A STUDY OF LIQUID PHASE EXFOLIATION
AND PROPERTIES OF 2D NANOMATERIALS

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A thesis submitted for the degree of
Doctor of Philosophy

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2015
I leave this as an exercise to the reader.
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Sebastian Tadeusz Barwich
ABSTRACT

Graphene and, more generally, two dimensional nanomaterials have been a focus of the scientific community for over a decade after Graphene’s isolation by Geim et al. in 2004. While these materials possess exceptional properties as they approach monolayer thickness, in order to fully exploit and utilise these materials production methods must be refined and the process and material behaviour during production must be well understood.

In order to address the practical issue of shipping large quantities of material, a method is outlined to “pre-treat” flaked graphite in order to yield a dry powder that can subsequently be dispersed in liquid media with ease. This technique is shown to produce a powder that reaches higher concentrations in significantly less time than the parent graphite. An optimised pretreatment time of ~26 hours is inferred from the data and a peak rate of exfoliation of 1 mg ml\(^{-1}\) min\(^{-1/2}\) is demonstrated for a pretreatment time of 16 hours without introduction of defects or reduction in the extent of exfoliation. While the technique is most effective in NMP, a known stabilising solvent for graphene, significant improvements over the parent graphite are seen for pretreatments in water despite the instability of graphene in water.

A potential refinement to this technique is presented in order to remove unexfoliated material in addition to residual solvent associated with the pretreatment itself. Through simply heating the pretreated material in water, residual NMP can be almost completely removed, albeit replaced with significantly lower amounts of residual water. This process is shown not to introduce any additional defects into the graphene basal plane, in fact the final material actually shows an improvement in quality when using chemical analyses.

A new method of exfoliating two dimensional materials; shear exfoliation using high shear mixers, was developed during the course of this work and understanding the process was of great interest. Exfoliation of graphite to form graphene was
demonstrated in a far more controlled shear environment using a rheometer and it was demonstrated that turbulence was unnecessary for exfoliation to occur. High concentration dispersions of up to ~39 mg ml⁻¹ were studied using the rheometer and the properties of these dispersions were used to gain an understanding of the flake interactions in solvent stabilised dispersions. This allowed an inter-flake bonding energy of ~20 k_BT to be inferred which would indicate the graphene flakes are joined with “point-like” bonds, likely the flake corners, with a limited spatial extent.

A simple model for the shear exfoliation mechanism was suggested when the method was developed. This mechanism was tested extensively in the hopes of further optimisation of the shear exfoliation method. The minimum shear rate required for exfoliation is measured for 3 different materials, graphite and two transition metal dichalcogenides; MoS_2 and WS_2. The behaviour of this minimum shear rate was investigated for graphene as a function of solvent surface energy and was curiously found not to vary. This can be explained as the flake size was seen to vary significantly between solvents. Varying the shear rate was also shown to be a method for controlling the flake size. However, this was found to be coupled with the flake thickness, meaning large flakes produced in this manner were also significantly thicker. The shear exfoliation model was seen to hold up, allowing potential routes to optimising the method toward different applications.


“I will work harder!”

(Boxer the Horse)

“I know that I know nothing”

(Derived from Plato’s account of Socrates)

ACKNOWLEDGEMENTS

It seems more than a little ironic to admit a few short pages after declaring this thesis my own work to admit that none of this would have been remotely possible were I truly working alone. First and foremost I must thank Professor Jonathan Coleman for allowing me to undertake this PhD in the first place. Through his expertise and guidance, frustrating results and failures were quickly cleaned up or brushed off in preparation for the next round. Professor Matthias Mobius has also been inconceivably patient with a student with no undergraduate experience in fluid dynamics.

Being perpetually surrounded by experienced researchers has been invaluable. Thanks to Umar, Claudia, Niall, Keith and Mustafa for their patience explaining and demonstrating both theory and procedures. I would also like to thank Dr. Marguerite Hughes who helped me to realise that doing a PhD was something I wanted to do while I was interning in the group as an undergrad. The senior postgraduates, Pete, Paul, Graham, Tom, Ronan Sophie, Arlene and Evie who have since finished, were given a thankless task of answering my many questions while they no doubt had something better to do and for that I thank them.

The social aspect inherent in the group has been a great source of stress relief and completing my PhD has been a pleasure because of it, anyone who has been to Trinity college can attest to the irresistible allure of sunny days outside the Pav. Westland row will remain a fond memory thanks to the great friends I have made. Conor and Damo, like a shoal of fish, by submitting together perhaps one of us will make it. Peter (L),
you’re up next, no pressure! Adam, Andrew, Dave, Auren and Ivan it’s closer than you think, best to start worrying early. Everyone in the (extended) group has made the years fly by and I’d like to thank (and blame) them for this. The top floor office may be far too warm with suspicious mushrooms in the plasterwork but it has been a home away from home for four years and has kept both my morale and my fitness up.

Last but certainly not least, I must thank Olivia and my Family who have always been supportive of me and my education. I wouldn’t be where I am today without my parents supporting me all the way and through college and I wouldn’t have made it this far without Olivia supporting and encouraging me over the years. Having so many sympathetic ears to vent to is a luxury not afforded to many and I am hugely thankful and forever indebted for it.
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Motivation and Thesis Outline

1.1 Motivation

It has always been the case that new materials with exploitable properties lead to great advances for mankind. It is clear to see how quickly a novel material can completely change our society when one considers a few notable examples; aluminium, plastics and of course silicon. Our ability to process silicon in such a precise manner, in a very interesting way, led to a “race to the bottom” of sorts. Feynman’s “There’s plenty of room at the bottom” was far more prophetic than perhaps even he realised and, with advancements across the field of science in sample processing and characterisation, science at the nanometre scale began to attract huge amounts of research and industrial interest.

Carbon nanomaterials could be said to have been discovered as long ago as 1976 when the first carbon nanotubes were described,[3] although a more widely acknowledged work was put forward by Iijima in 1991[4]. The carbon nanomaterial family further filled out with fullerenes, first prepared by Kroto et al. in 1985[5] and graphene, first isolated by Geim and Novoselov in 2004[6]. A common feature among these materials however, was the need to “exfoliate” them in order to fully harness their properties and further complicating the matter is the need to stabilise the materials once this exfoliation has been achieved. Efficient and scalable methods to de-bundle nanotubes and de-laminate graphite are still important areas of study today as well as stabilising the materials in their exfoliated state in order to allow these wonder materials to be utilised.

This comes with an important caveat however in that, in addition to a materials beneficial properties, a material must be easy to process and economical if it is to be widely utilised. Rather than a dull exercise in bookkeeping, this is a scientific
challenge to understand and model a very complicated process to such an extent that it convinces a sceptic to invest. By gaining a comprehensive understanding of the parameters involved in graphene production we gain a more robust understanding of the process with regards to applying theory to describe it, and furthermore we can highlight potential routes for material commercialisation.

In this thesis I aim to further our understanding of liquid phase exfoliation of layered materials, in particular graphite, through attempting to optimise exfoliation. I aim to probe the fluid dynamics of these materials in dispersion, testing a new exfoliation method, and, finally, rigorously testing the model used to understand the mechanism behind this new method. Furthermore, the processing techniques discussed in this thesis have been widely applied to a broad range of 2D layered nanomaterials widening the scope and applicability of the research. Through attempting to model these dispersions and comparing them to established theories it is hoped that a clearer picture of these materials will be revealed and allow potential pitfalls for other, similar, materials to be avoided, making this work important from a scientifically but also from an industrial viewpoint.

1.2 Thesis Outline

Chapter 2 - Introduction and Background

Here a brief overview of the chief materials used is given. The history and properties of these materials are discussed as well as the resultant applications owing to these properties. The process of liquid phase exfoliation is introduced and its progression over the years is summarised finishing with challenges which still remain in the process.

Chapter 3 - Theory

How solubility theory can be applied to the exfoliation of two-dimensional nanomaterials is introduced. Solution thermodynamics are discussed as well as solubility
parameters. It is briefly discussed how Hildebrand parameters can be used to understand the exfoliation process. The main concepts of rheology are introduced and how this is applied to oscillatory rheology is explained. How the rheology changes on introduction of nanoparticles into suspensions is briefly discussed.

Chapter 4 - Characterisation and Methods

The sample preparation methods and methods of characterisation of samples used in this thesis are discussed. The characterisation methods are each given an introduction, outlining their respective measurement parameters, and, in addition, some history of these methods is provided.

Chapter 5 - Graphite Pretreatment Technique to Allow Rapid Dispersion of Graphite

A method of treating graphite powder to allow it to be re-dispersed at higher concentration with less energy required for the final exfoliation step. This method is tested for various pre-treatment times and for two different solvents; one (NMP) known to be stabilising for graphene the other (water) known to be destabilising. The effects on the starting graphite are studied using SEM. These pretreated powders are then re-dispersed in fresh NMP and the resulting dispersions are characterised using UV-Vis spectroscopy and TEM. A metric to describe exfoliation efficiency is introduced to compare pretreatment times and solvents. A pathway to further refine this method is outlined and the material produced is tested using solution thermodynamics in order to compare it to previous work.

Chapter 6 - Rheological Behaviour of Liquid Phase Exfoliated Graphene Dispersions

The behaviour of graphite/NMP mixtures and graphene/NMP dispersions under shear is presented and exfoliation under non-turbulent shear conditions is demonstrated using a rheometer. Dispersions of pristine graphene at extremely high concentrations are prepared in NMP using a version of the pretreatment method outlined in chapter 5. The viscoelastic properties of these dispersions are studied for various
concentrations. A model is proposed to describe the system and a typical bond energy between the graphene platelets is inferred.

Chapter 7 - Testing Our Understanding of the Shear Exfoliation Mechanism

Graphite, MoS2 and WS2 are pre-treated using a version of the method outlined in chapter 5. These three materials are sheared at a variety of shear rates in order to discern any variation in the minimum shear rate required for exfoliation. The theory and model put forward to describe the process of shear exfoliation is tested for graphene through variation of solvent surface energy. The theory is then tested for all three materials by measuring the platelet lateral size and thickness as the shear rate is varied. The variation in mean flake thickness as a function of shear rate allows the minimum shear to be defined in a more concrete manner. This allows the theory and model put forward to describe shear exfoliation to be tested through variation of material surface energy, solvent surface energy, solvent viscosity and finally applied shear rate.

Chapter 8 - Conclusions and Future Work

The main results and conclusions of this thesis are highlighted and discussed with regards outstanding questions concerning this work in addition to further investigation avenues highlighted by these results.
2.1 INTRODUCTION

This chapter will introduce the materials used throughout this thesis. This includes a discussion on the physical structure of the materials as well as outlining the physical and electrical properties of each material. Various methods of producing these materials will be briefly discussed and the pros and cons of each production method will be touched upon. The potential applications of each of these materials is discussed. The first section will discuss graphene, the core material used in this work. After that transition metal dichalcogenides are then introduced as an extension of the methods used to all 2D materials. Finally, liquid phase exfoliation, the production method used in this thesis, will be discussed in more depth while outlining the challenges facing this production method with regards to sample production and storage and scaling up the method to industrial scales.

2.2 GRAPHENE

Broadly speaking, graphene is the name given to a two-dimensional (2D) sheet of graphite. More specifically, graphene is a mono-atomically thick sheet of sp² hybridised carbon atoms, arranged in a honeycomb lattice. It is considered to be a parent building block for all graphitic carbon forms; it can be rolled to form carbon nanotubes, sections of it can be formed into “buckyball” like structures (e.g. C₆₀) and layers of it stack to form graphite (see Figure 2.1). Although strictly speaking graphene refers to a single atom thick layer, the use of the term graphene has been stretched to include sheets of up to a few atoms thick with the term “few layer graphene”. Graphene was first
isolated and identified in 2004 by Geim et al in Manchester university. By peeling apart the layers of highly oriented pyrolytic graphite (HOPG) crystals using adhesive tape they obtained small amounts of graphene[6]. This discovery and the characterisation of the produced graphene sheets earned the Nobel prize for Geim and Novosolov in 2010.

