pressure differences between LF and dual frequency (DF) setups.

	Acoustic Pressure Increase P_{RMS} (%)			
Frequency Setup (%Power)	DIW	EtOH	DIW:EtOH	Glycerol
Pressure % Difference: 20% LF-DF	36.1	53.9	43.9	179.8
Pressure % Difference: 60% LF-DF	27.2	19.5	10.9	97.2
Pressure % Difference: 100% LF-DF	0.382	6.0	10.3	-13.2
	Acoustic Pressure Increase P_{Max} (%)			
Pressure % Difference: 20% LF-DF	7.6	20.3	20.0	58.1
Pressure % Difference: 60% LF-DF	19.4	28.0	17.4	159.6
Pressure % Difference: 100% LF-DF	-4.0	9.5	6.7	12.5

$$\text{Percentage Increase: } \frac{DF-LF}{LF}$$

Eq (3)

Table 6.3. Acoustic pressure measurements using the HF source at 50% input power.

HF Acoustic Pressure (kPa)	DIW	EtOH	DIW:EtOH	Glycerol
P_{RMS}	26.5	37.1	29.7	13.1
P_{Max}	80.1	91.3	81.5	46.4

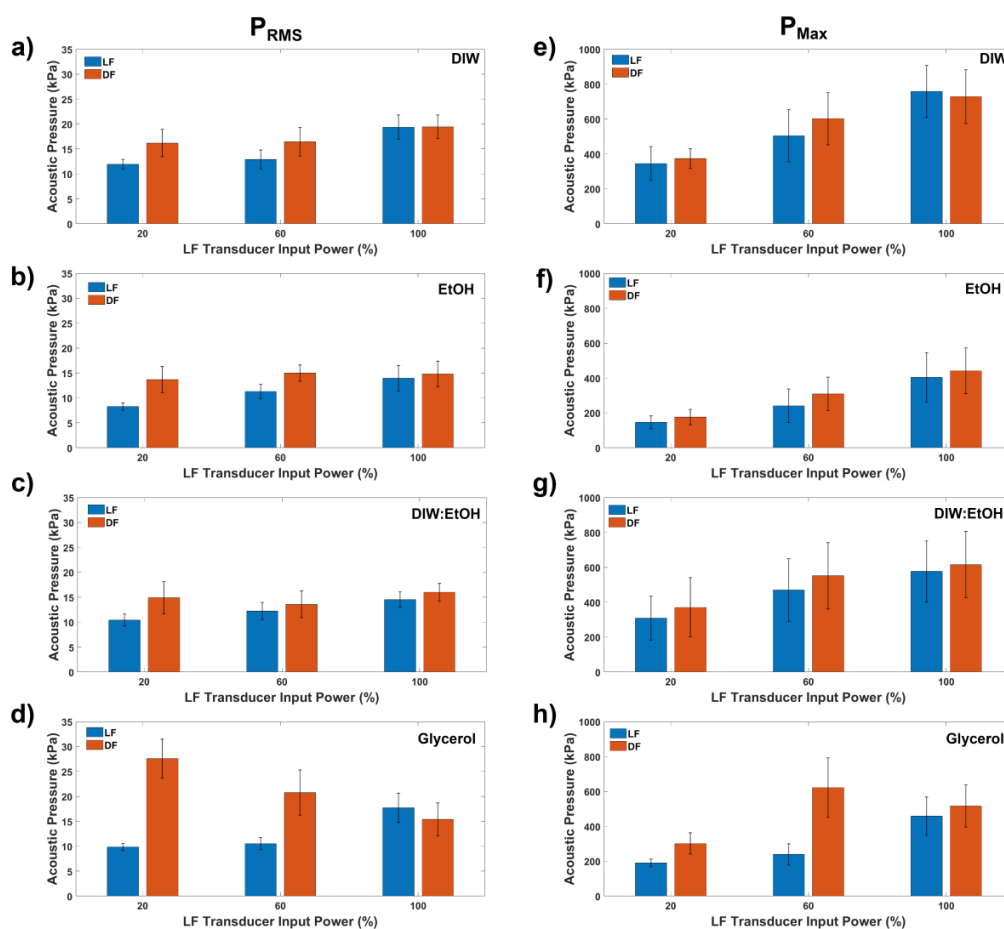


Figure 6.2. Acoustic pressure measurements for frequency setups LF and DF. (a-d) P_{RMS} , (e-h) P_{Max} . The acoustic intensity ($\times 10^{-6} \text{ W/m}^2$) corresponding to the sonication input powers for DF are as follows: DIW; 363 (20%), 1070 (60%), 1636 (100%); EtOH; 359 (20%), 925 (60%), 1349 (100%); DIW:EtOH; 504 (20%), 24 (60%), 1212 (100%); glycerol; 1084 (20%), 1175 (60%), 3272 (100%).

The pressure plots demonstrate that the enhancement of cavitation between the LF and DF setups reduces when increasing input power (Fig.6.2). The percentage difference between the frequency setups at 100% input power were much smaller than that of 20 and 60% input powers. This is likely due to the LF source gaining prominence and generating larger bubbly

clouds, therefore, increasing cavitation shielding, including suppressing the incident wave from the membrane transducer leading to the reduced contribution of the DF setup. Interestingly, despite P_{RMS} having an upward trend with input power for the LF case in glycerol, when the DF setup is activated the P_{RMS} trend decreases. The P_{RMS} obtains the maximum pressure value (28 kPa) among all liquid cases at 20% input power in the DF configuration, followed by a gradual decay when increasing the LF power (Fig. 6.2d). Glycerol's significant pressure increase in the DF setup may be a consequence of its physical properties. The viscosity of glycerol is much greater than the other investigated solvents. A possible explanation may lie in the contribution from the incident wave (at 1.174 MHz) that propagates in the bulk liquid without being disrupted by the cavitation cloud (due to weak cavitation zone development at that power setting) in addition to harmonics and the long lifespan of bubbles in glycerol as explained in [101]. Due to their tiny size, these HF bubbles are unlikely to collapse in such a viscous liquid [101]. Hence, the liquid is populated by tiny bubbles that tend to vigorously vibrate rather than collapse, overlaid to the emissions from the fundamental frequency as well as the main cavitation cloud (confined under the probe), which raises the overall pressure and cavitation noise at the MHz range (see Fig. 6.3a-c, green line). However, when the LF input power increases (meaning a larger cavitation zone and cloud penetration depth with more collapses and associated SWs, although more shielding and cushioning of the intensity of the SWs on top of the acoustic damping) these tiny bubbles suppress the signal as opposed to amplifying it, due to blocking the propagation of the incident wave (notice the suppression of the fundamental peak in Fig. 6.3b and c). Therefore, cavitation emissions from vigorously oscillating bubbles/clouds and SWs are suppressed (note the HF remains the same at 50% and thus the population of the bubbles). It is possible that these bubbles are captured within the parcel of liquid that is formed under the cavitation zone (as previously explained and discussed [101], [172]), absorbing the powerful shock while their vibrating emissions are blocked without being able to reach the sensor. Hence, a trade-off exists between the size of the cavitation zone from the LF source and the bubbles from the HF source (similar to data presented in Chapter 4 when selecting the optimum input power for the LF source). When the cavitation zone is small (i.e. 20% input power), there is less shielding and acoustic emissions, and propagating SWs reach the sensor, further amplified by the oscillating HF bubbles in the vicinity. Alternatively, when the LF cavitation zone increases (i.e. 100% input power), SW emissions dominate the pressure field whereas the HF bubbles play a significantly smaller role and their contribution to the overall spectrum is diminished (this is also apparent from Fig. 6.2d where the pressure level for both

setups is almost the same implying the insignificant role of the HF source at that input power from the LF). This is likely why the P_{Max} pressure plot for glycerol (Fig. 6.2h) has an increasing trend (indicating a dominant SW pressure field), whereas the P_{RMS} decreases with input power (Fig. 6.2d).

As previously mentioned, the FOH is primed to detect SWs (which are generally responsible for generating the largest acoustic emissions; Chapter 5 Methodology), hence, the P_{Max} plots are indicative of the inertial cavitation contribution. The P_{Max} acoustic pressures all gradually increase with input power (as more SWs are generated due to populated bubbly structures) and interestingly with the introduction of the HF membrane these pressures are further increased (with most cases between 5-30%, with larger increases in glycerol). This indicates that the DF mode improves the pressure magnitude of SWs by amplifying their intensity or by overimposing emissions (in the MHz range) by the tiny vigorously oscillating bubbles as shown previously [101].

Fig. 6.2e-h demonstrates that the DF setup again enhances the cavitation intensity (other than DIW at input 100% power that slightly dropped, indicating contribution of shielding from the numerous bubbles). However, these plots reveal less of a pressure increase between the LF and DF setups, overall, compared to the P_{RMS} plots (Fig. 6.2a-d)). We can attribute this phenomenon to the bubble dynamics of the HF source. The HF transducer membrane (1.174 MHz) does not produce transient cavitation, but rather tiny rapidly oscillating cavitation bubbles (i.e. stable cavitation, observed later in Section 6.3.2), hence, P_{Max} values demonstrate less of a difference. It does however, indicate that the addition of the HF source promotes more transient collapses, as speculated previously in [199], plus further contribution to the spectrum from the vigorously oscillating bubbles, as for example, shown in Fig. 6.3a) for DIW:EtOH (see multiple spikes generated in the range of 1-4 MHz) and EtOH (cavitation noise increase Fig. 6.3b-c). This was more prominent for EtOH. It is known that EtOH has a higher tendency to nucleate bubbles thus giving rise to prominent peaks at MHz frequencies due to long-lived vigorously oscillating bubbles [101] increasing the cavitation zone and therefore generating larger measured maximum pressure readings.

Analysis of the DF acoustic spectra for all input powers (Fig. 6.3a-c)) shows the 1st harmonic (1.174 MHz) to be the most prominent, with glycerol significantly standing out (corresponding to the pressure measurements in Fig. 6.2). This is probably related to the formation of well-defined standing waves compared to other liquids due to the high viscosity,

confined cavitation zone and smaller amount of HF bubbles which feature a lesser proclivity to nucleate in glycerol, thus, they do not destruct the nodes/antinodes. Interestingly, the 2nd and 3rd harmonic for glycerol were largely suppressed indicating that glycerol's driving frequency giving rise to its large measured pressures (P_{RMS}) are a consequence of the fundamental frequency of the HF transducer (as previously discussed). The prominence of these HF peaks for glycerol and EtOH are also consistent with the larger percentage increase in P_{RMS} pressure measurements (Fig. 6.2b and d). We also observe ultra-harmonics around the three HF harmonics (1.174, 2.347 and 3.522 MHz, Fig. 6.3a-c) insets, for DIW, EtOH and DIW:EtOH, respectively. Interestingly, these ultra-harmonics manifest at 24 kHz intervals around the HF peaks, perhaps an indication that they are regulated by the LF source. To the best of our knowledge, this is the first time this phenomenon has been noticed, and will require further investigation in the future.