The experimental method is perhaps almost misleading in its simplicity in that, before its isolation, graphene was thought to be thermodynamically unstable as a strictly 2D material.[7] The exfoliation of graphite was well known however with the earliest demonstration of the exfoliation of graphite dating back to 1840[8–10]. In the lead up to graphene’s isolation much work was being done with the aim of producing thinner and thinner graphite platelets. Experiments were performed to tear and fold carbon nanotubes[11] and HOPG[12, 13] using the tip of an atomic force microscopy probe with the aim of controlled manipulation of the material at the molecular scale. While, before its isolation, graphene was of interest as a theoretical material and a model system worthy of study, once it had been demonstrably produced there was an explosion of interest worldwide that is still going on today.

2.2.1 Properties

The reason that graphite crystals can be exfoliated into individual sheets is down to the atomic bonding within the crystal. This consists of sp2 hybridised carbon atoms, a hybrid orbital of the 2s and 2p_x and 2p_y orbitals. As a result, graphite is covalently bonded in plane with a bond angle of 120 degrees. These sheets are stacked in an AB configuration otherwise known as Bernal stacking seen in Figure 2.1. Each sheet is only bound via van der Waals interactions of the 2p_z orbitals to its neighbouring sheets with these forces being relatively much easier to overcome. This allows sheets of graphene to be exfoliated while maintaining much of the sheet’s lateral size.
Graphene earns its interest with a long list of physical properties surpassing those obtained for any other material and far superior to its unexfoliated parent crystal. A monolayer of graphene will absorb a significant portion of incident white light, 2.3%[14] despite only being one atom thick. It is also the strongest material measured thus far with a Young’s modulus and intrinsic strength of 1 TPa and 130 GPa respectively[15]. In addition to all of this, a monolayer of graphene is also completely impermeable to gases[16]. All of this combines to make graphene an attractive material for reinforcement[17, 18] and coating purposes[19].

Initially, interest in graphene surrounded the extreme electrical properties it possesses due to its unique band structure. Once it was isolated it was discovered it exhibited a number of novel properties including room temperature quantum Hall Effect[20, 21]. With an electron mobility[22] of $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (with previous work[23] showing the deposition method, substrate and ripples on the flake being a limiting factor), capable of sustaining extremely high current densities $10^6$ times that of copper[24] and a thermal conductivity[25] above 3000 W m K$^{-1}$ it is easy to see why graphene is considered such an exciting material. Combined with its robust physical properties,
its highly favourable electrical properties make graphene a very attractive option as a transparent conductive coating in electronics, particularly for flexible electronic devices.\cite{26}

2.2.2 Fabrication Methods

It has been suggested that graphene fabrication might ideally be performed in tiers.\cite{27} This simply separates the graphene production methods by application, with high quality, costly graphene reserved for electronic applications requiring high conductivity and transparency. On the other side of the spectrum; lower cost, bulk production methods would be used in applications such as composites, coatings and inks where the highest conductivities and Young’s modulus are not necessarily required. Below, four production methods are outlined and suggested applications of each production method are given.

2.2.2.1 Mechanical Exfoliation

The first reported method to produce graphene was the mechanical exfoliation of HOPG crystals reported by Geim et al.\cite{6} The starting HOPG was etched using oxygen plasma and peeled from the parent crystal to form platelets of lateral sizes from 20 μm to 2 mm. These individual platelets could then be peeled apart repeatedly using scotch tape in a process dubbed micro-mechanical cleavage. The resulting flakes could then be released using acetone and captured on a silicon substrate to be studied. The thinnest flakes were then found using a combination of optical microscopy, atomic force microscopy and electron-beam microscopy.

The flakes produced using this method have been shown to be of superb quality surpassing that of other methods with lateral sizes of up to 100 μm.\cite{28} The lack of defects and functionalities makes graphene produced by this method ideal for testing the fundamental properties of graphene. Of course as one might expect it is a low-yield process with very few graphene flakes produced as well as being highly laborious.
Being highly technical and low throughput means this method is more suited to laboratory testing and is unsuitable for large scale production.

2.2.2.2 Epitaxial Growth and Chemical Vapour Deposition

Producing silicon-based electronics with a “bottom-up” approach is common practice and similar modes of thought have been applied to graphene production. One such method is the annealing of silicon carbide (SiC) surfaces. If SiC is annealed at high temperatures under vacuum it has been shown to form a graphitic surface by sublimating Si atoms. This method has been refined to carefully control the number of graphene layers grown, can be patterned using lithography methods and has been shown to be capable of producing graphene platelets hundreds of micrometers in size.

The graphene produced by this method is of high quality and SiC itself is well suited to high-frequency semiconductor devices allowing high-frequency graphene based transistors to be grown using this method. This process requires annealing at temperatures above 1000 ºC under vacuum, a costly process that is not compatible with many electronics production technologies, somewhat limiting its development. However, SiC devices are being developed for consumer application due to their capability at high voltage and temperature allowing circuit simplification.

Another “bottom-up” approach that has shown much promise is chemical vapour deposition (CVD). In this method a carbon containing gas (normally methane) is decomposed at high temperatures in the presence of a process gas (normally hydrogen) to grow a layer of graphene on a substrate (typically copper). This method was shown to be able to reliably produce monolayer graphene up to a centimetre in size in 2009 although the earliest reference to monolayer growth can be traced to 1979. While this process is also operated at high temperatures ~1000 ºC through careful choice of precursor gas and substrate this can be lowered to ~750 ºC. This method has been shown to be very effective and significant strides towards scaling it to production levels have been made with large area graphene layers already having been produced in a roll-to-roll process using copper foils and wafer-scale single crystal monolayers being grown on a germanium substrate.
Similar to SiC grown graphene, problems of cost face CVD graphene. As a high
temperature process it is simply very energy hungry, limiting its use to high quality ap-
plications in electronics. Furthermore, there are problems in transferring the graphene
from the growth substrate as copper is often incompatible with device fabrication pro-
cedures. There are also problems terminating the graphene deposition once a complete
monolayer has been formed on the substrate as thickness has been seen to increase
with growth time.\cite{39} The transfer process can lead to damage to the sheet reducing
its usefulness and there are further problems with adhering the sheet to the target
substrate sufficiently with solution processing techniques adding a further dimension
of trapped solvent. One solution is to directly pattern the graphene into devices and
etching away the underlying copper substrate,\cite{40} a highly technical process, further
reinforcing CVD as a production method only suited to high quality applications.

2.2.2.3 Chemical Modification

Another method of exfoliation is that of chemically altering graphite or its analogues
and thus facilitating exfoliation, after which the exfoliated layers can be subsequently
stabilised for example in liquid media. This can be achieved via the application of
intercalating compounds, through rapid heating or application of harsh reagents which
break apart the in plane bonding of the starting material.

One such method is through conversion of graphite to form graphite oxide (GO).
Known as a modified Hummers’ Method,\cite{41, 42} this consists of treating graphite
flakes with harsh oxidising agents to introduce hydroxyl groups and other function-
alities (see Figure 2.2) into the graphene flakes.\cite{43} This has the effect of converting
graphite, a hydrophobic material, into graphite-oxide which is hydrophilic, facilitating
its dispersion in polar solvents such as water. It also has the effect of increasing the
inter-planar spacing of graphite which also aids attempts to exfoliate the layers by
reducing the energy required to separate them.\cite{44} The GO can then be exfoliated
easily through sonication in water and the unexfoliated material removed through
centrifugation or settling. Monolayers were produced in this manner in 2006\cite{45} and
dispersions of graphene oxide are reported to be stable at concentrations of up to 4 mg
mL$^{-1}$ with flakes having lateral dimensions of up to of 7 $\mu$m.\cite{46} High concentration
dispersions of up to 13.35 mg mL$^{-1}$ have been reported and have been seen to behave as liquid-crystalline viscoelastic gels.[47]

With this method however the defect free lattice of the graphene layers is disrupted by the oxidising process to such an extent that GO is non conducting. In essence the monolayer flakes produced can no longer be called graphene. While graphene oxide produced in this manner can be partially reduced using either using reductants such as hydrazine to form graphene once more, many defects still remain[43, 45, 48] which have large detrimental effects on the properties of the graphene sheets.[49] Thermal methods of further reducing graphene oxide show promise but significant oxygen quantities still remain.[50] The presence of large quantities of defects and the small size of the flakes produced limits reduced graphene oxide to applications where the highest achievable strength and conductivity are not needed for it to be advantageous. For example spray coatings and conductive inks[51, 52] or applications where the increased surface area of the small flakes is beneficial, such as gas sensors[53] or electrochemical capacitors[54].

![Figure 2.2: Structural model for graphene oxide modified from[43]](image)

Another route which accomplishes the task of exfoliation and reduction of graphene oxide simultaneously is that of thermal reduction. By heating the GO rapidly (heating rates of $>2000$ °C min$^{-1}$) thermal decomposition of the GO causes it to split with enough force to exfoliate the GO into graphene sheets[55, 56]. This process removes the oxygen from the platelets releasing it as CO, CO$_2$ and H$_2$O.[55] These gases being released creates extremely high pressures (as high as 100 MPa) forming a reduced, exfoliated
product, i.e. graphene sheets. A benefit of this method over chemical reduction is that
it avoids the introduction of hetero-atomic impurities into the graphene lattice.

Despite this many defects are still introduced into the basal plane as vacancies as
carbon is released with the oxygen containing functionalities.[57] Furthermore not all
the oxygen is removed with a significant amount remaining in the material.[56] Both
thermally reduced graphene oxide and mechanically exfoliated reduced graphene
oxide have similar drawbacks with the relatively small flake size and presence of large
quantities of defects. While the removal of hydrazine from the process is beneficial, the
process still requires rapid heating to temperatures ~ 1000 °C[56] making this process
arguably more expensive while having similar prospects for its applications.

Finally, there are methods of producing graphene in a highly controlled manner
through chemical means. This method of producing graphene flakes with a narrow size
distribution is the “unzipping” of carbon nanotubes to form graphene nanoribbons.
This unzipping can be achieved by cutting the nanotubes by etching them using an
argon plasma[58], by oxidisation of the nanotubes, akin to the Hummers method
for graphene[59, 60] shown in Figure 2.3, or another method using metallic nano-
clusters to split open the nanotubes by catalysing hydrogenation along the length of
the nanotube.[61]
These methods have the benefit of producing graphene with a very narrow size distribution, allowing the material to be tailored to the application, however using carbon nanotubes as a starting material makes the process extremely expensive. Alternative methods exist for growing graphene nanoribbons through surface coupling of molecular precursors to form a linear polymer before subsequent cyclodehydrogenation to form the graphene nanoribbon.\cite{62} The growth of graphene from precursor monomers is a fascinating area however it will have to compete with CVD methods of nanoribbon growth in terms of both cost and reliability.

2.2.2.4 **Liquid Phase Exfoliation**

The method of liquid phase exfoliation is central to this thesis and a more in depth look at the method can be found in Chapter 4.2.1 with the theory surrounding liquid stabilisation being covered in more detail in Chapter 3.2. Liquid phase exfoliation
is a method in which the exfoliation of graphite and the subsequent stabilisation of graphene is performed in liquid media. The exfoliation of graphite is facilitated by large shear forces in the liquid either through sonication, high-shear mixing or alternative processes such as wet ball milling. While these processes can be applied to exfoliate GO as mentioned in the previous section, for clarity the process of liquid phase exfoliation will be used to refer to exfoliation of “pristine” graphene and not GO.

Liquid exfoliation is not a newly discovered method and can be traced as far back as 1859, when Brodie reported a process akin to wet ball milling of graphite flakes. While the process has changed somewhat, the principles remain the same; apply shear forces to the graphite layers in order to delaminate them from the parent crystal and subsequently stabilise the exfoliated sheets (see Figure 2.4). In 2004, Bunch et al reported a procedure for making graphite quantum dots using sonication in solvent (di-chlorobenzene) and demonstrated graphite particles of the order of 500 nm, although no monolayer graphene was reported. Both these methods might have succeeded in creating monolayer graphene, albeit in incredibly small amounts, however with no stabilisation the flakes would have quickly re-aggregated.

In 2008 Hernandez et al reported a method of producing monolayer graphene using sonication in organic solvents such as N-methyl-pyrrolidone (NMP). This followed on from work seeking to stabilise exfoliated, or de-bundled, carbon nanotubes in solvents by matching the surface energy of the solvent to that of the nanotubes.
By minimising the energetic cost of creating the extra solvent-material interface, the energetic barrier to exfoliation was lowered and simultaneously the energetic drive to re-aggregate was minimised. The theory surrounding the energetics will be covered in more detail in Chapter 3.2 on page 24. Since its initial discovery the method has been expanded to include a large range of solvents, surfactants and polymers as stabilising agents. This is highly welcome as the solvents first used during exfoliation, such as n-methylpyrrolidone, are highly toxic.

While this method can produce large quantities of graphene, with batch sizes of 1 litre having been produced in a sonic bath, scalability of sonication remained an issue. This issue was addressed by Paton et al. in 2014 by replacing sonication with exfoliation using a high shear mixer. High-shear mixing was demonstrated to be able to produce monolayer graphene with the same quality as had been produced using sonication making it an ideal method to scale up the production of liquid exfoliated graphene. This method is a much lower energy process and led to alternative exfoliation methods being sought with exfoliation later being demonstrated in a kitchen blender.

Figure 2.5: Simplified schematic of proposed exfoliation route of platelets under shear with exfoliation progressing from left to right, the energetics of each stage are displayed underneath, $E_{LL}$ is the liquid-liquid interaction energy, $E_{PP}$ platelet-platelet and $E_{LP}$ the liquid-platelet interaction energy, modified from [81].

Shear exfoliation demonstrated some interesting behaviours such as a minimum shear rate required before a well exfoliated dispersion was observed. Because of this a mechanism was proposed in order to understand the shear exfoliation of layered materials. This mechanism, shown schematically in Figure 2.5, involved the platelets delaminating laterally with the related energetic cost of breaking the inter-platelet
interactions being balanced by the introduction of solvent-platelet interactions. Paton et al. showed that the energetics of this proposed mechanism could be expressed as

\[ \dot{\gamma}_{\text{min}} = \frac{\left( \sqrt{E_{S,G}} - \sqrt{E_{S,L}} \right)^2}{\eta L} \]  

(2.1)

Where \( \dot{\gamma}_{\text{min}} \) is the minimum shear for exfoliation, \( E_{S,G} \) and \( E_{S,L} \) are the graphene and solvent surface energies respectively, \( \eta \) is the solvent viscosity and \( L \) is the flake length. The understanding of this mechanism will be the focus of Chapter 7 on page 113.

Some issues still remain with the graphene flakes produced using liquid phase exfoliation. The flakes produced, either using sonication or high-shear mixing, are typically between 0.5 \( \mu \text{m} \) - 1 \( \mu \text{m} \) with samples being very poly-disperse. While this can be remedied somewhat by application of controlled centrifugation[83] flake sizes remain smaller than those obtained from oxidative methods. Low concentrations are also an issue although much work has been done to address this. From the first dispersions of 0.01 mg mL\(^{-1}\), the concentrations have been improved significantly[70, 72] with the highest concentration samples having reached 63 mg mL\(^{-1}\) with 26 - 28 mg mL\(^{-1}\) dispersions remaining stable[84].

Graphene produced in this manner is unsuitable for high quality electronic purposes due to its small flake size reducing the electrical conductivity of large films due to the large number of inter-flake junctions.[85] Graphene produced in this manner is ideal for spray coating however, for example conductive inks[86, 87]. Dispersed flakes can be mixed with polymers for reinforcement[18, 88] and addition of graphene in this manner can also be utilized to produce conductive composites and is a economical way of producing high quality strain sensors[89]. The high surface area of graphene produced in the manner makes it ideal for sensors[90], making use of the size limitations of the process. While reduced graphene oxide is a similar process that can be performed in water producing larger flakes, the lower strength and conductivity of the resulting material makes LPE graphene an attractive alternative in addition to the fact that the harsh treatments of oxidation/reduction can be avoided.
2.3 GROUP VI TRANSITION METAL DICHALCOGENIDES

Transition metal dichalcogenides (TMD’s) is the name given to a family of compounds of the general form MX$_2$, where M represents a transition metal and X represents a chalcogen atom. This can be shown schematically in Figure 2.6. There are approximately 60 TMD’s to choose from,[91] each with their own sets of properties spanning the full range from insulators such as HfS$_2$, semiconductors such as MoS$_2$ and WS$_2$ and true metals such as NbSe$_2$ and TaS$_2$.[92]

However in this work only two such materials are employed, molybdenum disulphide (MoS$_2$) and tungsten disulphide (WS$_2$) and so the focus will be on these materials. TMD’s adopt a planar structure that, when viewed from the side, sandwiches the metallic atom between two chalcogen atoms with each layer being 3 atoms thick unlike the mono-atomic layers of graphene. When viewed from above these layers can be viewed as 3 hexagonal lattices, the top and bottom of which are chalcogens, with individual layers stacked in either an A-B-A configuration, corresponding to trigonal prismatic, or an A-B-C configuration, corresponding to octahedral. The A-B-A configuration can be seen schematically in Figure 2.6.
Properties

TMD’s have a wide range of electronic properties depending on the combination of metal and chalcogen, see Table (cross ref). While there are many TMD’s this discussion will focus on the materials used in this work; MoS$_2$ and WS$_2$ which are so called group VI TMD’s. As seen in Figure 2.6 these materials are planar in structure and, similar to graphene, these layers are bound strongly in plane with the layers only bound to each other by van der Waals interactions, allowing the bulk crystals to be exfoliated into monolayer or few layer platelets.
Exfoliation of these materials is beneficial for a few reasons. The simplest being the increased surface area of exfoliated flakes being beneficial for catalysis of the hydrogen evolution reaction.[93, 94] An interesting property of monolayer group VI TMD’s is that they shows significant photoluminescence (PL) seen for both MoS$_2$[95] and WS$_2$[96, 97] once obtained in monolayer form. This compares to very weak emission observed in the bulk form.[92]

This is a consequence of a larger effect of exfoliation effecting the band structure of the material. In the case of group VI TMD’s, this changes the material from an indirect band gap semiconductor into a direct band gap semiconductor.[98] This is a result of quantum confinement effects due to restricting the wave function to two dimensions.[99] Exfoliation of these materials also has the effect of increasing the band gap from $\sim$1.2 eV to $\sim$1.9 eV for MoS$_2$ and from $\sim$1.3 eV to $\sim$2.1 eV for WS$_2$.[99] The effects on the band structures can be calculated from first principles using density functional theory (DFT) and these are shown in Figure 2.7 for bulk and monolayer MoS$_2$ and WS$_2$.

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![Table 2.1: Electronic character of various layered TMD’s adapted from[92]](chart.png)
2.3.2 Fabrication Methods

As a layered crystal, many of the methods of exfoliation are functionally very similar to those of graphene. However there are some notable differences in the chemistry and crystal structure of layered TMD’s when compared to graphene that would lead to some unexpected difficulties were the same exfoliation methods applied. In this section a brief outline of production methods of MoS$_2$ and WS$_2$ is given alongside the drawbacks of the method and potential applications of material produced in these manners.

2.3.2.1 Chemical Vapour Deposition

Bottom up methods for producing monolayer flakes can be found for both MoS$_2$ and WS$_2$. A method demonstrated for both is the chemical vapour deposition reaction of...
the metal tri-oxide with sulphur. This has been shown for WS$_2$\cite{100} and MoS$_2$\cite{101} with wafer scale uniformity. Both materials utilise a similar method, albeit on different substrates with MoS$_2$ being grown on sapphire and WS$_2$ on SiO$_2$. In both cases a layer of MoO$_3$ of desired thickness is deposited on the substrate (MoO$_3$ using thermal deposition methods and WO$_3$ using atomic layer deposition) and subsequently sulphurised by flowing sulphur gas over the oxide layer at high temperatures. A similar process has been demonstrated for both where the metal it is sulphurised during the process of sublimation and deposition although this results in much smaller flake production.\cite{102,103} This is likely a result of a lessened control of the rate of sulphur addition as this has been demonstrated to improve the size of crystalline domains for WS$_2$.\cite{104}

These processes all have similar downsides as CVD methods with graphene, high temperatures, difficulties in transferring layers while avoiding damage to the material and scalability issues as the process is limited by the substrate. An alternative for MoS$_2$ has been demonstrated with a method of dip coating a surface in a precursor, ammonium thiomolybdate. This thin layer can then be thermally decomposed in the presence of sulphur to produce large area MoS$_2$.\cite{105} This method is potentially much more scalable, however control of the number of MoS$_2$ layers is more difficult, with only tri-layer demonstrated. Furthermore high temperatures are still required, meaning film transfer is still required for many applications. As with graphene, CVD processes are best suited for high quality electronic applications.

2.3.2.2 Exfoliation of Bulk Crystal

As with graphene, exfoliation of crystalline TMD’s is a process that has been known for some time. In fact, a method akin to the micro-mechanical cleavage method utilized by Geim, Novosolov et al. was demonstrated to produce layers of MoS$_2$ as thin as 3 nm in the 1960’s.\cite{91} Monolayer production was demonstrated by Novosolov et al. in 2005 by applying the same methodology used to produce monolayer graphene to MoS$_2$.\cite{106} As with graphene however this process is hardly a scaleable one and is limited to production of samples for property testing or lab-prototype testing.
Intercalation, that is to say methods of introducing chemical species that diffuse between the layers of the crystal, expanding the interlayer spacing and thus lowering the interlayer binding energy, was also employed in order to exfoliate TMD’s. One common and very successful method is lithium intercalation through immersion in concentrated n-butyl lithium, or BuLi, in hexane for extended periods. This must be done under dry conditions in an inert atmosphere, as BuLi is highly reactive with water. After the lithium has diffused between the layers the resultant intercalated material can be fully exfoliated through simply exposing it to water, ethanol, methanol or isopropanol and rapidly heating the material is enough to exfoliate it. By exposing the lithiated MoS$_2$ to water, hydrogen is rapidly released and builds up adequate pressure to force the flakes apart.

BuLi, being highly reactive and requiring an inert atmosphere for the intercalation step is far from ideal, requiring immersion in BuLi for at least 48 hours. By pre-exfoliating MoS$_2$ in hydrazine followed by intercalation using sodium naphthalenide and dipping in water while applying sonication it can be achieved without BuLi and the flakes obtained have a width of up to 4 μm ~ 4x larger. However, this method not only requires 48 hours for the intercalation to proceed but also requires heating (130 °C) during the “pre-expansion” step. Furthermore both methods must be performed under an inert atmosphere and it has been found that lithium intercalation alters the phase of the MoS$_2$ from 1T to 2H. This changes the material from semiconducting to metallic due to the formation of a complex, Li$_x$ MoS$_2$ and consequently it ceases to exhibit photoluminescence. While the semiconducting phase can be recovered through mild annealing some lithium will likely always remain. This is not necessarily a negative result as the negative charges introduced into the flakes can be exploited to functionalise the MoS$_2$ basal plane and the metallic phase of MoS$_2$ is known to be more catalytically active for the hydrogen evolution reaction. The use of harsh chemical agents and moderate heating drives up the price of these methods although a natural application is as an anode material for lithium ion batteries for which high end electronics applications are abundant.

Another method, that is also the exfoliation procedure employed in this work, is liquid phase exfoliation. Functionally this method is identical to that described for
graphene. Through applying sonic energy to the bulk material in a solvent the layered crystals can be exfoliated and by using appropriate solvents the dispersed flakes are stabilised against reaggregation.\[112\] This has been demonstrated using surfactants\[74\] and using shear exfoliation in place of sonication\[81, 113\]. This method can produce flakes of lateral size in the range 50-1000 nm for MoS\(_2\) and WS\(_2\)\[112\] for sonication and \(\sim 40 - 220\) nm with the possibility of size selection by controlling initial surfactant concentration for shear exfoliation\[113\].