Comparing the SW peak (Fig. 6.3d-i)) we observed larger peaks for the DF setups (Fig. 6.3d-f)). Particularly, DIW and DIW:EtOH at 20% and 60% input power demonstrate the largest increase of this peak, corresponding with the P_{Max} pressure readings (Fig. 6.2), again, indicating the increased prominence of transient cavitation effect using a DF setup. At 100% input power (Fig. 6.3e, h) and f, i)), a larger SW peak is less evident for DIW and DIW:EtOH compared to the LF setup (in confirmation with Fig. 6.2). This may also be in line with a larger contribution of shielding from the numerous bubbles at 100% input power using the DF setup. For EtOH and glycerol, this peak is not evident and appears as noise. It has been previously noted that this peak has a lesser tendency to manifest in these liquids, possibly consequential to attenuation of the wave, whereby acoustic damping occurs from the highly viscous glycerol [172] and also seen in [200]. For EtOH, the lower speed of sound (compared to the other liquids) generates quicker decaying SWs, therefore, the SW peak becomes imperceptible (above noise). The large vapour pressure of EtOH is also a contributing factor to the absence of this peak for both DF and LF setups, decreasing the tendency for bubble collapse, therefore, giving prominence to the harmonic peaks via additional rapid bubble oscillation [101]. The SW peak was also observed to shift upwards in frequency for DIW:EtOH, aligning with a faster speed of sound propagating in the liquid as previously discussed in [38], [172].

Interestingly, we observe that these humps of DIW:EtOH at 20% input power (Fig. 6.3d)) are overimposed with acoustic emissions of oscillating bubbles evidenced by the sharp secondary peaks across the hump, indicating the presence of the “mist” cavitation with tiny oscillating

bubbles as observed in Chapter 5 [101] and [172]. The occurrence of these high intensity peaks in the HF domain of the spectra can be correlated with linear pulsations of resonating tiny bubbles that are also in line with the Minnaert equation (explained in Chapter 2.2) [108] i.e. a peak at 3.5 MHz corresponds to a resonance radius of $\sim 1 \mu\text{m}$. This observation demonstrates the benefits of this liquid combination for producing nanomaterials, where these active tiny bubbles may be a key factor for quality exfoliation as previously seen in [191].

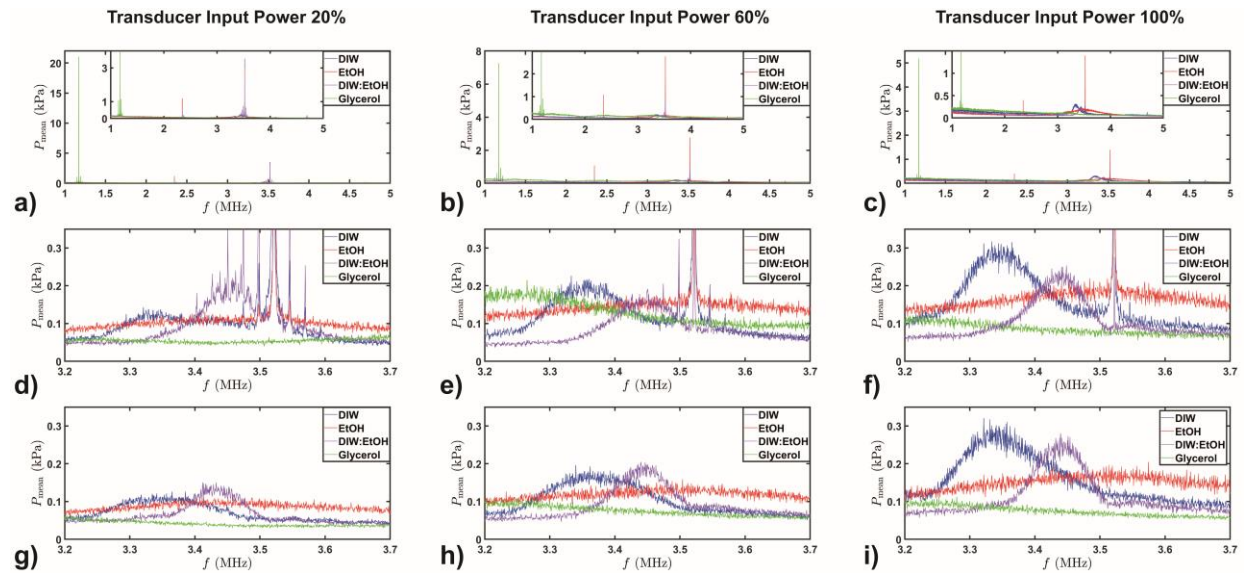


Figure 6.3. Acoustic spectra showing DF and LF setups for each solvent, over an averaged acoustic pressure. (a-c) Full DF spectra for 20, 60 and 100% input powers, respectively. (d-f) DF spectra displaying the SW peak range (~ 3.2 - 3.7 MHz) for 20, 60 and 100% input power, respectively. (g-i) LF spectra displaying the SW peak range (~ 3.2 - 3.7 MHz) for 20, 60 and 100% input power, respectively. Note that the spectra range shows only between 1-5 MHz as at higher frequencies the magnitude of the harmonics becomes negligible and only low level broadband noise is generated (refer to the Appendix Section C Fig. C2).

6.3.2. Shadowgraphic High-speed Imaging

In light of the acoustic pressure measurements, high-speed camera imaging was used to elucidate bubble dynamics for the selected liquids providing qualitative analysis. The behaviour and development of cavitation under different frequency setups was investigated to observe what effect the HF transducer had on the liquids. Initial observations were taken for DIW as a reference liquid in Fig. 6.4, followed by the other studied liquids (Fig 6.5). The HF setup produced no cavitation cloud (it should be noted that observations were made ~ 75 mm from the surface of the membrane due to the design of the transducer). Due to the slow motion of the HF induced bubbles while having the camera recording at 1 Mfps (Fig. 6.4a) it was not feasible to capture their movement (as they appeared to be stationary). However, standing waves from the membrane were recorded, as indicated by the red arrows in Fig. 4a

(and was also the case for the other investigated solvents; EtOH, DIW:EtOH and glycerol). By reducing the frame rate (Fig. 6.4b, 10 kfps) we were able to see through the camera footage with the field of view now populated with myriads of active bubbles. The majority of the HF bubbles are non-transient (no bubble implosion) with vigorous oscillating motion observed and as expected and discussed in Section 6.3.1 (note that the standing waves are far more evident in the video and should be watched at the published version of this Chapter; <https://doi.org/10.1063/5.0136469>). However, larger HF cavitation bubbles of about 100 μm were observed to oscillate with as much change as $\sim 43\%$ of their overall diameter when shrinking/expanding implying a vigorous oscillating behaviour (note that the specific size changes of smaller HF bubbles cannot be resolved due to camera limitations, watch at <https://doi.org/10.1063/5.0136469>). In addition, HF bubble velocities were calculated in the range of $\sim 0.02\text{--}0.08\text{ ms}^{-1}$ for approximate bubble diameter sizes of 4–100 μm , respectively (corroborating with previous experimental observations [54]; Note that some larger bubbles derive from pre-existing large in size gas bubbles as liquids were not degassed).

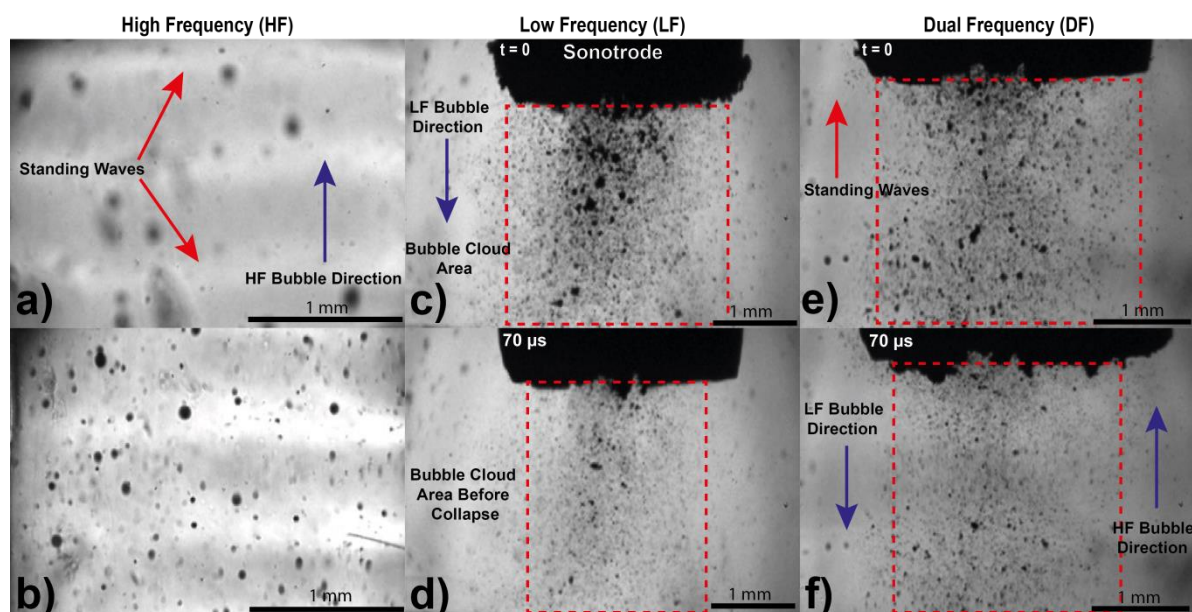


Figure 6.4. Representative frames selected from multiple high-speed image sequences showing three ultrasonic frequency setups for DIW; (a–b) HF, (c–d) LF, (e–f) DF. **a)** Shows the HF set to 1174 kHz producing pressure nodes and antinodes (shadowgraphic imaging at 1 Mfps). **b)** Shows the same conditions but at the lower frame rate of 10 kfps; whereby the slower moving HF induced bubbles (compared to the LF induced bubbles) can be captured in motion. **c)** Shows the LF transducer during the formation of a bubble cloud (1 Mfps). **d)** Shows the LF transducer just before the same cloud collapses, 70 μs after c) (1 Mfps). **e)** Shows the DF setup during the formation of a bubble cloud (1 Mfps). **f)** Shows the DF setup just before the same cloud collapses, 70 μs after e) (1 Mfps). The corresponding videos can be accessed with the published version of this chapter at <https://doi.org/10.1063/5.0136469>; b); e). Note scale bar is at 1 mm.

Fig. 6.4c-d) shows high-speed imaging for the LF induced cavitation bubbles and respective cavitation zone in DIW. The large bubble cloud formed under the sonotrode tip generated strong collapses of the cavitating clouds, producing high pressures. Fig. 6.4e-f) shows the DF setup consisting of the LF sonotrode and HF transducer membrane, hence, both the bubble cloud and the HF standing waves are visible (watch at <https://doi.org/10.1063/5.0136469>). One observation between the LF and DF setup was the size of the cavitation cloud. Fig. 6.4c) and Fig. 6.4e) show a cloud of bubbles forming under the sonotrode. Just before the cloud is about to collapse ((Fig. 6.4d) and (Fig. 6.4f)), the DF setup is seen to retain a larger bubble cloud volume (Fig. 6.4f)), with an increase of $\sim 9\%$ in size. It is likely that these tiny bubbles are difficult to collapse due to their small size and surface tension; therefore, they tend to remain suspended in the liquid medium thus retaining an active cavitation zone. Due to their long lifespan, the HF bubbles have time to grow and reach resonance size (due to rectified diffusion [201]) associated to LF transducer (around $100\text{ }\mu\text{m}$ in radius), or merge into clouds (secondary cavitation) therefore becoming unstable and thereafter collapsing. Therefore, the DF setup retains a larger active cavitation zone, increasing the propensity of SW generation due to more bubble cloud collapses (also in-line with the larger measured P_{Max} values in Fig. 6.2e-h and qualitatively seen in the recordings corresponding to Fig. 6.4 & 5 at <https://doi.org/10.1063/5.0136469> where SW generation is more evident). The HF bubbles play an active role in replenishing cavitation nuclei, and in turn increasing the cavitation zone under the sonotrode tip (shown later in Fig. 6.6 schematic). Interestingly, the larger cavitation zone is also formed at the edges under the sonotrode tip in DF mode, demonstrating additional nucleation of cavitation bubbles (Fig. 6.4f). A larger cavitation zone generates stronger collapses complemented by numerous SW emissions. Previous research has suggested that small bubbles generated in the HF field nucleate cavitation bubbles in the LF cavitation zone [202].

Shadowgraphic imaging of the remaining liquids (Fig.6.5) re-enforced these observations. EtOH under the DF setup was shown to produce a larger range of satellite bubbles (bubble fragments or secondary bubbles that move or form away from the sonotrode tip) that oscillated more rapidly, with a 57% more contraction from their maximum size than their LF counterpart (Fig. 6.5(a1-2 to b1-2)). This enhanced bubble oscillation also corroborates with the pressure data presented in Fig. 6.2b). The case of DIW:EtOH also demonstrated retention of more bubbles in the cavitation zone (notice that the cloud “mist” retains formation) during the collapse of the bubble cloud for the DF setup (Fig. 6.5(c1-2)) compared to the LF setup

(Fig. 6.5(d1-2)). For the case of glycerol (Fig. 6.5e1-f2)), significant observations of the cavitation zone were limited using the high-speed camera. However, image analysis did reveal an increase in the cross-sectional area of the cavitation zone under DF ultrasound. Interestingly, analysis of the cavitation zone enhancement of the liquids coincided with the pressure measurements using the FOH (Fig. 6.2). These percentage increases in cross-sectional area were calculated for glycerol, EtOH, DIW:EtOH and DIW to be 17.2, 16.5, 11.9 and 8.7%, respectively (Table 6.4). Apart from glycerol where viscosity is the dominant property, the surface tension values of the studied liquids follow the same trend. The lower surface tension produces a higher propensity to nucleate bubbles, hence, increasing the cavitation zone, a phenomenon also delineated under the influence of a DF setup.

Table 6.4. Cavitation zone cross sectional area under the sonotrode tip calculated using high-speed images in ImageJ software.

Liquid Medium	Maximum Cavitation Zone Area under sonotrode (mm ²)	Percentage Increase DF-LF (%)
DIW LF	4.5	8.7
DIW DF	4.9	
EtOH LF	6.7	16.5
EtOH DF	7.9	
DIW:EtOH LF	5.1	11.9
DIW:EtOH DF	5.7	
Glycerol LF	1.3	17.2
Glycerol DF	1.5	

We can therefore summarise the most salient observations of the DF setups to demonstrate bubble clusters and LF bubbles moving away from the sonotrode tip to sustain longer lifecycles while rapidly oscillating. By analysing the LF and DF image sequences (Fig. 5) and corresponding video recordings (at <https://doi.org/10.1063/5.0136469>), we observed that these satellite bubbles/fragments of bubbles appear to have a higher tendency to remain in the cavitation zone whereby the interaction with travelling SWs re-energises them, promoting growth and further collapses (that is also in line with recent observations [203]).

In the DF scenario we also noticed that the size and oscillating motion of the bubble fragments are sustained for longer periods of time under the HF pressure field (most noticeable in EtOH Fig. 5(b1-2)), in addition to higher probability of bubble coalescence. The larger cavitation zone and additional satellite bubbles are likely a contributing factor for the larger measured acoustic pressures by the FOH (Fig. 2e-h), detecting more SWs from more transient cavitation collapses and overall cavitation activity. These observations are

graphically portrayed in the schematic, whereby the LF source (Fig. 6a) generates a smaller cavitation zone with lesser secondary cavitation such as oscillating satellite bubbles. Additionally, it is also evident that the spatial distribution of the satellite bubbles formed from the cavitation cloud increased under the influence of the HF transducer being activated as merging with tiny HF bubbles occurs sustaining a larger/expanding active cavitation zone (Fig. 6b, and demonstrated by the high-speed camera, Figs. 6.4 and 6.5).

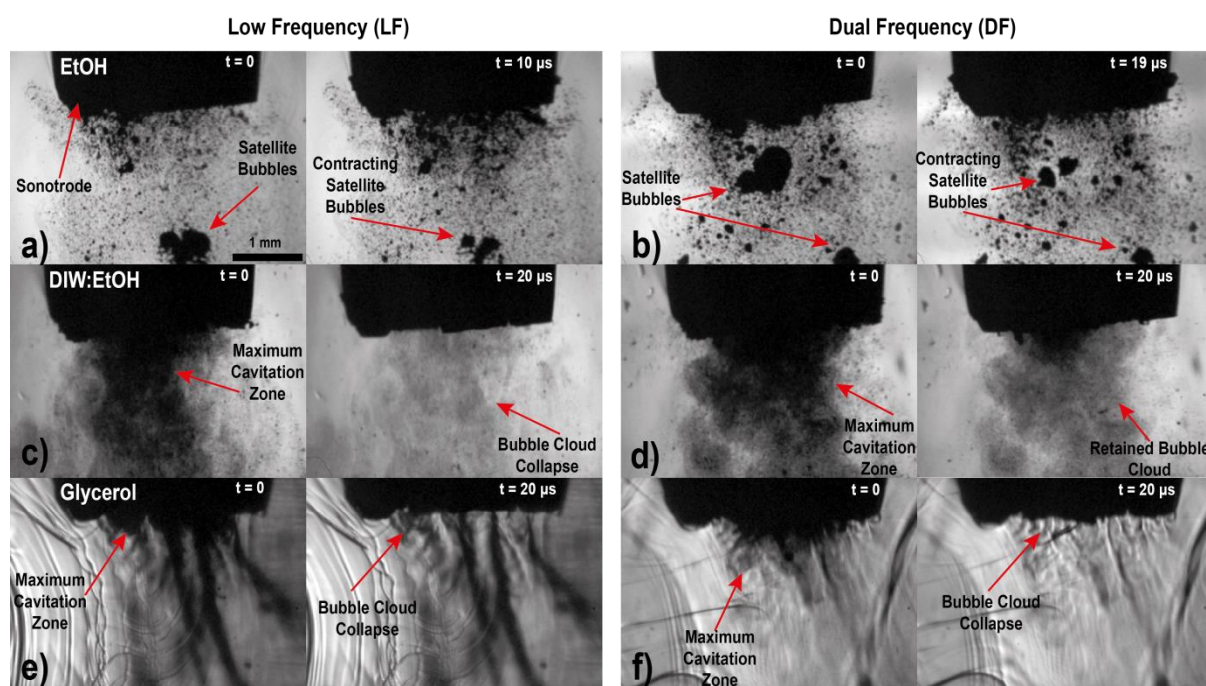


Figure 6.5. Representative frames selected from multiple high-speed image sequences showing the difference between two ultrasonic frequency setups; **a)** EtOH, showing the cavitation zone and oscillating motion of satellite bubbles under the LF source. **b)** EtOH, showing the cavitation zone and oscillating motion of satellite bubbles under the DF source. **c)** DIW:EtOH, showing the maximum cavitation zone and during cloud collapse for the LF source. **d)** DIW:EtOH, showing the maximum cavitation zone and during cloud collapse for the DF source. **e)** glycerol, showing the maximum cavitation zone and cloud collapse for the LF source. **f)** glycerol, showing the maximum cavitation zone and cloud collapse for the DF source. Time duration between images is shown for each sequence. Imaging was taken at 1 Mfps. The videos can be accessed with the published version of this chapter at <https://doi.org/10.1063/5.0136469>; a); b). Note scale bar is at 1 mm.

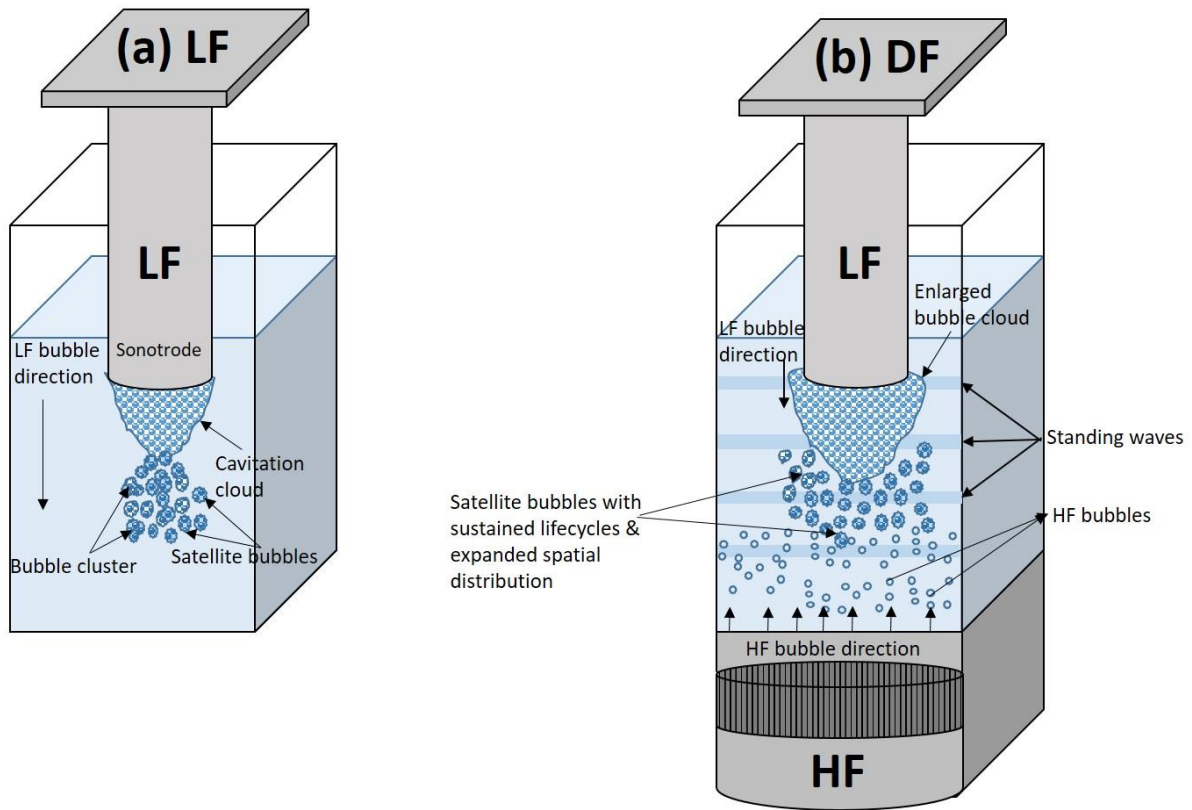


Figure 6.6. Schematic of cavitating environment under **a)** the sonotrode, producing LF cavitation bubbles, and **b)** the DF setup, combining the LF and HF cavitation bubbles for DIW. **a)** Shows the sonotrode produce a cavitation zone, mostly directly under the tip. **b)** Shows the combination of the two frequencies to enhance the cavitation activity. The cavitation zone under the sonotrode tip is expanded, with the lifecycle of the satellite bubbles extended, in addition to their increased spatial distribution in the liquid medium. HF bubbles are seen to oscillate with much smaller radii, moving upwards, in the opposite direction of the sonotrode, mixed with the satellite bubbles and suspended clouds, replenishing cavitation nuclei and facilitate enlargement of the cavitation zone under the sonotrode tip.