This method is scalable and relatively low energy compared to the alternatives and has been demonstrated for a huge variety of TMD’s. The main drawback of this method is the size of the flakes produced, typically no larger than 1 \(\mu\)m. Although compared to lithium intercalated flakes there is a trade off between flake size and residual exfoliant as the liquid exfoliation route allows a more suitable solvent/surfactant to be chosen with regards to the application. The size of the flakes produced in this manner makes them ideal for printed applications however\[86, 114\] and liquid processing techniques allow the exfoliated material to be mixed with other materials to form composites\[115\]. The production of exclusively small flakes is in fact beneficial for catalysing hydrogen evolution as it has been shown that the flake edges are much more catalytically active and one suggested route is a hybrid thin film of MoS\(_2\) deposited on graphite.\[94\]
3

THEORY

3.1 INTRODUCTION

In this chapter the key theories utilised in this thesis will be discussed. Firstly an introduction to solubility theory will be given, initially discussing the thermodynamics of mixtures and surface energies, then discussing the more specific solvent solubility parameters. This is directly relevant to Chapter 5 in which a solvent survey, comparable to that performed by Hernandez et al.[71] is performed using pretreated material and again in Chapter 7 where it is applied to shear exfoliation in order to test our understanding of the process. Following this an introduction to the rheology of nanoparticle suspensions is given in order to better understand the processes involved in Chapter 6 in which the properties of graphene dispersions are probed using a rheometer.

3.2 SOLUBILITY THEORY

All nanomaterials utilized in this thesis are prepared using solvent-based liquid phase exfoliation techniques. This method, pioneered by Hernandez et al. in 2008,[66] is based on a theory used to understand exfoliation techniques used to de-bundle and stabilise debundled carbon nanotubes in solvents.[67, 68, 79] Liquid phase exfoliation of nanotubes has been well studied though, typically, these dispersions were stabilised against re-aggregation using surfactants or polymers. Without such stabilisation samples could be dispersed using sonication but would quickly sediment out as aggregated bundles. It was later found that certain solvents did not require stabilising agents in order to reliably produce exfoliated nanotubes and furthermore, simple
dilution was enough to de-bundle the nanotubes in these solvents.[67] Understanding the energetics of the interaction between the nanotubes and the dispersant, in this case specific amide solvents, was crucial in order to minimise the energetic cost of exfoliating the material. This theory was later directly applied to graphene and due to the similarity between the graphene surface and that of carbon nanotubes it was reasoned that the interaction between solvent and dispersed material might be similar.

3.2.1 Solution Thermodynamics

If we look at the exfoliation in solvent in its base state it can be viewed as simply a mixture of two species. The energetics of mixtures is well known in thermodynamics, with two substances mixing there is a change in entropy (\(S\)) and depending on the interactions between the two species there is a corresponding change in enthalpy (\(H\)) for the whole system; with the system encompassing both species before mixing and the total mixture after mixing has occurred. In general the solubility of two materials can be described by the Gibbs free energy of mixing (\(\Delta G_{\text{mix}}\)) which, if performed under isothermal conditions, is given by

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \tag{3.1}
\]

where \(\Delta H_{\text{mix}}\) and \(\Delta S_{\text{mix}}\) are, respectively, enthalpy and entropy changes due to the mixing. In terms of solubility, for these materials to be soluble the process needs to be energetically favourable i.e. \(\Delta G_{\text{mix}} \leq 0\).

Entropy can be understood as a measure of disorder and the mixing of two substances will always increase the disorder of each, therefore the second term in Equation 3.1 will always be negative. This might be seen to imply that most solvents would be suitable as long as \(\Delta H_{\text{mix}}\) is not too large a positive value however it is important to note that the nature of the particles being dispersed complicates matters. The dispersed flakes in this work are very large and rigid macro-molecules, much larger than the molecules involved in mixing two solvents for example. This means that while \(\Delta S_{\text{mix}}\) is positive,
it is not very large and so $\Delta H_{\text{mix}}$ is the dominating factor in determining $\Delta G_{\text{mix}}$.\[79\] This means that in order to produce a stable dispersion the enthalpy of mixing must be minimised. If it is large, there will be a significant energetic drive towards aggregation, crashing the dispersion.

The work by Hernandez et al. in 2008 derived an approximate expression for $\Delta H_{\text{mix}}$ in order to express it in terms of properties that were easily obtainable for solvents. This relates to the energetic “cost” of separating the graphite sheets to infinity, minus the energy to bring them back together in a solvent-graphite dispersion.\[66\] This showed that the energy cost of exfoliating 2D nanosheets could be expressed as

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} \approx \frac{2}{T_{\text{flake}}} (\delta_{\text{graphene}} - \delta_{\text{solvent}})^2 \phi$$ \hspace{1cm} (3.2)

where $V_{\text{mix}}$ is the total volume mixture, $T_{\text{flake}}$ is the thickness of the dispersed flakes, $\delta_{\text{graphene}}$ and $\delta_{\text{solvent}}$ are the the square root of the surface energies for graphene and solvent respectively and $\phi$ is the volume fraction of the flakes in the mixture. This energetic “cost” is associated with the fact that surface atoms, either in liquids or solids, exist in a different state to those in the bulk as they lack interactions with neighbouring atoms at the interface. Thus they exist in a higher energetic state. This naturally tends to minimise and this is known more intuitively with surface tension.

While the surface energies of solvents are not readily available they can be related to surface tension, $\gamma$, which is a well documented quantity for most available solvents. The two can be related via

$$\gamma = E_{\text{surface}}^{\text{solvent}} - T S_{\text{surface}}^{\text{solvent}}$$ \hspace{1cm} (3.3)

Where $E$ represents the surface energy, $T$ the temperature and $S$ represents the surface entropy. Surface entropy again is not a common property but it was shown to be $\approx 0.1$ mJ m$^{-1}$ K$^{-1}$ in amide solvents.\[79\] Thus, at room temperature ($\sim 20$ °C), to convert from surface tension to surface energy can be approximated by adding $\sim 29$ mJ m$^{-1}$ K$^{-1}$.

If this is combined it can be seen that in order to effectively exfoliate graphene in solvent the surface energy, or alternatively surface tension, difference between graphene
and solvent must be minimised. This minimises the bracketed term in Equation 3.2 which in turn minimises the enthalpy of mixing and minimises the Gibbs free energy of mixing in Equation 3.1. However, while the surface energy match is the most important term for minimising enthalpy, a few other important factors are contained in Equation 3.2. For example, the effect of flake thickness. Thicker flakes present a smaller enthalpy term, indicating that, in order to produce thinner flakes, one must combat the increase of enthalpy through careful selection of well-matched solvents in order for thinner flakes to be stable. Furthermore to obtain higher concentrations, and so volume fractions, the solvents should be well matched with it being more difficult to stabilise higher concentrations in poorly matched solvents.

3.2.2 Solvent Solubility Parameters

The matching of surface energies seen in the previous section is reminiscent of a very basic chemistry principle of “like dissolves like”. This very simple principle is taught as a way of understanding immiscible liquids with the prime example being oil and water. The rational being that polar water only mixes well with other polar solvents and non-polar oil can only be mixed with another non-polar solvent. Of course the reality is much more complex than polar or non-polar with solvents existing at varying degrees of “polarity”.

This gives rise to solvent solubility parameters, values assigned to solvents describing their character which are used to predict suitable solvent-solute combinations.[79, 116, 117] These parameters are determined from the solvents cohesive energy density which is the energy required to completely overcome the van der Waals bonding holding the liquid together. This is also known as the vaporisation energy and is formally the energy required to remove all the molecules in a unit volume to infinite separation.

The simplest solubility parameter comes directly from the cohesive energy density can be expressed as

$$\delta_{T,j} = \sqrt{\frac{E_{c,j}}{V}}$$  (3.4)
where $E_{c,i}$ is the cohesive energy density of species i in the mixture, $V$ is the molar volume and $\delta_{T,i}$ is known as the Hildebrand solubility parameter for species i. Using this parameter the following expression can be derived for the enthalpy of mixing per unit volume

$$\Delta H_{mix} \approx \phi (1 - \phi) (\delta_{T,a} - \delta_{T,b})^2$$

(3.5)

Where, again $\phi$ is the volume fraction of the solute and $\delta_{T,a}$ and $\delta_{T,b}$ represent the Hildebrand solubility parameters for the solute and solvent, respectively. This is known as the Hildebrand-Scratchard equation and is valid for small molecular species, an important assumption when considering the exfoliation of graphite platelets. This expression also does not consider negative values for the enthalpy of mixing due to the geometric mean approximations made in its derivation, meaning this approximation may break down where specific interactions between solvent and solute are notably stronger than the solvent-solvent or solute-solute interactions of the unmixed components.[68, 79]

An alternative formulation, used extensively in polymer science for solubility calculations is the Flory-Huggins equation[118] which gives the enthalpy of mixing per unit volume as

$$\Delta H_{mix} = \frac{\chi k T \phi (1 - \phi)}{v_0}$$

(3.6)

where $k$ is the Boltzmann constant, $T$ is the temperature, and $v_0$ is the solvent molecular volume. $\chi$ is known as the Flory-Huggins interaction parameter and is a dimensionless constant for each combination that describes the interaction energy between a solvent and solute. Recalling how the enthalpy of mixing affects the Gibbs free energy of mixing, $\chi$ determines whether or not mixing is energetically favourable between two species. If $\chi < 0$ mixing is energetically favourable and $\Delta G_{mix}$ will also be negative making the mixture a true solution. If $\chi > 0$ then the solute molecules will have a greater affinity for themselves and mixing is not energetically favourable.

Equations 3.5 and 3.6 can be combined to give $\chi$ in terms of the Hildebrand solubility parameters as follows[118]
\[ \chi \approx \frac{u_0}{kT} (\delta_{T,a} - \delta_{T,b})^2 \] (3.7)

This relation, as with Equation 3.5, does not allow for negative values of \( \chi \) and is an approximation. However it can be successfully applied to systems absent of polar interactions where London dispersive forces are dominant. As \( \chi \) cannot be negative, a successful solvent-solute combination can only aim to minimise \( \chi \) through matching the Hildebrand parameters.

As previously mentioned, the Flory-Huggins parameters are somewhat limited in that they provide no allowances for bonding forces outside of van der Waals. This was addressed by Charles Hansen who expanded the theory to deal with the various types of interactions that exist between solvent and solute.[117] He separated the terms into; dispersive (D), the strongest for organic molecules arising from atomic interactions, polar (P), polar forces on the molecules arising from permanent dipole-dipole interactions and hydrogen bonding (H), a more specific interaction arising from hydrogen bonding to a highly electronegative element. These three components were then used to form so called Hansen solubility parameters (HSP) from the cohesive energy density by first splitting it into D, P and H components as follows

\[ \frac{E_{c,T}}{V} = \frac{E_{c,D}}{V} + \frac{E_{c,P}}{V} + \frac{E_{c,H}}{V} \] (3.8)

Followed by obtaining the square root of each respective energy density component as in Equation 3.4 to yield the three HSPs. These three components can then be related to the Hildebrand solubility parameter seen below

\[ \delta^2_T = \delta^2_D + \delta^2_P + \delta^2_H \] (3.9)

By using these parameters in place of the Hildebrand parameters Equation 3.7 can be expressed instead in terms of the HSPs, expanding the expression considerably

\[ \chi \approx \frac{u_0}{kT} [ (\delta_{D,a} - \delta_{D,b})^2 + (\delta_{P,a} - \delta_{P,b})^2 + (\delta_{H,a} - \delta_{H,b})^2 ] \] (3.10)

where the subscripts a and b denote the solute and solvent parameter respectively. By expressing the Flory-Huggins parameter in the fashion the use of this expression to
describe the behaviour of a wide range of solvents can be justified. Whereas previously the expression did not consider polar interactions this expression has a wider scope. Furthermore, documented HSPs are available for a wide range of solvents which allows this methodology to be easily and thoroughly tested.