6.3.3. Synchronised high-speed imaging and acoustic pressure measurements

Figure 6.7 shows a series of images and waveforms obtained using a synchronisation technique of high-speed recordings with real-time acoustic pressure measurements (Fig. 6.7, for 20% input power). Initial observations reveal that DIW (Fig. 6.7a) appear the least enhanced with the addition of the HF transducer. The largest difference between the LF and DF setup is demonstrated by glycerol, followed by EtOH the DIW:EtOH (Fig. 6.7 d, b & c)), coinciding with the previously measured pressure increases (Fig. 6.2). An increase in cavitation noise is evident for all the DF cases, where particularly, DIW and DIW:EtOH (Fig. 6.7a & c), respectively induce more SWs (indicated by the sharp peaks) which generate approximately 2.5 times larger peaks than for EtOH and glycerol (Fig. 6.7b & d),

respectively). Glycerol is shown to generate multiple bubble collapses (Fig. 6.7d)), however, due to high viscosity of the liquid the SW power rapidly diminishes (reaching up to ~ 400 kPa) and produces sparse individual peaks. EtOH generates even fewer individual peaks (Fig. 6.7b)) with less cavitation intensity (a few reaching up to ~ 200 kPa) indicating less SWs, with a fluctuating pressure time plot. This may be a consequence of prominent vibrating bubble oscillation which is non periodic inducing a non-consistent pressure time domain. The plots of Fig. 6.7 b) and d) especially indicate that the addition of the HF transducer predominantly enhances rapid bubble oscillation, as opposed to increasing transient cavitation (whereby bubble collapses would produce more prominent individual large pressure peaks indicative of SW generation). For instance, the largest recorded pressure peaks are over 1000 kPa for the DF DIW and DIW:EtOH setups (Fig. 6.7a & c)), whereas, more uniform pressure distributions (smaller difference between bulk pressures and maximum peaks) are evident for the DF EtOH setup (Fig. 6.7b)), and especially for the DF glycerol setup (Fig. 6.7d), with both generally generating less than 400 kPa peaks and demonstrate a prominent acoustic contribution from the fundamental frequency (shown in Fig 6.3a-c)). It should be noted that SW energy as evidenced by the negative and positive pressure time traces (measured by the FOH) is dissipated as broadband noise in the frequency domain, with only a very small portion (as explained previously [112]) contributing to this small rise (a few kPa) at ~ 3.2 - 3.6 MHz as shown in Fig. 6.3d-i).

High-speed imaging using the Photron camera (non shadowgraphic imaging) was unable to capture the standing waves propagating from the HF transducer. Hence, the difference between the insets (Fig. 6.7) of the LF and DF setups are harder to distinguish. However, the basic pattern for both setups demonstrates a growing cavitation cloud over the first 10 ms (insets (1-4)), followed by a stabilised period with a smaller cavitation zone (insets (5-6)). As analysed in chapter 5, EtOH again produced a larger cavitation cloud than DIW, and the mixture of DIW:EtOH produced the “mist” cavitation extending the cavitation zone with smaller dispersed cavitation bubbles [172], [191]. Glycerol’s cavitation zone is localised at the sonotrode tip in both frequency setups with a more homogeneous waveform (indication of continuous contribution from the incident wave) and pressure surges from the DF setup. The higher viscosity of glycerol, and the high vapour pressure of EtOH, both inhibiting bubble collapse, may promote bubble oscillation under the DF setup. This may explain why these two solvents are subject to an increase in cavitation intensity (P_{RMS} for EtOH and P_{Max} for glycerol) when combining both a LF and HF source. DIW:EtOH demonstrates an enhanced

pressure field from LF to DF (43%) and an enlarged cavitation zone (12%) populated via tiny microbubbles in the form of cavitation “mist”, which strongly supports why this combination of liquids under a DF source is favourable for exfoliation as observed previously [20]. Additionally, the formation of these tiny cavitation bubbles may penetrate in-between the layers of layered materials, therefore, facilitating exfoliation; agreeing with the results in Chapter 3 [191].

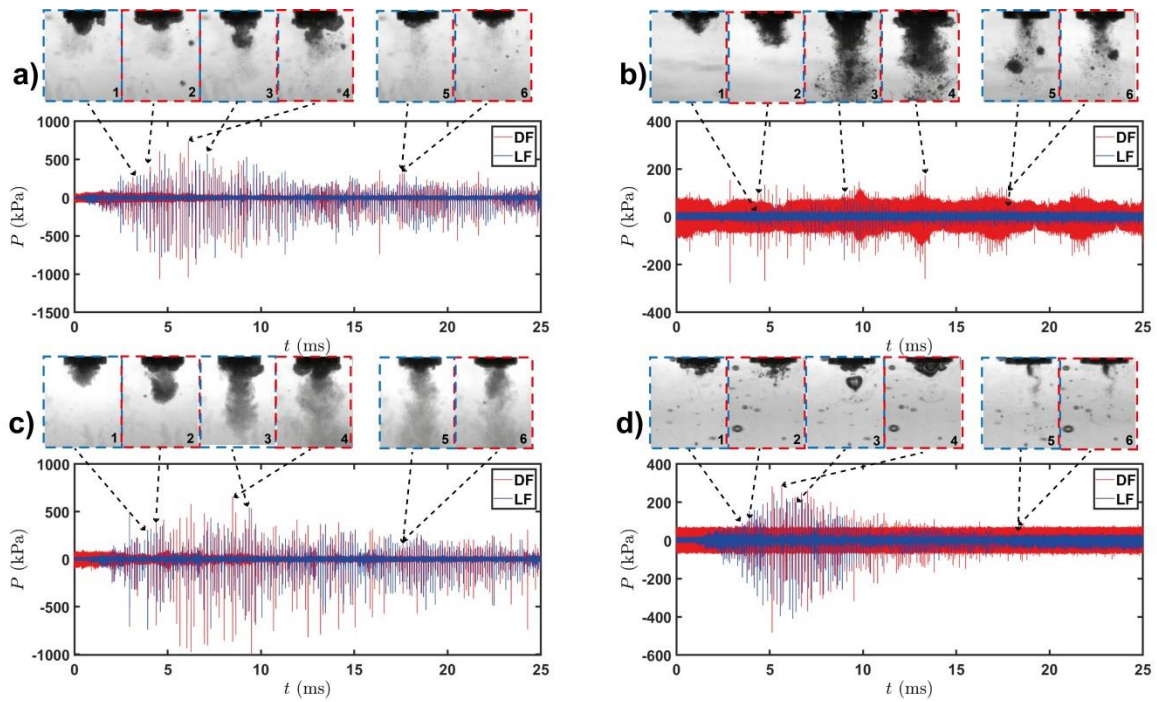


Figure 6.7. Synchronised high-speed images (insets) with acoustic pressure plots for each studied liquid; **a)** DIW, **b)** EtOH, **c)** DIW:EtOH & **d)** Glycerol, whereby the DF (red) and LF (blue) data are plotted together for comparison. The period of 25 msec is recorded once the LF source is activated. The insets display four representative moments (indicated via the arrows, blue boxed images are LF, while red boxed images are DF) of the developing bubble dynamics for each solvent; (1) initial activation of the sonotrode for the LF setup, (2) initial activation of the sonotrode for the DF setup, (3) maximum cavitation cloud before collapse for the LF setup (thereafter, a large corresponding pressure spike is induced), (4) maximum cavitation cloud before collapse for the DF setup, (5) stabilised cavitation period for the LF setup, (6) stabilised cavitation period for the DF setup. Imaging was taken at 100 kfps, with intensity measured via a FOH and converted to acoustic pressure. The transducer input power was set to 20%.

6.3.4. Dual-frequency Exfoliation of Graphite & Its Characterisation

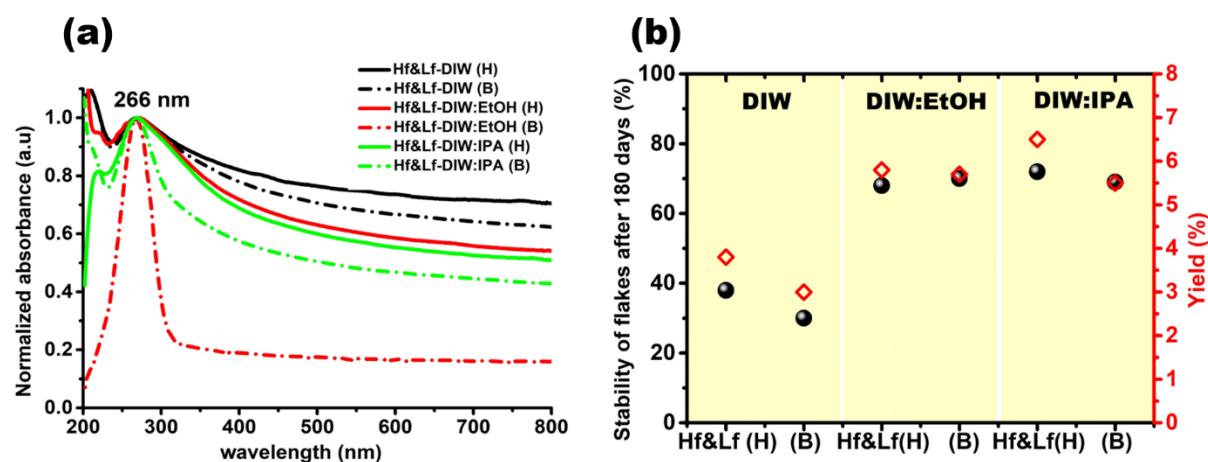


Fig. 6.8 (a) Normalized UV-Vis absorbance spectra of obtained graphene supernatants; (b) stability of graphene flakes recorded after 180 days (on left Y-axis) and yield estimations of produced graphene (on right Y-axis) obtained after Hf&Lf ULPE in DIW, DIW:EtOH and DIW:IPA.

Following the experiments performed in this chapter, ULPE utilising the DF setup and characterisation of resultant samples was taken. Fig. 6.8(a) displays the normalized UV-Vis absorption spectra recorded for Hf&Lf-DIW (H), Hf&Lf-DIW (B), Hf&Lf-DIW:EtOH (H), Hf&Lf-DIW:EtOH (B), Hf&Lf-DIW:IPA (H) and Hf&Lf-DIW:IPA(B). The solid and dashed absorption curves indicate the representative spectra obtained for samples sonicated with the horn and bell sonotrode, respectively. The characteristic graphene related absorption peak centred on ~ 266 nm was found in each sample (ascribing to π - π^* transitions of C=C sp^2 bonds). However, a distinct variation in the slopes of the curves between horn and bell samples was also observable. The bell samples Hf&Lf-DIW (B), Hf&Lf-DIW:EtOH (B) and Hf&Lf-DIW:IPA(B) demonstrate more decreasing nanosheets thickness in comparison to Hf&Lf-DIW(H), Hf&Lf-DIW:EtOH (H) and Hf&Lf-DIW:IPA (H). Therefore, manifestations of sharper peaks in bell-sonicated samples for each solvent reveal the majority of thinner exfoliated flakes in them. The improved exfoliation while using the bell sonotrode can be understood on the basis of its double diameter (40 mm) which generates an extended cavitation zone explaining both the enhanced circulation of GP particles into treatment volume and substantial generation of SWs for layer delamination.

From the graph given in Fig. 6.8(b), it can be inferred that the amount of produced graphene (indicated with red diamonds) in DIW:EtOH (5.8% (H), 5.75% (B) and DIW:IPA (6.5% (H), 5.5% (B)) is almost double the amount produced in DIW (3.75% (H), 3.0% (B)). These

results correlate with chapter 5 ULPE characterisation, demonstrating the utility of the alcohol content in the solution. The stability (indicated with black spheres) (Fig. 6.8(b)) of suspended graphene flakes is also in correlation with chapter 5. DIW:EtOH (68%(H), 70%(B)) and DIW:IPA (72% (H), 69%(B)), were shown to withhold a stability of two times more in contrast to DIW(38% (H), 30% (B)) for the duration of approximate 180 days.

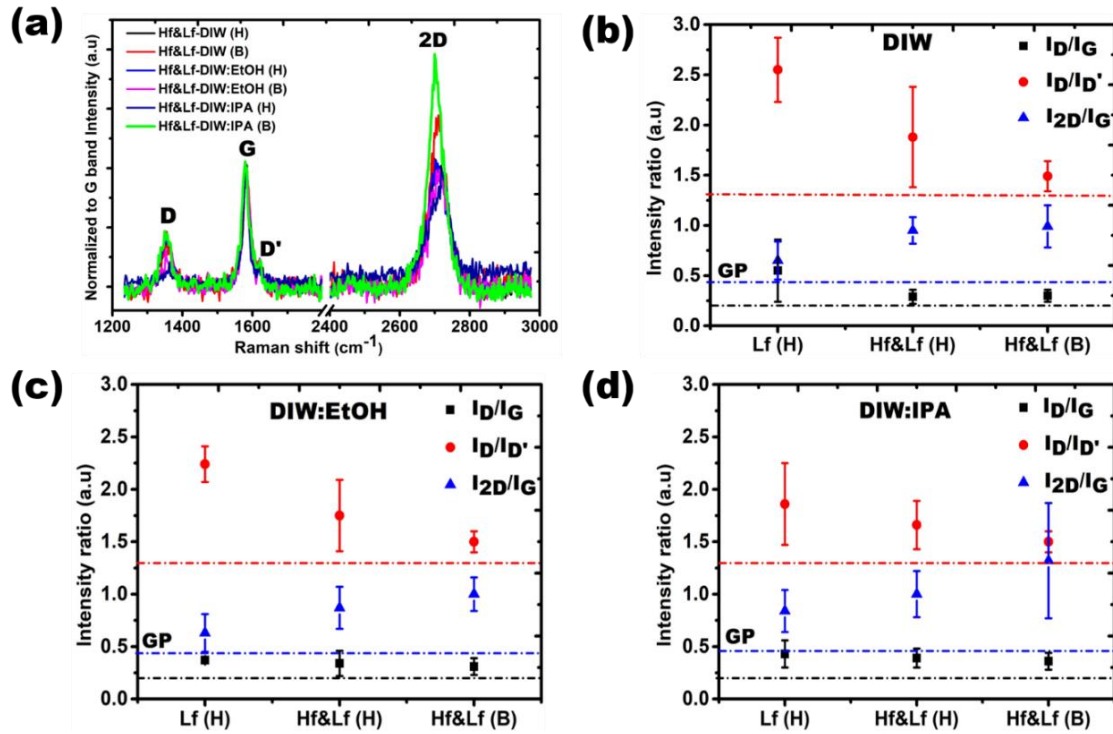


Fig. 6.9 (a) Representative Raman spectra of flakes exfoliated in each sample featuring D, G, D' and 2D peaks, spectra are normalized to the G band intensity; (b)-(d) averaged intensity ratios of peaks, I_D/I_G (black squares), $I_D/I_{D'}$ (red circles) and I_{2D}/I_G (blue triangles) of registered flakes in DIW, DIW:EtOH and DIW:IPA, respectively. The data for the original GP is indicated with dashed line of same colour for reference.

Raman spectroscopy was also carried out for analysing the quality of exfoliated flakes in terms of their defects quantification and qualitative estimations of thicknesses [204]. Figure 6.9(a) demonstrates the representative Raman spectra of investigated graphene flakes exfoliated in the samples, Hf&Lf-DIW (H), Hf&Lf-DIW (B), Hf&Lf-DIW:EtOH (H), Hf&Lf-DIW:EtOH (B), Hf&Lf-DIW:IPA (H) and Hf&Lf-DIW:IPA(B). From the spectra, first thing to note the characteristic signatures of sp^2 hybridized carbon, i.e. D, G, D' and 2D bands centred on $\sim 1350 \text{ cm}^{-1}$, 1580 cm^{-1} , 1620 cm^{-1} and 2720 cm^{-1} respectively [204]. All the spectra are linear baseline subtracted and normalized to the G-band intensity for a clear comparison.

From Fig. 6.9(b-d), we observe a drop in defect ratios in registered graphene flakes exfoliated in DIW (0.55 to 0.30), DIW:EtOH (0.37 to 0.30) and DIW:IPA (0.43 to 0.36) in Hf&Lf ULPE configuration in comparison to Lf only. This decreased trend of defect ratios manifests the lesser defective graphene flakes produced in the Hf&Lf set-up in contrast to Lf. This data aligns with the chapter 3 observation that smaller cavitation bubbles able to fit in-between the layers can facilitate a more gentle exfoliation inducing less defects (where the HF transducer nucleates these tiny bubbles). The observed defect ratios are above the level of GP ($I_D/I_G \sim 0.22$, black dashed line), which suggests the evolution of structural defects occurs due to thinning of GP crystallites after ULPE. Interestingly, defect ratios (I_D/I_G) appear to remain constant for the flakes exfoliated with both the horn (H) and bell (B) sonotrode, implying a similar quality under both ULPE setups. Additionally, the values of I_{2D}/I_G are populated within a narrow range of 1 ± 0.2 , revealing the majority production of FLG in both the Hf&Lf (H and B)-DIW and DIW:EtOH (Fig. 6.9(b-c)). Interestingly, there is also not a significant difference in I_{2D}/I_G values for the Hf&Lf-DIW(H) and Hf&Lf-DIW(B).

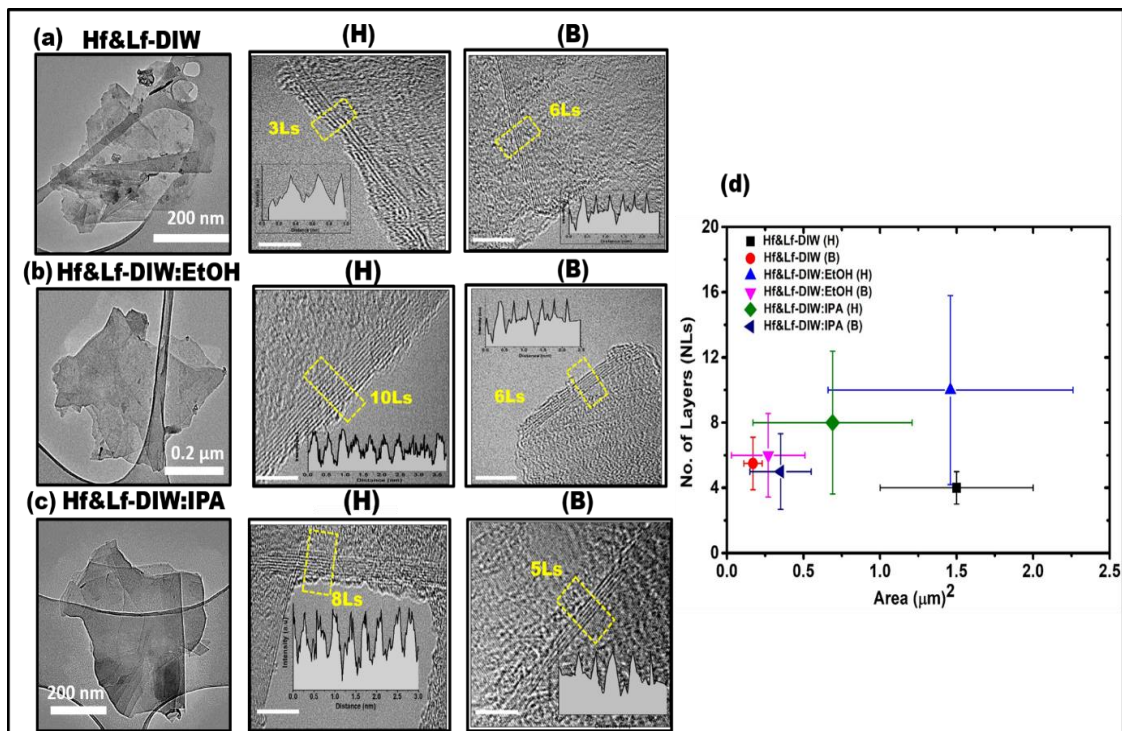


Fig. 6.10 (a-c) Representative TEM images (both low and high resolution) of graphene flakes; **(d)** statistical data for area and number of layers exfoliated in DIW, DIW:EtOH and DIW:IPA for both horn (H) and bell (B) sonotrode.