One assumption which has not so far been addressed is that Equation 3.5 is applicable to small molecular species, an assumption that is quite a stretch when applied to dispersed graphene sheets. This was addressed in 2012 by Hughes et al. wherein the dispersive, dipole-dipole and dipole-induced dipole interactions were explicitly calculated in a manner to apply to 1D rods and 2D platelets.\[119\] This work showed that the dispersive and polar HSPs could be applied to yield the enthalpy of mixing of species a and b, through the use of a pre-factor to account for the dimensionality, d, of the solute

$$\left( \frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} \right)_d = (1 - \frac{d}{3}) \phi (1 - \phi) [(\delta_{D,a} - \delta_{D,b})^2 + (\delta_{P,a} - \delta_{P,b})^2]$$ (3.11)

with d = 0 representing small molecules, d = 1 being rods and d = 2 representing platelets. It is worth noting that the dipole-induce dipole interactions are excluded from the above expression as they were largely determined to have a near negligible effect.\[119\] The maximum dispersed volume fraction described by Hughes et al. for nanotubes\[120\] could be expanded using this method to describe 2D platelets and was shown to be

$$\phi \propto \exp \left[ - \left( 1 - \frac{d}{3} \right) \frac{v_N}{RT} \left( [\delta_{D,a} - \delta_{D,b}]^2 + [\delta_{P,a} - \delta_{P,b}]^2 \right) \right]$$ (3.12)

where v_N is the molar volume of the dispersed phase, R is the gas constant and T is the temperature. While this expression does not deal with hydrogen bonding parameters it does show that the form of the Hansen solubility theory is conserved when applied to large 2D platelets and further shows the importance of matching parameters in order to successfully create a well exfoliated, stable dispersion.
Rheology is a field of study interested in the deformation behaviors of soft matter. The term “rheology” itself is Greek for the study of flow of matter and the field concerns itself primarily with the flow of fluids. This is not limited to simple liquids but is extended to viscoelastic fluids and soft solids and is even extended to stiff solid materials in some instances. The materials of rheological importance range from flame-throwers to plastic processing to non-drip paints and contact adhesives.[121] At its most basic, studying these materials comes down to applying a force to the material in a controlled manner and precisely measuring the resultant deformation.

There are a variety of manners in which to achieve this, for example viscometers, while not a rheometer, measure viscosity by applying a controlled force to a liquid and measuring the resultant flow. When considering rheometers there are two types, rotational and the less common extensional rheometers. However, for the purposes of this work a rotational rheometer was used and so that will be the focus of the theory outlined.

### 3.3.1 Basic Concepts

In order to study our system, we apply a shear force to the sample while measuring the displacement of that phase. As shown in Figure 3.1, the shear force applied moves the mobile phase through a displacement (D) and these values are then measured as well as the known parameters for the experiment; the area of the mobile phase (A) the mobile/stationary phase separation (H) and the time taken for the displacement to occur (t). By knowing these parameters some simple values can be calculated such as the shear stress, $\sigma = F/A$, and the shear strain, $\gamma = D/H$. Additionally the shear rate, formally the velocity gradient between the mobile phase and stationary phase, $\dot{\gamma} = \dot{D}/H$ (for a linear system) can be obtained. Note that this assumes laminar flow, i.e. fluid flowing in parallel layers with no disruption between the layers, and the absence of slippage between adjacent phases. This allows the viscosity of a fluid, $\eta$, to
be calculated as $\sigma = \eta \dot{\gamma}$, an expression which holds true for many materials, known as Newtonian fluids. This expression holds true as long as shear stress and shear rate remain linearly proportional or to put it another way, as long as the viscosity itself is not a function of the strain or the shear rate.

![Diagram](image)

Figure 3.1: Schematic showing applied shear force resulting in a deformation

The reality is more complicated than this for the experimental setup. A rotational rheometer typically involves two circular plates, a top plate which can be rotated through a very precise application of torque, and a fixed bottom plate. The strain is then obtained by measuring the angular deviation of the mobile phase. This means the shear strain is greatest at the edges of the plate where the plate moves through a greater arc. This can be dealt with by either taking a more general average strain across the disk or this can be compensated for somewhat by using a conical upper plate where the centre protrudes and so the separation height is smaller. The angle of the cone can be tailored so that the material is stressed uniformly at all points along the radius of the cone but this limits the cone-plate setup as it is tailored for one separation height setting. Cone-plate geometries are not ideal for particle suspensions as the gap setting is typically very small (~ 50 $\mu$m). This can lead to issues such as jamming and irreproducibility when the particle diameter is of the order of the gap.
3.3 Rheology of Nanoparticle Suspensions

length. The specifics of the rheometer used in this work and the method of converting torque/angular deviation to stress/strain will be discussed in Section 4.3.7 on page 63.

There are a number of deviations from this behaviour however, fluids can be shear thinning/thickening and some fluids, known as Bingham plastics, behave as a solid at low shear stresses but display Newtonian behaviour above a certain stress (known as a yield stress, $\sigma_y$), flowing as a viscous fluid. These are shown graphically in Figure 3.2.

A Bingham plastic is an example of a Herschel-Bulkley fluid, a generalised model for non-Newtonian fluids, in which the strain is related to the stress as follows

$$\sigma = \sigma_y + k\dot{\gamma}^n$$ (3.13)

which allows for shear dependant behaviour as well as reducing to Newtonian behaviour when the yield stress is zero and $n = 1$, leaving $k$ as the viscosity.

Figure 3.2: A generalised plot of shear stress vs shear rate showing different fluid behaviours, modified from [122]

Some further fluid behaviours which cannot be displayed in the previous figure are variation of viscosity with temperature (a phenomenon well known outside the field of rheology), variation of viscosity with pressure, thixotropic fluids; which become less viscous as they are strained or agitated or the inverse of that, rheopectic fluids; which become more viscous as they are strained or agitated. This is a time dependent behaviour and such fluids will recover their original characteristics if left standing.
Thixotropic behaviour is typically seen with clays which are known to form “networks” within the dispersion which is broken down progressively as the sample is sheared and reforms again if given adequate ageing time.[122–124]

3.3.2 Viscoelastic Fluids and Oscillatory Shear

With more complex materials exhibiting properties not typically associated with simple liquids we begin to approach viscoelastic fluids, fluids which exhibit both a viscous and an elastic component. While an ideal fluid exhibits a stress proportional to shear rate, \( \sigma = \eta \dot{\gamma} \), an ideal Hookean elastic solid exhibits a stress proportional to strain \( \sigma = k\gamma \), where \( k \) is the rigidity modulus. It is useful when discussing viscoelastic behaviour to utilise a simple model, combining these two elements. In Figure 3.3 a simple theoretic system, known as the Kelvin viscoelastic model, has been set up. In this simple model a combination of viscous and elastic must be considered giving

\[
\sigma = k\gamma + \eta \frac{\delta \gamma}{\delta t}
\]

(3.14)
a differential equation which yields some interesting results. If a stress is applied at it is easy to see that while the spring will reach the strain governed by Hooke’s law, the viscous component damps the spring meaning it takes some time, \( t \), depending on the viscosity, to do so.[121]

![Figure 3.3: The simple Kelvin model of viscoelasticity](image)

In order to study such materials and separate the two components, a new method is required, oscillatory shear. This method of measurement involves applying a small
amplitude sinusoidal oscillation (either strain or stress) to the material. The frequency of oscillation is typically given in radians per second as \( \omega = 2\pi \nu \) where \( \nu \) is the frequency of oscillation in Hertz. For a perfectly elastic solid, as an oscillatory stress is applied, the strain oscillates with the same frequency and remains perfectly in phase, however for a perfectly viscous fluid, the strain maintains the frequency but “lags behind” the applied stress, or alternatively the stress is in advance of the strain. For a viscoelastic fluid being tested, the time lag, \( \triangle t \), can be measured to obtain the phase angle shift \( \delta = \triangle t \omega \). This means we can express strain and stress as

\[
\gamma(t) = \gamma_0 \sin(\omega t) \tag{3.15}
\]

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{3.16}
\]

where \( \gamma_0 \) and \( \sigma_0 \) are the strain and stress amplitudes respectively.

For oscillatory shear of viscoelastic fluids, instead of viscosity, stress and strain are linked using a complex shear modulus \( G^* \) giving a generalised form

\[
\sigma(t) = G^*(\omega) \gamma(t) \tag{3.17}
\]

where \( G^* \), which may also be a function of the oscillation frequency, can be broken up into elastic and viscous components as follows:[121, 122] \( G^* = G' + iG'' \) with the components being known as the storage modulus (\( G' \)) and loss modulus (\( G'' \)) and \( i = \sqrt{-1} \). These components can be thought of as describing the extent of the “solid-like” behaviour for \( G' \) and “liquid-like” behaviour for \( G'' \) and are defined as follows:

\[
G' = \frac{\sigma_0}{\gamma_0} \cos \delta = |G^*| \cos \delta \tag{3.18}
\]

\[
G'' = \frac{\sigma_0}{\gamma_0} \sin \delta = |G^*| \sin \delta \tag{3.19}
\]

As mentioned previously, for a perfectly elastic solid the stress and strain are perfectly in phase which means \( \delta = 0 \) and for a viscous fluid they are completely out of phase,
i.e. $\delta = 90^\circ$. This reduces the above cases so as to remove the opposing modulus for either purely viscous or elastic materials. A viscoelastic material exhibits a phase angle shift between these two limiting cases and so the relationship between stress and strain can be expressed as a contribution from both a viscous and elastic component as follows

$$
\sigma(t) = G'(\omega)\gamma_0 \sin(\omega t) + G''(\omega)\gamma_0 \cos(\omega t)
$$  (3.20)

### 3.3.3 Incorporating Dispersed Nanoparticles

When studying the fluid dynamics of a dispersion of particles in a fluid it is important to consider the interactions between said particles. In all cases there are attractive van der Waals forces and random dispersive forces arising from Brownian/thermal motion. In specific cases there are electro-static attractive/repulsive forces arising from charged particles in the suspension or even steric repulsion from adsorbed polymer/surfactant molecules. The balance of these forces determines what state the particles will adopt in the dispersion. If thermal/Brownian motion dominates the particles (if non-spherical) will be randomly oriented. If attractive forces dominate, the particles will aggregate leading to a number of structures that can form and this can potentially lead to flocculation and separation of the dispersed and continuous phase. If the attractive forces are of the order of the repulsive forces, many interesting structures can form and some are shown schematically in Figure 3.4. If repulsive forces dominate the particles can form a less traditional form of lattice with a regular particle distribution formed by the repulsion between particles. This is of particular interest in this work as a dispersion increases in concentration and inter-flake interactions begin to dominate, this is discussed in detail in Chapter 6 on page 94.
In discussing dispersions and colloids it is common to use relative viscosity, $\eta_r$, defined as the measured dispersion viscosity divided by the viscosity of the dispersant without the dispersed material. The earliest work studying viscosity as a function of suspended particle concentration showed relative viscosity will scale with the volume fraction of the dispersed phase giving\[125\]

$$\eta_r = 1 + 2.5\phi$$ \hspace{1cm} (3.21)

The pre-factor of 2.5 is the intrinsic viscosity for dispersed spheres and the above has been modified to describe dilute dispersions of platelets, yielding an intrinsic viscosity of 1661.\[126\] This however does not take into account particle size or in fact any particle properties as it neglects inter-particle interactions. This limits the above expression to dealing with low concentrations where the assumption of non-interaction is a fair approximation. These interactions can be accounted for through inclusion of higher order terms of $\phi$. One such attempt to account for the inter-particle interactions is the Einstein-Batchelor equation

$$\eta_r = 1 + 2.5\phi + 6.2\phi^2$$ \hspace{1cm} (3.22)

However this holds for extensional flow, dealing with extensional viscosities and attempts to apply it to shear have yielded a large variation in the pre-factor term for the $\phi^2$ component\[121\].
An attempt by Ball and Richmond, based on an averaging technique, summed the effects of each particle allowing the Einstein relation to be written differentially

\[ \eta_r = (1 - K\phi)^{-\frac{5}{2}K} \]  

(3.23)

Where K is a factor to account for the finite volume of the added particles. This equation leads to an infinite viscosity for \( \phi = 1/K \) which leads to an important concept of a maximum packing fraction \( \phi_m \). The particles of finite size will eventually, with increasing volume fraction, begin to stack in whatever manner they fit. With spheres, there are various well-known maximum packing fractions depending on the packing arrangement with hexagonally close packed being the most efficient packing at \( \phi_m = 0.74 \), though random close packing is more appropriate and is commonly used, where \( \phi_m = 0.64 \). Various packing arrangements and their packing efficiencies can be seen in Table 3.1. If Equation 3.23 is modified with the maximum volume fraction and the exponent of \( 5/2 \) is replaced with the solutes intrinsic viscosity, a measure of a solute’s contribution to the viscosity of a solution, the result is the Krieger-Dougherty equation

\[ \eta_r = \left( \frac{1}{(1 - \frac{\phi}{\phi_m})} \right)^{\left[ \eta/\phi_m \right]} \]  

(3.24)

For rigid spheres at infinite dilution, \([\eta_r] = 5/2\), and this reduces to Equation 3.23.

<table>
<thead>
<tr>
<th>Packing Arrangement</th>
<th>Maximum Packing Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Cubic</td>
<td>0.52</td>
</tr>
<tr>
<td>Minimum Thermodynamically Stable Configuration</td>
<td>0.548</td>
</tr>
<tr>
<td>Hexagonally Packed Sheets Just Touching</td>
<td>0.605</td>
</tr>
<tr>
<td>Random Close Packing</td>
<td>0.637</td>
</tr>
<tr>
<td>Body-Centred Cubic Packing</td>
<td>0.68</td>
</tr>
<tr>
<td>Face-Centred Cubic/Hexagonal Close-Packing</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 3.1: Packing efficiencies for various arrangements of mono-disperse spheres from [127]
The concept of a “critical volume fraction” for mixtures past which a particular material property varies asymptotically has been applied in many different ways. Much work has been done to show percolation behaviour in low dimensional nano-structures, be it electrical properties in thin films of 1D nano-tubes[128] or polymer-graphene composites[129]. Here we are interested in physical percolation of the particles, i.e. the concentration reaching a point where a significant proportion of the particles are in contact such that a weak structure is formed. Of particular interest is high aspect ratio “needles” and platelets which have been modelled previously[130, 131].

![Graph showing viscosity vs. percentage volume concentration for differently shaped particles.](image)

Figure 3.5: Effects on viscosity of differently shaped particles in water at fixed shear rate (300 s⁻¹) showing decreased packing efficiency and lower maximum packing fraction for, from left to right; rods, platelets, grains and spheres, fitted to equation 3.24. From [121]

The values for \( \phi_m \) also vary strongly with particle size distribution with increasing polydispersity increasing the maximum packing fraction. Thus far all derived equations have been for mono-disperse, spherical particles with deviations and particle shape being compensated for in pre-factors or crowding terms. Some work has been done to investigate continuous particle distributions however it is likely more accurate to determine \( \phi_m \) for each system.[121] Similarly the shape of the dispersed particle has
dramatic effects on the critical volume fraction as modelled in Figure 3.5, with lower particle symmetry lowering the packing efficiency. This has the effect of increasing the particle loading effect of platelets on the mixture viscosity compared to the same volume fraction of spherical particles. Another interesting property of these platelet/needle dispersions is the ability to load a dispersion beyond this critical volume fraction, in contrast to spheres for which the viscosity diverges at that point, and this of particular relevance to the work in this thesis.
Characterisation and Methods

4.1 Introduction

In this chapter, the various experimental procedures for sample preparation and characterisation will be discussed. Dispersion preparation in all cases begins with either sonication or high-shear mixing exfoliation of the bulk layered material being studied. Sonication was used initially as the method of shear exfoliation was not known. Once shear exfoliation was known, it was used for preparation of large quantities of material and testing the theory used to understand shear exfoliation. Tip sonication is a highly energetic process and so was only used where comparisons to previous work were of importance or small volumes of highly-concentrated dispersions were required. Bath sonication however is a much lower energy process and so was used only to prevent aggregation in highly concentrated samples.

Dispersions can then be first characterised through absorbance spectroscopy of the uncentrifuged sample over extended periods of time for sedimentation analysis. Where the sedimenting phase was not of interest, the samples were centrifuged to remove the larger, unexfoliated bulk material from the exfoliated supernatant. Once the exfoliated dispersion was obtained, it could be studied using ultraviolet-visible absorption spectroscopy over an extended wavelength range to determine concentration but also lateral size and thickness of transition metal dichalcogenides.[132]

The extent of exfoliation could then be studied by producing films from these dispersions using vacuum filtration although some re-aggregation is likely to occur during filtration. An alternative method of investigating the extent of flake exfoliation is transmission electron microscopy (TEM), wherein a direct representation of the flakes can be obtained and flake dimensions observed and measured. Solid samples can also
be imaged using scanning electron microscopy (SEM) where flakes can similarly be observed and measured.

Continuing the study of solid samples, X-ray photoelectron spectroscopy can be performed on powdered samples to study the chemical composition, giving an indication of defects and residual solvents in the sample. A further method to study the chemical composition of solid samples is thermo-gravimetric analysis. Coupled with mass-spectrometry this technique provides an in-depth analysis of the chemical make up of the sample, again revealing residual solvents or other unwanted chemical species while providing insight into defects in the sample. All of these techniques are described in this chapter in greater detail with reference to sample preparation and treatment as well as the specific processing settings and conditions used.

4.2 Dispersion Preparation

4.2.1 Sonication

Sonication is a shorthand term that is commonly used to refer to the application of ultrasonic energy to either a sample or in some cases a piece of equipment as a method of cleaning. Ultrasonic is a broad term which refers sound waves with a frequency far above that which human ears are sensitive to, typically greater than 16 kHz. These high frequency transverse waves have many applications such as medical imaging (i.e. ultrasound diagnostic imaging), navigation and industrial scale mixing. As mentioned previously this is commonly used for cleaning and ultrasonic baths are commercially available to clean jewellery. The applied energy in these baths is enough to remove material from the surface of objects and it is a device in the same vein as these that was used to separate the layers of graphite in suitable solvents to form graphene [66].

In the work presented in this thesis, the method of sample preparation is liquid-phase exfoliation. On applying sonic energy to a liquid sample, the solvent molecules therein begin to oscillate about their mean positions at the frequency of the applied sonic energy. This sound wave goes through compression and rarefaction cycles with solvent
molecules being forced towards one another and apart respectively. For ultrasonic cycles this can exceed the critical molecular distance necessary to hold the liquid intact and so a cavity is formed which will grow during the rarefaction cycle. These bubbles subsequently contract or collapse entirely once the rarefaction cycle ceases releasing large amounts of energy in the form of a shock wave.\[133]\] These shock waves generate large local shear stresses, large enough to delaminate the van der Waals bound layered materials used in this work.

The process must be carefully monitored however as large amounts of heat are generated during sonication. This is largely due to energy losses to the acoustic wave due viscous frictional losses as well as thermal conduction from areas of high pressure to low pressure areas.\[133]\) This means, particularly for higher power sonication, that cooling must be employed either through circulating cooled water about the sample or, in the case of sonic baths, circulating cooled water through the bath itself. Furthermore, the applied energy is large enough to break apart the basal plane of the particles being exfoliated in a process known as sonication-induced scission. This has been observed for carbon nanotubes\[134, 135]\), graphene\[72]\) as well as MoS$_2$\[136]\). The final length of the exfoliated material has been observed to reduce to a lower limit approximately as $l \propto t^{-1/2}$, a factor that must be taken into account when employing long term sonication.

4.2.1.1 Equipment

The equipment used in this work employs piezoelectric transducers to convert high-frequency electrical energy into high-frequency sonic energy. In the case of the sonic bath, a number of transducers supply energy to a steel tank filled with water. Liquid samples are then held in this tank in vials or beakers and the sonic energy supplied to the tank passes from the tank to the water in the vessel and is then transmitted into the sample. Care must be taken to ensure the liquid level in the sonic bath does not fall below the marked operating levels. In the case of a sonic tip, the transducers supply the energy to a titanium probe that is directly immersed in the sample allowing more direct control of the energy input into the sample. Samples sonicated in this manner must be secured such that the tip does not come into contact with the sample holder.
and that the tip is placed centrally in the sample a few millimetres from the bottom to ensure consistency.

All sonication tools used in this work has a fixed frequency output of 20 kHz in the case of the sonic tip and 40 kHz in the case of the sonic baths. An ultrasonic bath (Branson 1510-MT, 16 W) was used to prevent sample re-aggregation in Chapter 6 and was not used for sample exfoliation due to reproducibility issues. The sonication time is controlled via a timer on the bath and for the short timescales it was used for, cooling was not required. Samples were moved regularly to avoid the possibility of it remaining in a “dead spot” within the bath, i.e. an area in which the ultrasonic wave has formed a node due to it forming a standing wave within the bath.

For powder pre-treatment in Chapter 5 and for high concentration dispersion preparation in Chapter 6 a sonic tip was used (Vibracell, GEX750) shown in Figure 4.1. For all samples the tip was run at 40% amplitude and the application of sonication was pulsed to facilitate sample cooling. The samples were cooled using an external chiller or an ice bath to prevent overheating and evaporation of the solvent. For powder pre-treatment, larger volumes were used so the flat-heat probe was utilised. In the case of high concentration dispersion preparation, lower volumes were needed and so a tapered tip was used.
4.2.2 Shear Exfoliation

In this work, shear exfoliation is used to refer to the application of high shear rates to layered materials in liquid media using high shear mixers or in one instance a high shear setup for a rheometer (described in more detail in its own section) and is not to be confused with other methods in which high shear stresses play a vital role. Shear stress, shear rates and the proposed shear exfoliation mechanism have all been outlined in detail in the previous chapters and will only be mentioned in this section in brief. High shear mixing in the liquid phase is known well as a household process, achievable in any household blender and can be accomplished in a variety of ways. A rotating blade immersed in the sample is the most common method, however alternatives can drive the mixture through small gaps or have a rotating phase and stationary phase with a precise gap between them to create a region of high shear.

Figure 4.2: Silverson high shear mixer with operation shown diagramatically adapted from [2]
The high shear mixer used in this work is what is known as a rotor-stator mixer, consisting of a electrically driven steel rotor within a perforated housing, called a stator. This can be seen in Figure 4.2 on the preceding page. The rotor is spun at a high rotation rate which draws liquid mixtures into the bottom and forces it out laterally, driving it through the perforations. There are a few high shear regions in this process, the rotor-stator gap is one, as are the perforations in the stator, and finally turbulent eddies near the mixing head are a potential high shear region. While the region of high shear is found only near the mixing head, the process mixes the sample well and utilises all available material. The approximate shear rate (\(\dot{\gamma}\)) generated can be calculated by noting the rotor speed in rotations per second (N) by the following equation

\[
\dot{\gamma} = \frac{\pi ND}{\delta}
\]

where \(\delta\) is the rotor-stator gap and D is the rotor diameter.

### 4.2.2.1 Equipment

A Silverson High-Shear Mixer model L5M is used in this work with two separate mixing heads. The mixer can deliver between 100 and 7000 rpm and samples were kept at 15 °C using an external chiller supplying a water bath surrounding the sample. Liquid samples in appropriately sized beakers were secured in place in the water bath and the mixing head lowered directly into the sample to a few mm above the bottom of the sample beaker. The mixing head was always placed slightly off centre in the sample container to avoid “whirl-pooling” and spillage of the sample. Care must be taken to ensure the mixing head is completely covered to prevent damage to the mixer. Sample mixing time was then controlled via the built in timer in the shear mixer. The large 32 mm diameter rotor is used for volumes above 180 ml in conjunction with the square hole high shear screen and this mixing head has a rotor-stator gap of \(\sim 220 \mu m\). For volumes below 180 ml, a 12 mm diameter rotor tubular mixer was utilised with the circular shear screen and this setup has a 115 \(\mu m\) rotor-stator gap.
4.2 Dispersion Preparation

4.2.3 Centrifugation and Sedimentation

Dispersions produced either using shear exfoliation or sonication will still contain large quantities of large, unexfoliated material, unstable dispersed material and in the case of successful exfoliation, a small portion of exfoliated nanosheets. In order to study and characterise the produced nanosheets they must first be separated from the bulk material and unstable phases. This will happen naturally over time as the larger particles settle to the bottom of the container and the unstable particles flocculate and follow suit. This process is itself of interest in certain cases and is also studied. However for practical purposes of dispersion preparation centrifugation is used to speed up this process. This drives the large unstable particles to the bottom of the sample vial and the remaining stable dispersion (the supernatant) can then be decanted from the top to be kept and characterised.