Figure 6.10 presents data on dimensions and layer-count of the produced flakes in DIW, DIW:EtOH and DIW:IPA, for both low and high resolution TEM (HR-TEM). Fig. 6.10(a-c) demonstrate low-resolution representative TEM images of graphene flakes exfoliated in all

cases of DIW, DIW:EtOH and DIW:IPA with both the horn and bell sonotrode, respectively. The same procedure detailed in Chapter 5 was used calculate the flake sizes. Fig. 6.10(d) provides statistical data for area and thickness of the analysed flakes, which is plotted for each case. The average area of exfoliated flakes in Hf&Lf-DIW (H), Hf&Lf-DIW:EtOH (H) and Hf&Lf-DIW:IPA (H) was measured to be $1.5 \mu\text{m}^2$ (black square), $1.46 \mu\text{m}^2$ (blue triangle) and $0.7 \mu\text{m}^2$ (olive diamond), corresponding to average number of layers 4, 10 and 8, respectively. Large-sized graphene flakes with a spectrum of layer-count ranging from 4-15 were produced in Hf&Lf-DIW:EtOH (H). This result is similar to the TEM characterisation presented in chapter 5 (where the Lf-DIW:EtOH (H) produced high-quality FLG (3–5 Ls) with an average area of $\sim 1.15 (\mu\text{m})^2$). On the other hand, the area of produced graphene flakes in the Hf&Lf-DIW (B), Hf&Lf-DIW:EtOH (B) and Hf&Lf-DIW:IPA (B) lie in a lower regime with average areas of $0.17 \mu\text{m}^2$ (red sphere), $0.27 \mu\text{m}^2$ (pink triangle) and $0.35 \mu\text{m}^2$ (navy triangle) having an average number of layers 5, 6 and 5, respectively. Therefore, we can deduce from the TEM statistical plot (Fig. 6.10(d)) that the samples sonicated with the bell sonotrode contain comparatively thinner flakes having a smaller area as opposed to the horn sonotrode.

In the last two chapters we have investigated the bubble dynamics, cavitation development and the acoustic pressure regime of specifically selected green solvents for both a single LF ultrasonic source and a DF source consisting of a LF and HF transducer. The corresponding results from ULPE aligned with the fundamental analysis, whereby the selected parameters were shown to improve exfoliation results.

DIW:EtOH produced an average area of $1.15 \mu\text{m}$ with 3-5 layers from the single LF source. Introducing the DF setup produced layers within the range of 10 ± 5 but with a larger area of $1.5 \mu\text{m}$ and yield of 5.8%. This data implied that the DF setup produced more favourable results overall. When shifting to the larger area sonotrode (40 mm bell) we witnessed an improved degree of exfoliation in half the sonication duration, however, at the expense of producing small sized FLG flakes ($0.3 \mu\text{m}$). DIW:IPA performed similarly to DIW:EtOH (yields of 5.5, 5.75% respectively), whereas DIW performed the worst, generating lesser FLG yields (3%) also at the cost of more induced defects and much shorter stability. The overall progression of research throughout the thesis would indicate the use of a water/alcohol solution sonicated from a DF setup, with moderated temperature and input power (40°C at 50%) can produce high quality and high yield graphene for ULPE. However, further research would be needed to refine this system and generate a larger output of nanomaterial.

6.4. Conclusions

The benefits of using a DF transducer setup was recently demonstrated for the production of 2D nanomaterials in the studied liquids [154]. This work took the next step and presented analysis into a DF ultrasonic system (24 kHz & 1.174 MHz) providing insightful information on the reasons behind this advancement. Bubble dynamics, acoustic pressures, spectra and generated SWs were elucidated and compared with a single (standard setup), LF sonotrode source (24 kHz) for various liquids (DIW, EtOH, DIW:EtOH and glycerol). This was demonstrated using ultra-high-speed imaging, showing how the combination of a LF and HF source improved cavitation activity and enhanced the cavitation zone. In general, the DF setup generated greater acoustic pressures (up to 180% increase). This data was re-enforced with the aid of synchronised high-speed imaging and acoustic pressure measurements that showed bubble dynamics in real-time with acoustic emissions. The selected image sequences also showed an increased size of the cavitation zone directly under the sonotrode tip (9-17 % increase). In addition, the DF setup increased the spatial distribution of satellite bubbles and bubble clusters from the LF source, while extending their lifecycles by maintaining a larger cavitation zone (Fig. 6.4e-f and Fig. 6.5d), therefore, increasing the propensity of more powerful bubble collapses and hence more SW emissions. Furthermore, utilising the DF setup also promoted vigorous bubble oscillations due to many smaller additional cavitation bubbles unable to collapse, hence, enhancing the overall cavitation activity. This was particularly the case for DIW:EtOH liquid that was recently found to be a suitable solvent for cavitation exfoliation of graphene [20], [191]. This was further proved through ULPE utilising a DF setup. DIW:EtOH produced an average area of 1.5 μm^2 with 10 ± 5 layers and 5.8% yield with the horn sonotrode. Further optimization can include using a larger area sonotrode (40 mm bell), which exhibited improved degree of exfoliation in half the sonication duration, however, at the expense of producing small sized FLG flakes. DIW:IPA performed similarly to DIW:EtOH, whereas DIW performed the worst, generating lesser FLG yields also at the cost of more induced defects and much shorter stability. The analysis and observations from this study can contribute to developing and validating multifrequency numerical models, in addition to optimizing and controlling a cavitation processing method for multifrequency systems and ULPE.

Chapter 7

Concluding Remarks & Future Outlook

From the research presented in this thesis entitled ‘On the fundamental mechanisms & optimisation of ultrasonic assisted liquid phase exfoliation of two-dimensional nanomaterials’, there are various key points that can be summarise the significance of the experimental work and relevant discussions. A brief description of these results will be followed by potential future work that could be conducted.

1. An investigation and experimentation into the sono-exfoliation mechanism of graphite was undertaken. Ultra-high-speed shadowgraphic imaging of laser induced single bubble interactions with fixed graphite flakes were recorded at 1 Mfps. High-speed imaging of bubble cloud interactions with fixed graphite flakes induced via an ultrasonic probe were recorded at 100 kfps. Finally, acoustic pressure measurements were taken using a calibrated FOH to estimate acoustic emissions required to initiate and propagate delamination of layered graphite (found to be up to 5 MPa). The most salient sono-exfoliation mechanisms were identified, which demonstrated that initiation of exfoliation has generally induced via SWs, and further propagated by liquid jets and rapidly oscillating cavitation bubbles. The experiments were limited as only one orientation of the graphite flake was exposed to acoustic emissions. Different positions could be conducted and investigated. Further investigation could also include a fixed graphite flake observed under X-ray photons to elucidate multi-bubble interactions and view bubble interfaces.
2. A systematic study to determine optimum solution temperature and transducer input power conditions for ULPE was conducted. A calibrated cavitometer was used to measure the acoustic pressure of GP and GF, in DIW solutions between temperatures of 10-70 °C, using three input powers (20, 50, 100%). The optimal sono-exfoliation parameters were determined to be 20% input power at 10°C for a GF solution, and 100% input power at 40°C to 50°C for a GP solution. Future work could include a systematic study analysing input powers of 5% intervals and temperature changes in 5°C intervals to fine tune the optimum parameters further i.e. input power between 45-55% maybe further enhance cavitation characteristics for ULPE. Additionally, the use of a needle hydrophone and FOH could complement the cavitometer in these experiments to provide a full cavitation picture. This would enable a larger range of

calibrated frequencies along with high sensitivity and precise detection of acoustic emissions due to exhibiting high spatial resolutions.

3. Analysis of solvents bubble dynamics and acoustic emissions were taken to identify a suitable eco-friendly solution for ULPE. Synchronised high-speed imaging with acoustic pressure measurements were taken for potential green solvent candidates as a replacement for NMP. Additionally, shadowgraphic high-speed imaging was taken to analyse shock wave generation of the solvents. The optimum solution (in terms of cavitation activity and acoustic pressure) of DIW:EtOH was then used to sonicate graphite for 2 h and found that the yield was twice that of using pure water as a liquid medium. Additionally, the stability of 87% of the graphene yield remained after 3 months. Future work could include further investigation into the ratio of DIW to EtOH in the solution. This may increase the performance of graphite exfoliation if cavitation is enhanced. Additionally, other water/alcohol mixes (such as DIW:IPA or methanol) could be investigated and may facilitate exfoliation through more favourable chemical interactions with layered materials or enhancing cavitation within the liquid medium.
4. An investigation of the effect of dual-ultrasonic frequencies on eco-friendly solvents bubble dynamics and acoustic emissions was conducted. Comparison of a single frequency probe (24 kHz) and a dual-frequency setup (24 kHz + 1174 kHz) was carried out using synchronised high-speed imaging with acoustic pressure measurements in conjunction with shadowgraphic high-speed imaging. Through the use of a dual-frequency system bubble fragments and satellite bubbles were able to extend their lifecycle, increase spatial distribution, thus, extending the boundaries of the cavitation zone (up to a 17% increase). Furthermore, this combination of ultrasonic frequencies generated higher acoustic pressures (up to 180%) and enhanced the characteristic shock wave peak, indicating more bubble collapses and the generation of additional shock waves. Graphene characterisations using the established dual-frequency setup in DIW:EtOH produced an average area of 1.5 μm with 10 ± 5 layers and 5.8% yield with the horn sonotrode. When using the bell sonotrode the yield was approximately the same (5.75%) in half the sonication duration. However, this achievement came at the cost of producing smaller sized FLG flakes (0.3 μm). Future work may include analysing the selected eco-friendly solvents with the addition of surfactants such as sodium cholate, which has been shown to enhance the cavitation zone by providing additional nuclei for cavitation. The

water/alcohol solution in combination with glycerol could also be investigated to optimize acoustic emissions. As demonstrated in Chapter 6, glycerol greatly boosted the acoustic emissions, and could aid with the chemical nature of material dispersion required to stabilise the exfoliated nanomaterials.

Appendix

Section A: Bubble Simulation & Acoustic Pressure Mapping

Figure A1 distances 0.77 and 1.5 mm represent the range of distances a cavitation bubble was generated from the graphite flake in Fig. 3.8. This range of LIB interactions provided a more representative comparison to how graphite layers may exfoliate under a typical LPE sonicated environment. From this we can obtain a representative picture of bubble oscillating force estimates which made contact with the graphite flake, and hence, provide an indication of the fatigue process that occurred during graphite flake layer exfoliation.