A centrifuge operates by rotating the samples in a sample holder about a fixed axis at a known rotation rate, typically given in RPM, for a known period of time. However the effective force applied to samples is dependent on more than simply the rotation rate and so to allow comparisons to other devices the centrifuge rate can be converted to relative centrifugal force (RCF) which is quoted relative to gravity. This can be calculated from

\[ RCF = \frac{r\omega^2}{g} \]  \hspace{1cm} (4.2)

where \( g \) is the gravitational force, \( r \) is the radius of the rotor and the angular rotation \( \omega = 2\pi N \) where \( N \) is the rotation rate in rotations per second.

Centrifugation will separate particles on the basis of mass. While centrifugation is used in order to yield a stable dispersion, particles may continue to drop out even after a centrifugation step. This can be due to an insufficient centrifugation or it could be indicative of an unstable dispersion in which particles are aggregating and falling out of suspension. This process can be studied using optical methods. By monitoring the absorption of the sample over time an indication of the concentration of dispersed material can be obtained. This is based on the Beer-Lambert law stating that
\[ A(t)/l = \alpha C(t) \]

where \( A \) is the absorbance, \( l \) the thickness of the sample the light must pass through, \( \alpha \) is the absorption coefficient for the suspended material and \( C \) is the concentration of suspended material. As material falls out of suspension, concentration falls and the absorbance follows suit. This is covered in more detail in Section 4.3.1 on the next page.

As previously stated, a sample produced through sonication or shear exfoliation will potentially contain a mixture of thin well exfoliated material, unstable exfoliated material and thick unexfoliated material. Each phase will sediment at a different timescale, with stable material remaining dispersed. It has been shown that sedimenting phases decay exponentially with each phase having its own time constant.\(^{[137]}\) From this, the concentration of a dispersion during sedimentation can be written as

\[ C(t) = C_0 + \sum_n C_n e^{-t/\tau_n} \quad (4.3) \]

where \( \tau_n \) is the time constant for phase \( n \) and \( C_0 \) represents a stable concentration and can be excluded for completely unstable dispersions. As concentration is not directly measured, this can be expressed in terms of absorbance as

\[ \frac{A(t)}{l} = \alpha_0 C_0 + \sum_n \alpha_n C_n e^{-t/\tau_n} \quad (4.4) \]

where \( \alpha_0 \) and \( \alpha_n \) are the extinction coefficients for the stable phase and the \( n \)th sedimenting phase respectively.

### 4.2.3.1 Equipment

The centrifuges used in this work are a Hettich Mikro 220R and a Thermo Scientific Heraeus Megafuge. The Hettich can be either used with a low speed rotor (radius of 90 mm), capable of holding 6 samples tubes of up to 28 ml and operating at 500 - 6000 RPM or a high speed rotor (radius of 87 mm) capable of holding 24 samples of up to 1.5 ml and operating at 6000 - 18,000 RPM. The Megafuge was used with a TX-200 swinging rotor (radius of 168 mm) which can hold up to 16 samples of up to 50 ml and operates at 500 - 15,200 RPM. All centrifuges have refrigeration capabilities and this was used to prevent overheating during high speed centrifuge cycles.
The sedimentation absorption analysis was performed using a house built apparatus. This consists of a vertical array of four synchronised pulsed lasers (633 nm) and photodiodes as illustrated in Figure 4.3. A cuvette containing pure solvent with no material is run before testing a sample containing solvent and material to obtain $I_0$. The solvent is removed and then the sample is then placed into the cuvette and the pulse settings and length of test can be set to monitor how the intensity of the transmitted laser signal varies with time. This can be converted into the absorbance of the sample and can also be used to obtain how the sample concentration varies over the course of days, weeks or even months. Each laser in the array produces its own signal and the measurements across the array are expected to be in sync. Some degree of evaporation can occur, particularly with low boiling point solvents and care was taken to discount affected lasers when this occurred.

4.3 CHARACTERISATION METHODS

4.3.1 Optical Absorption Spectroscopy

Optical absorption spectroscopy is a technique based on the interaction of light with the sample. While the method gets its name from absorption, light can interact with a sample in a variety of ways. First and foremost, incident light may be reflected back
along its path or refracted at the air/cuvette interfaces or cuvette/sample interfaces. Light can interact with the sample in such a manner that the incident photons change directions, known as scattering, in a process that can either leave the energy unchanged (elastic) or the photon can exchange energy with the sample (inelastic). Finally the incident photon may be absorbed by the sample being tested. This can occur when the energy of the photon matches an electronic transition of a material within the sample or when the photon energy matches that of a rotational or vibrational energy mode within the sample.

In the absorption spectroscopy in this thesis, the wavelength of the incident light is varied within the range of UV (200 - 400 nm) through visible (400 - 700 nm) and into the near IR (700 - 800 nm). Within this frequency range it is chiefly electronic transitions and vibrational modes that are observed. The peaks and troughs measured at specific wavelengths are characteristic to each material and reveal these properties for the samples tested. This can be used to reveal important information about the samples such as concentration and in certain cases, platelet size and thickness.\[132\] The concentration of the dispersion can be obtained using a relation known as the Beer-Lambert law that relates the measured absorption to the concentration of material in the sample at a characteristic wavelength using a constant known as the extinction coefficient. Typically this is applied at a specific peak or trough within the spectrum.

If a beam of monochromatic light passes through a sample, an interaction between the sample and the light can be observed by measuring the ratio of the transmitted light (I) to the incident light (I\(_0\)). This is known simply as the transmission (T)

\[ T = \frac{I}{I_0} \]  \hspace{1cm} (4.5)

The law states the transmitted intensity decreases as a function of path length (l) such that

\[ I = I_010^{-el} \]  \hspace{1cm} (4.6)

Where \( e \) is a proportionality constant known as the absorption coefficient (with units m\(^{-1}\)). A more useful constant, \( \alpha \), known as the extinction coefficient (with units mL}
mg^{-1} m^{-1}) can be used in place of the absorption coefficient where $e = \alpha C$. Taking this and manipulating Equation 4.6 to extract the concentration gives

$$\alpha Cl = -\log_{10} \left( \frac{I}{I_0} \right)$$  \hspace{1cm} (4.7)

This can be further simplified by substituting in a term known as the absorbance, defined as $A = -\log_{10} T$, yielding a simple and very useful equation

$$\frac{A}{T} = \alpha C$$  \hspace{1cm} (4.8)

where $A$ is the measured absorbance, $l$ is the sample path length, $C$ is the sample concentration and $\alpha$ is extinction coefficient for that material and is wavelength dependent. These are all shown schematically in Figure 4.4.

![Figure 4.4: Graphical representation of the Beer-Lambert law, showing key parameters](image)

4.3.1.1 Equipment

The UV-Vis spectrometer used in this work is a Varian Cary 50 UV-Vis spectrophotometer. This utilises a xenon lamp capable of operating between 190 - 1100 nm using a monochromator with an approximate 1.5 nm fixed spectral bandwidth.[138] Baselines were run for each solvent, solvent mixture and surfactant/water mixture concentration in a quartz cuvette in the relevant wavelength range. Samples were placed in a quartz cuvette and spectra were obtained in the range of 200 - 800 nm and the absorbance of
the dispersed material calculated by subtraction the baseline contribution. All samples were run in either a 4 mm path length cuvette or a 10 mm with the shorter path length used for samples of higher concentration. Highly concentrated samples exhibit an absorption value above that which is measurable by the instrument (instrument limit is approximately $\text{Abs} = 3$) and so high concentration samples were diluted with the appropriate solvent/surfactant:water mixture so as to be measurable.

4.3.2 Raman Spectroscopy

The interaction of light with a sample mentioned in the previous section mentioned that the scattering of light was a potential interaction. The scattering of light involves the material absorbing the incident photon and re-emitting it. This can occur in a number of ways. If the emitted photon has the same wavelength, or alternatively; energy, as the incident photon (or is “elastically” scattered) this is known as Rayleigh scattering. However if the emitted photon is different in wavelength, the photon is inelastically scattered by the material in a process known as Raman scattering.

Raman scattering is named after Sir C.W. Raman who first observed the scattering phenomenon in 1928[139] and this discovery eventually earned him the Nobel prize in 1930. The original paper focuses on the modification of the frequencies of light scattered by certain liquids and gases and attributes this to the material absorbing a portion of the incident photon energy and scattering the remainder. This is now understood to be the absorption of a photon followed by the emission of another photon of either lesser energy, and so leaving the molecule in a higher energy state (known as Stokes Raman scattering), or of greater energy, leaving it in a lower energy state than it started in (known as anti-Stokes Raman). These processes are shown graphically in Figure 4.5. In practical terms this means if a monochromatic source of light interacts with a material, a small portion of the incident light is scattered and shifted in wavelength. These shifts can be measured yielding the Raman spectrum revealing information about the molecular vibrations and rotations occurring within the sample being tested.
Raman scattering occurs due to the incident light interacting with the molecules in the sample being tested and ultimately results in a change in vibrational energy of the molecule, providing complementary information to infrared (IR) spectroscopy. In contrast to IR absorption spectroscopy, a single photon process where an incident photon is absorbed when it is in resonance with a particular vibrational frequency of the molecule, Raman scattering is a two photon process involving the polarisability of the molecule with respect to its vibrational motion. Furthermore certain vibrational transitions that are inaccessible to IR spectroscopy are easily observed using Raman spectroscopy and vice versa.

In this process the molecule absorbs an incident photon and is briefly excited into a virtual energy state before emitting another photon as it decays down to a different vibrational state. The difference in energy between the start and end vibrational states determines the frequency of the emitted photon. In terms of intensity, Rayleigh scattering is a far more common transition and so must either be filtered out in order to observe Raman or the Raman signal must be enhanced using photo-multipliers. Anti-Stokes Raman scattering is the least intense signal, as the molecule must already be in a higher energy state for it to be observed. The signal generated by Raman scattering is proportional to the change in polarisability of the molecule being tested. This makes it an ideal spectroscopic tool to use for layered compounds due to their easily polarised πorbitals between layers.

Figure 4.5: Energy level diagram showing IR absorption and scattering processes
Raman Spectroscopy has been shown to be very successful for studying graphene and carbon based materials, although it can also be used to study inorganic layered compounds and 1D nanomaterials. In this work, Raman is used primarily to investigate graphite and graphene films. Graphite itself has a very distinctive spectrum with several characteristic peaks; the D band: occurring at \( \sim 1350 \text{ cm}^{-1} \), the G band: occurring at \( \sim 1580 \text{ cm}^{-1} \) and the 2D band: occurring at \( \sim 2700 \text{ cm}^{-1} \) and the latter two bands can be seen in Figure 4.6 A.

The G band is so called as it is characteristic of, and first observed in, graphitic systems. It is related to the stretching of the carbon - carbon bonds within the graphite layers and has been shown to change notably when the basal plane of the platelet is significantly altered as can be seen in graphite oxide. The D band is so called because of its relation to defects. The band will only be present if the symmetry of the basal plane is interrupted, be it by interstitial defects, vacancies or dislocations in the basal plane, including flake edges. This band is particularly useful in this work as it has been shown that in the absence of basal plane defects, the D band can be used to approximate flake size. Finally, the 2D band is perhaps the most informative as it gives information on the extent of exfoliation of the graphene sample.