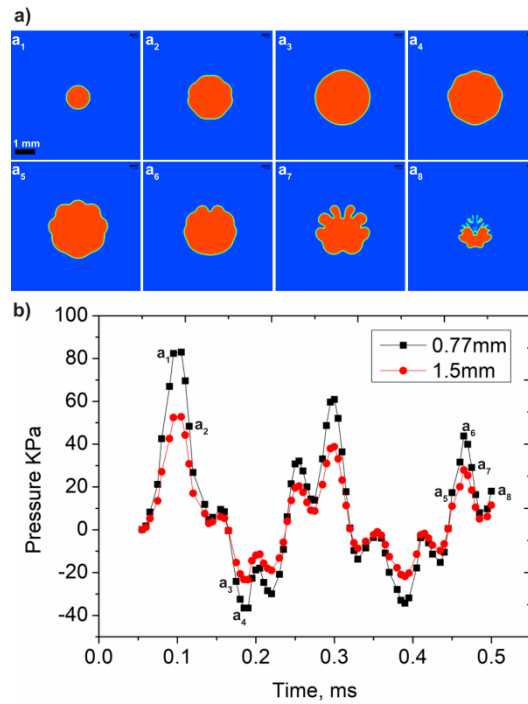


Figure A1. (a) Displays bubble oscillation dynamics, with a1-a8 highlighting eight oscillating points (where the red area represents the bubble shape). (b) Shows the corresponding pressure profile around the bubble as a function of time for two different distances to replicate the range of generated bubbles from the graphite flake. Using bubble parameters from Fig. 3.8 (“branching” manifestation), estimates for bubble oscillating forces by stable cavitation was demonstrated using 2D VOF modelling based on compressible flow. The pressure profile around the oscillating bubble as well as the time points of the eight typical frames in (a) are marked and displayed on (b). (a1) A single bubble is compressed. (a2-5) After compression to a certain extent, this bubble expands immediately and the surrounding fluid also develops outward. (a6-8) The bubble contracts sucking in the sounding liquid. Correspondingly, the pressure around the bubble also fluctuates in the range of $\sim -35+80$ kPa over the eight points. Hence, when this bubble continues to oscillate near the graphite flake, this high-speed oscillating flow pattern around it continues to act on the graphite as proposed in the “branching” manifestation (Fig. 3.8-3.9).

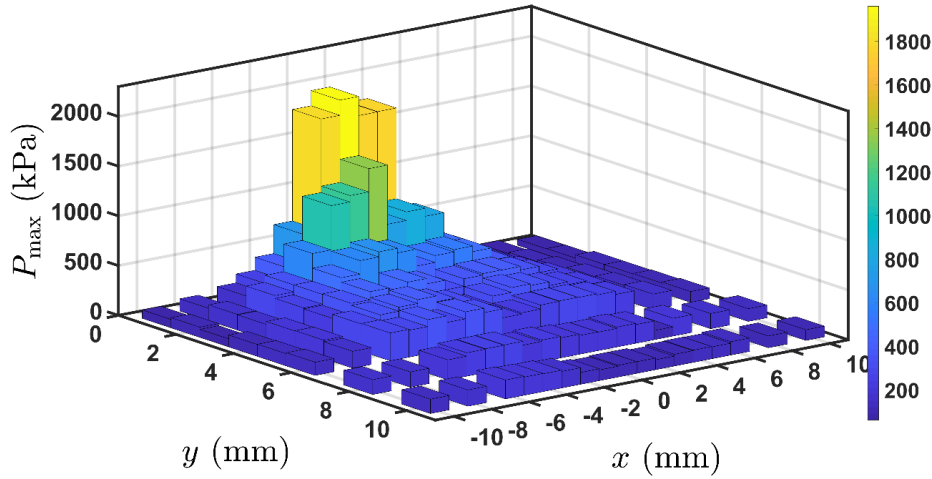


Figure A2. Pressure distribution mapping from fibre optic hydrophone: (0,0) is the tip of the sonotrode. Where x denotes the horizontal position of the hydrophone, and y the vertical (depth).

An effort to characterise and quantify the SW emissions by local cavitation bursts that clearly promote exfoliation (see all evidence in the previous sections) was made. In all cases described in Section 3.2 the calibrated FOH was deployed to recreate experiment conditions, and placed at the exact position as the tip of the graphite sample to measure acoustic pressure values from the propagating SW. Since the hydrophone was calibrated in the MHz range (1-30 MHz), the detected signals fed into the oscilloscope can only be received as a consequence of SW emissions from inertial cavitation.

Section B: Acoustic Pressure & Graphene Literature Comparison

Table B1. Non-dimensional numbers calculated to compare NMP at 20 °C and 40 °C.

	ND Number	NMP 20 °C	NMP 40 °C
Reynolds	$Re = \rho VL/\mu$	8.76×10^4	1.22×10^5

Our group has previously conducted a non-dimensional analysis of water-ethanol mixes. The relevant information on calculation can be found elsewhere [172].

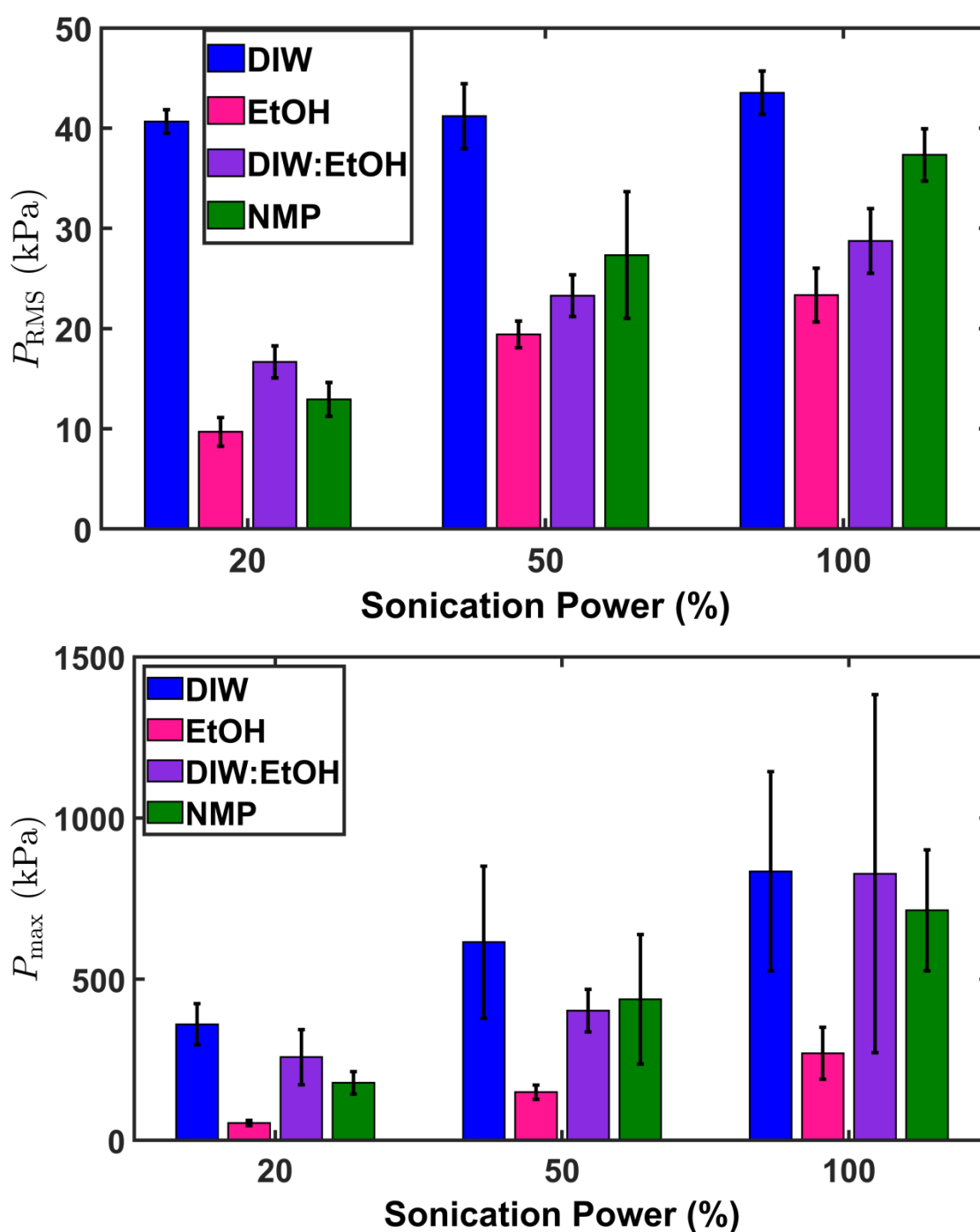


Figure B1. (a) Root means square pressure (P_{RMS}) measurements taken with the fibre-optic hydrophone (FOH) for solvents under investigation. (b) Maximum pressure (P_{max}) measurements taken with the FOH for solvents under investigation. Data was recorded for solvents at 20 °C.

The plots from Fig. B1 display similar pressure trends as for the solvents taken at 40 °C in Chapter 5, albeit lower overall pressure magnitudes. The largest distinction was lower pressures measured for NMP compared to that of the 40 °C NMP solution.

Table. B2. Acoustic intensity for each solvent under investigation at various input powers, with an uncertainty of $\pm 0.2 \times 10^{-4}$ W/m².

Solvent	Temperature (°C)	Input power (%)	Peak to peak amplitude (μm)	P _{liquid} (Watts)	P _{air} (Watts)	Acoustic Intensity (×10 ⁻⁴ W/m ²)
DIW	20	20	9.2	48	12	10
		33	15	68	14	14
		50	23	97	18	21
		100	46	199	50	39
	40	20	9.2	46	12	9
		33	15	64	14	13
		50	23	93	18	20
		100	46	190	50	37
DIW:EtOH	20	20	9.2	42	12	8
		33	15	62	14	13
		50	23	97	18	21
		100	46	197	50	39
	40	20	9.2	25	12	3
		33	15	48	14	9
		50	23	84	18	17
		100	46	178	50	34
EtOH	20	20	9.2	18	12	2
		33	15	31	14	4
		50	23	55	18	10
		100	46	169	50	31
	40	20	9.2	24	12	3
		33	15	39	14	7
		50	23	57	18	10
		100	46	162	50	30
NMP						
	20	20	9.2	30	12	5
		33	15	47	14	9
		50	23	87	18	18
		100	46	201	50	40
	40	20	9.2	44	12	8
		33	15	64	14	13
		50	23	92	18	20
		100	46	202	50	40

Using the formula; acoustic intensity = $\frac{P_{\text{liquid}} - P_{\text{air}} \text{ (W)}}{\text{Area of sonotrode (m}^2\text{)}}$

Where P_{liquid} is the acoustic pressure measured in the solution, P_{air} is the pressure measured when the sonotrode was activated in the atmosphere, and the *Area of sonotrode* was calculated to be (22 mm diameter) $3.79 \times 10^{-4} \text{ m}^2$. The resulting acoustic intensity was used for the plots in Chapter 5.

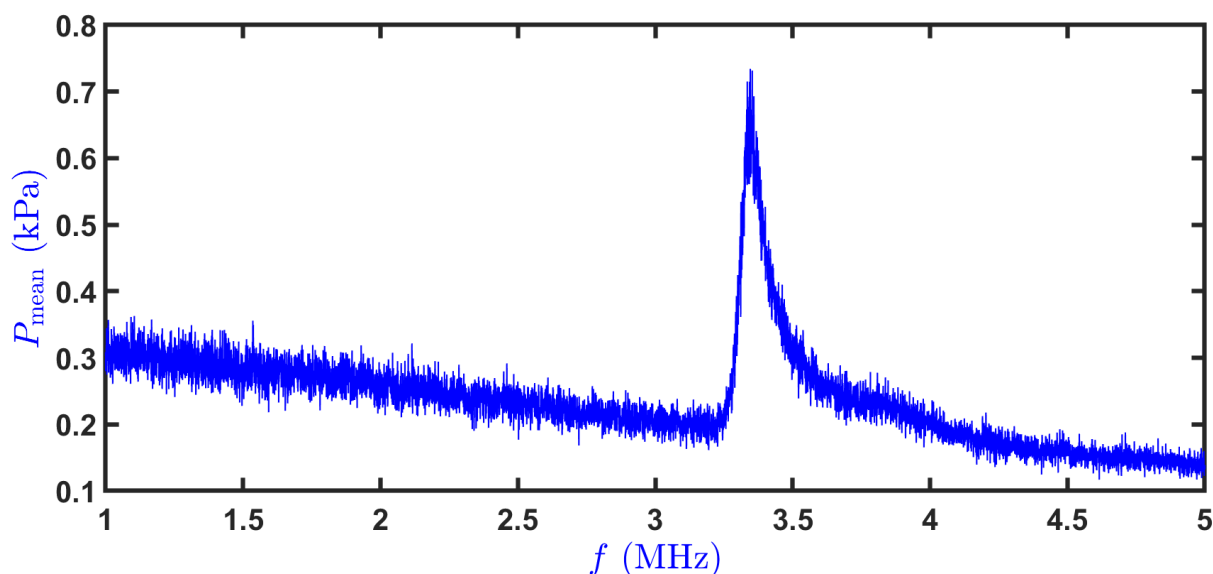


Figure B2. Spectra of NMP taken with a FOH demonstrating the inherent shock wave (SW) peak at ~ 3.3 MHz. The manifestation of the peak in Fig. B2 provided additional evidence that NMP bubble dynamics feature SWs as a prominent mechanism. The data indicates that NMP used with ultrasonic cavitation facilitates the exfoliation of 2D materials, utilising powerful cavitation shearing forces in addition to its chemical properties which delaminate layers.

For Chapter 5, the use of various sonication powers provided an appropriate range to analyse the SW generation for the four solvents. Due to SWs deceleration over long distances, SW velocities were calculated over ~ 1 mm after generation in order to fairly compare propagation through each solvent (calculated using *ImageJ* software).

Table B3. Literature comparison of degree of exfoliation, yield, quality and stability of produced graphene in NMP with DIW and DIW:EtOH in the present work.

Ref	Degree of exfoliation	Yield%	Stability	Quality
Liang et al. [205] LPSE of graphite in NMP	FLG with lateral size 1-1.5 μm	1.2-1.6% (corresponding to initial concentration 1-2 g/L)	Data not available	Average Wrinkled and folded graphene flakes with D/D' ratio $\sim 3.3 \pm 0.05$
Haar et al. [173] Bath sonication of graphite in NMP	FLG with lateral size >200 nm	85 $\mu\text{g/ml}$	Data not available	Good D/D' ratio not available
Bracamonte et al. [96] ULPE of graphite in NMP	Multilayers with lateral size 200 nm – 2 μm	Data not available	Data not available	Defective with D/D' ratio $\sim 4.5 \pm 0.5$
Manna et al. [206] Bath sonication of graphite in NMP	FLG with lateral size 0.5-2 μm	Data not available	Data not available	Average D/D' ratio less than 4.5
Teng et al. [207] Ball Milling in NMP	Multi layers with lateral size 0.2-0.5 μm	26%	Data not available	Data not available
Paton et al. [9] Shear mixing in NMP	FLG with lateral size 300-800 nm	3%	Data not available	Defective with D/D' ~ 4
Hernandez et al. [8] Bath sonication in NMP	Multi-layer graphene with lateral size tens of μm	12% (sediment recycling)	Data not available	Good quality D/D' ratio not available
Rangappa et al. [208] Supercritical fluid exfoliation (SCF) of graphite in NMP	<10 layers 0.1-2 μm	8.3%	Data not available	Defective (D/D' not available)
ULPE in DIW (present work)	3-5 layers Lateral size, 0.5-1 μm	1.25-5.62% [#]	8%	Good quality with D/D' ratio ~ 2.5
ULPE in DIW:EtOH (present work)	3-5 layers including SLG and BLG Lateral size, 0.5-1 μm (66% higher than produced in DIW)	3.75-21.86% [#]	78%	Good quality with D/D' ratio ~ 2.2

Centrifugation speed: 300-1500g

Section C: Acoustic Intensity, Spectra and Transducer Design

Table. C1. Acoustic intensity values for sonication input powers (from 20 °C solutions).

Solvent	Input Power (%)	P_{liquid} (W) Lf	P_{liquid} (W) HF @ 50%	Acoustic intensity (W/m ²)×10 ³ LF	Acoustic intensity (W/m ²)×10 ³ HF	Acoustic intensity [#] (W/m ²)×10 ³ Total (LF&HF)
DIW	20	7	157	283	80	363
	60	14	157	990	80	1070
	100	28	157	1556	80	1636
EtOH	20	7	149	283	76	359
	60	13	149	849	76	925
	100	26	149	1273	76	1349
DIW:EtOH	20	8	158	424	80	504
	60	15	158	1132	80	1212
	100	28	158	1556	80	1636
GLYCEROL	20	12	185	990	94	1084
	60	21	185	1081	94	1175
	100	43	185	3678	94	3372

* P_{air} (Watt) = 5, 7 and 17 for 20%, 60% and 100% input powers, respectively.

Note: P_{air} is considered only for LF only, as the HF transducer can only be operated safely with liquid.

$$\text{\#Acoustic intensity} = \frac{P_{\text{liquid}} - P_{\text{air}} \text{ (W)}}{\text{Area of sonotrode (m}^2\text{)}} \quad (1)$$

Volume of liquid = 200 ml.

Diameter of sonotrode used is 3 mm with peak to peak amplitude of 210 microns at 100% input power,

Diameter of the membrane used is 50 mm.

The acoustic intensity was calculated from equation 1. Where P_{liquid} is the power measured in the solvents, P_{air} is the power measured in the atmosphere, and the area of the sonotrode is πr^2 .

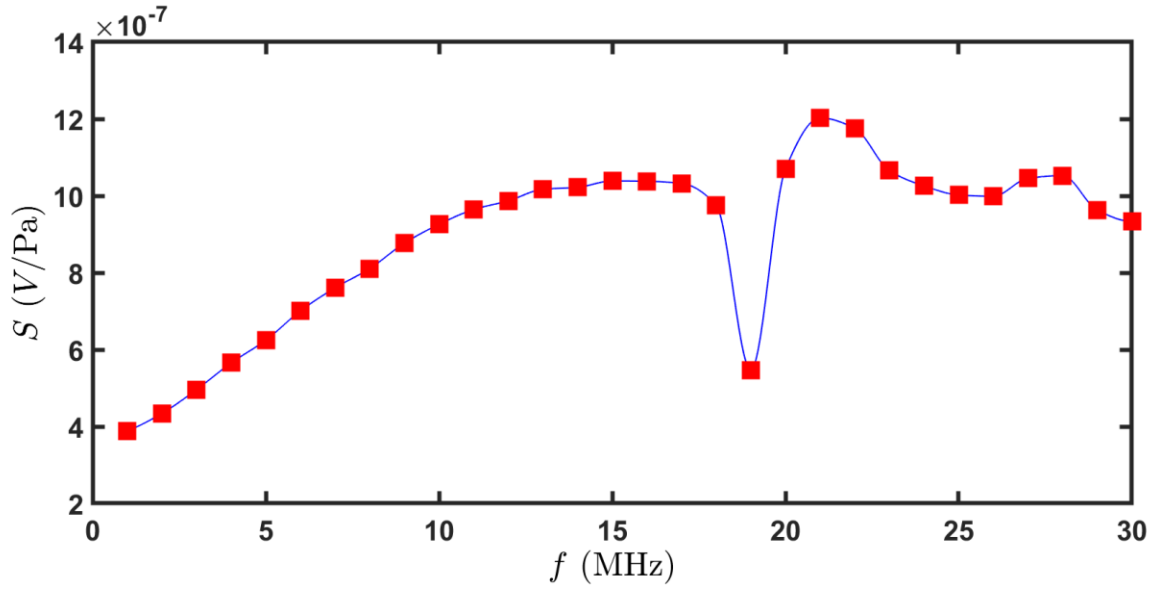


Fig. C1. Sensitivity plot of the fibre optic hydrophone used to take acoustic pressure measurements.

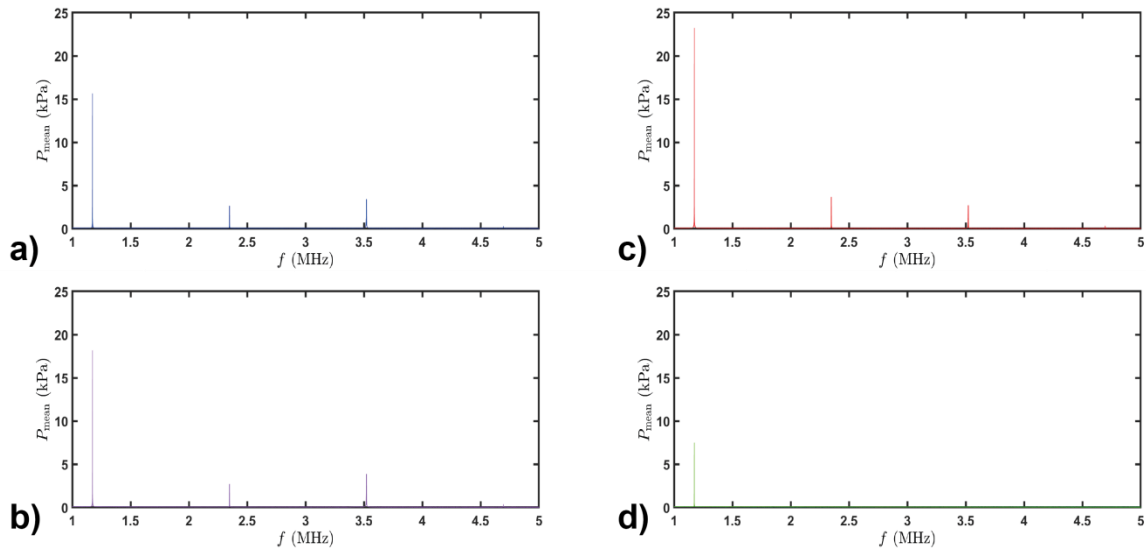


Fig. C2. Acoustic spectra showing HF only setups for each solvent, over an averaged acoustic pressure. **a)** DIW, **b)** EtOH, **c)** DIW:EtOH, **d)** Glycerol.

HF spectra are shown to generate the three HF harmonics at 1.174, 2.347 and 3.522 MHz as seen in Fig. 6.3. EtOH harmonics dominate due to its high vapour pressure, inhibiting bubble collapse and perhaps promoting bubble oscillation under the HF source as also previously seen in [9]. Interestingly, glycerol which has the more prominent spectra harmonics (Fig. 6.3) is seen to produce the smallest peak here indicating the low power input from the HF and the

unique combination of the LF and HF that facilitates significant acoustic intensity and cavitation development.



Fig. C3. Shows the base of the transducer membrane.

References

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