![Figure 4.6](image)

Figure 4.6: (A) Raman spectra of graphite and graphene, (B) Showing variation in 2D band of graphite/graphene as the number of layers decreases. Modified from [145]
In 2006 Ferrari et al. first observed how the 2D shape changes with respect to flake thickness,[145] shown in Figure 4.6 B. It was shown that while graphite has a 2D peak consisting of two sub-peaks 2D\textsubscript{1} and 2D\textsubscript{2} of approximately 1/4 and 1/2 the height of the G peak respectively, graphene consists of a single sharp peak situated at ~2640 cm\textsuperscript{-1}. This variation is a strong function of the number of layers and so analysis of the 2D peak has been used to assess the extent of exfoliation of graphene.

4.3.2.1 Equipment

In this work Raman spectra were obtained using a Horiba Jobin Yvon LabRam HR spectrometer using a 532 nm 50 mW laser excitation source. The spectra were taken using a 600 mm\textsuperscript{-1} diffraction grating, a 100x optical lens and a holographic notch filter was used to filter the Rayleigh scattered light. Before measuring any spectra the apparatus was calibrated using a white light source and subsequently a Si reference sample. Multiple spectra (no less than 10) were obtained from each sample at various points across the film to ensure that an average returned a representative spectra of the entire sample. Care was taken to ensure the signal to noise difference for the G peak was ~10\textsuperscript{3} by managing the filter applied to the incident beam and the acquisition time measurements were taken for. This was done in order to obtain clear spectra with minimal noise but also to prevent damage to the sample at high powers.

4.3.3 Transmission Electron Microscopy

While the previously discussed absorption and Raman scattering spectroscopies measure the interaction of light with a sample, electron microscopy measures the interaction of electrons with a sample. In the case of transmission electron microscopy (TEM) a coherent beam of electrons is first emitted from a heated filament (normally made of Tungsten or LaB\textsubscript{6}) and accelerated through a voltage into a column under high vacuum. This beam is focused as it passes through a number of magnetic lenses, known as the condenser lenses, before passing through the sample in the middle of the column. The electrons having interacted with the sample are further focused as they pass down the
column by the objective lenses followed by projector lenses focusing the beam onto a screen. As the initial momentum of the electrons is known, the interaction of electron and sample can be worked out by changes to the final electron energy and the angle through which it has been deflected. The method of image formation is akin to an optical microscope however the source of contrast in the case of TEM is the various electron scattering events that occur on passing through the sample. A schematic of a TEM column and the beam path can be seen in Figure 4.7.

The advantage of using electrons over conventional optical spectroscopy is due to a phenomenon known as the Abbe diffraction limit. Discovered by Ernst Abbe in 1873, this states that the smallest object that can be resolved is proportional to the wavelength of the wave used to image it, roughly \( d \approx \lambda/2 \). This means using a conventional microscope and visible light (~400 - 800 nm) the smallest object that can be resolved is ~200 nm if all sources of aberration have been minimised. Thus to reliably image objects smaller than this, the wavelength must be decreased and while this could be achieved by using light of a lower wavelength, focusing ultraviolet (UV)
light requires specialist lenses due to optical glass absorbing UV light and going to extremely small wavelengths makes focusing using optical lenses impossible. By using electrons the wavelength of the beam is determined by the de Broglie wavelength

$$\lambda = \frac{h}{mv} \quad (4.9)$$

where $h$ is the Planck constant and $m$ and $v$ are the particle mass and velocity respectively. This means the wavelength of the beam can be controlled by varying the voltage ($V$) the electrons are accelerated through in the electron gun

$$eV = \frac{1}{2}mv^2 \quad (4.10)$$

such that

$$\lambda = \frac{h}{\sqrt{2meV}} \quad (4.11)$$

This must then be modified to compensate for relativistic effects giving

$$\lambda = \frac{h}{\sqrt{2m_0eV \left(1 + \frac{eV}{2m_0c^2}\right)}} \quad (4.12)$$

Thus, using an acceleration voltage of 100 kV, the theoretical lower resolution limit is $\sim 2 \text{ pm}$. In practice however, these resolution limits are far from being achieved due to the presence of aberrations in the magnetic lenses with typical high contrast point resolution limits of $\sim 0.31 \text{ nm}$.\cite{150}

On passing through the sample, a variety of interactions are possible. Energy loss electrons that lose energy through exciting a core electron of sample material provide a fingerprint of the element involved. Zero-loss, small angle scattered electrons are used to produce a so called “bright-field” TEM image with the beam intensity varying spatially. Finally, diffracted or high-angle scattered electrons can be used to obtain the image, either through moving the detector or tilting and shifting the incident electron beam using the condenser lenses to yield a so called “dark-field” image. This highlights the species within the sample which cause the diffraction or scattering, a useful trait when characterising some samples. This also provides a diffraction pattern
from the material due to the electron wavelength being close to the lattice spacing and can reveal information about the crystal structure of the sample. A schematic of the various electron interactions with a sample can be found in Figure 4.8 with reference to a characterisation technique discussed in the next section.

![Possible electron interactions with a sample](image)

Figure 4.8: Possible electron interactions with a sample from [151]

4.3.3.1 Equipment

TEM samples in this work were prepared by drop-casting a few ml of dispersed material onto holey carbon grids (Cu 400 mesh) and vacuum drying the grids to remove residual solvent. Bright-field TEM micrographs were obtained in this work using a Jeol 2100 TEM system operating at a voltage of between 100 and 200 kV depending on sample stability under the beam. This machine uses a LaB6 electron source and can operate between 80 and 200 kV. A 5 sample sample holder was used to load the samples into the column and representative images were taken from multiple points from various points across the grid. Samples were left in the airlock of the
column under high vacuum to further remove residual solvent from the sample to prevent the introduction of material to the high vacuum column.

Statistical information was obtained from TEM images to obtain length and width statistics for the dispersion. Care must be taken when undertaking analysis such as this to ensure images are clear and at the correct focus. Images were taken at low (~5000x) and high (up to ~20000x) magnification, depending on the sample to ensure no bias towards imaging predominantly large or small flakes occurred. Length was defined as the longest dimension of the flake being measured with width being defined as the dimension perpendicular to the length. A large number of counts is necessary to obtain any insight into the sample using a technique such as this and the total flake count was maximised for each sample (>100 counts).

4.3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is similar to TEM in that it uses electrons accelerated through a voltage and focused using electromagnetic lenses in order to image the sample however the two processes are quite different. SEM is a surface sensitive technique in which a focused beam of electrons is scanned across the surface and back scattered electrons are then collected to work out an image of the surface. As with TEM, the electrons are typically emitted from a tungsten filament or a LaB₆ tip into a column under vacuum. The electrons are accelerated through a voltage and then focused using an electromagnetic condenser lens and passed through an aperture to ensure the beam is coherent. This beam is then passed through the scanning coils which control the imaging process as the beam is scanned over the area being imaged as well as the objective lens focusing the beam on the sample surface. This can be seen schematically in Figure 4.9.
In SEM, electrons are directed into a thick sample and the incident beam penetrates the sample surface and scatters inside the sample. This causes a teardrop shaped volume with which the beam is interacting with the depth/width of this shape depending on the sample material properties and beam energy. On interaction with the sample, backscattered electrons and secondary electrons are predominantly used to obtain an image of the sample while characteristic X-rays and Auger electrons can also be collected to further characterise the sample. Backscattered electrons consist of high energy electrons from the beam being scattered elastically by the sample and are typically high energy making them less surface sensitive although this is useful to study sample composition past the surface. Secondary electrons are electrons that have been ejected from the sample by inelastic collisions with electrons from the beam. These are lower energy and so secondary electrons can be used as a more surface sensitive imaging mode. A diagram showing the teardrop interaction region and the signal generated from different depths can be seen in Figure 4.9. As electrons are fired into the sample, and not through the sample as with TEM, it is important the sample...
is either conducting or is coated with a conducting layer to prevent the build up of charge as this would distort any obtained image of the sample.

4.3.4.1 Equipment

SEM samples were prepared by adhering small quantities of the solid sample to be tested to a sticky carbon tab. This tab is then adhered to a metallic SEM stub and, as the graphite/graphene samples being tested are adequately conductive, no metallic coating procedures were necessary. SEM micrographs were obtained using a Carl Zeiss Ultra Plus SEM with a LaB$_6$ source with an acceleration voltage of 5 kV. Images were obtained using the SE2 imaging mode which utilises secondary electrons to form an image. This mode was used as secondary electrons can produce a higher resolution image and the samples being tested did not require material analysis.

4.3.5 X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS) is a surface sensitive technique that can be used to measure the elemental composition of a sample. Sometimes called “electron spectroscopy for chemical analysis” (ESCA) the technique can be used to obtain chemical information in addition to the elemental information of a sample. Spectra are obtained by directing a beam of X-rays at the sample held under high vacuum (typically $< 10^{-9}$ mbar) and measuring the kinetic energy of electrons that escape from the top ~10 nm of the sample surface. Electrons are collected and focused using electromagnetic lenses and are directed into an energy analyser to obtain their kinetic energy. Spectra obtained are plotted as electron count versus the binding energy ($E_{\text{binding}}$) with the binding energy calculated as

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \quad (4.13)$$

where $E_{\text{photon}}$ is the photon energy of the incident X-ray, $E_{\text{kinetic}}$ is the kinetic energy of the expelled electron and $\phi$ is the work function of the material being tested in the sample.
4.3.5.1 Equipment

The spectra shown in this work were obtained under ultra-high vacuum (<5x10⁻¹⁰ mbar) using monochromated Al Kα X-rays (1486.6 eV) from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. Samples were dried under vacuum at 70 °C for 5 hours before insertion into the vacuum chamber. An Omicron CN10 electron flood gun was used to charge compensation and the binding energy scale was referenced to the adventitious carbon 1s core-level in the survey spectra at 284.8 eV. C1s core-level regions were recorded at an analyser pass energy of 15 eV and with slit widths of 6 mm (entry) and 3 mm x 10 mm (exit), resulting in an instrumental resolution of 0.49 eV. After subtraction of a Shirley background, the core-level spectra were fitted with Gaussian-Lorentzian line shapes and using Marquardt’s algorithm.

4.3.6 Thermogravimetric Analysis with Mass Spectrometry

Thermogravimetric analysis (TGA) is a technique in which a known mass of sample is heated either at a fixed heating rate or to a constant temperature and the resulting change in mass is monitored. This provides information about a sample as it monitors sample vaporisation, sublimation and adsorption/desorption as a function of temperature/time, allowing the components in a sample to be identified. TGA measurements can be performed under atmospheric conditions to monitor oxidation effects or they can performed under inert gas to exclude such effects.

Mass spectrometry is an analytical technique used to identify the quantity and type of chemical species present in a sample being tested. This is achieved by vaporising the sample, ionising the gaseous particles and accelerating the particles into a curved chamber lined with electromagnets. The mass to charge ratio of these ions can then be measured as they pass through an electromagnetic pathway by measuring their deflection as they pass through the magnetic field of known strength. This can be seen schematically in Figure 4.10. The gaseous input into a mass spectrometer can be coupled with the output of a TGA setup, to further characterise the material that is being vaporised/desorbed from the sample.
In this work a mass spectrometer coupled to TGA was carried out on a Netzsch STA 409 CD equipped with a Skimmer QMS 422 mass spectrometer (MS/EI). Samples were run with a programmed time-dependent temperature profile of 30 - 500 °C with a 10 K/min gradient. Initial samples of ~10 mg were used and measurements were performed under an inert atmosphere of helium gas flow of 90 mL/min.

4.3.6.1 Equipment

The basics of the function and theory of rotational rheometers has already been covered in Section 3.3 on page 31 and so this section will focus entirely on the specifics of the apparatus used in this work.
4.3.7.1 Equipment

The rheometer used in this work is an Anton Paar MCR 301 which has a minimum torque resolution of 0.001 μNm and can operate at torques of 0.1 μNm - 200 mNm. The system was used with a PP50 parallel plate and CC28.7 measuring system for high and low viscosity samples respectively. The parallel plate measuring system has a radius of 25 mm with a user set gap width which was set to 0.5 mm. This system is calibrated using the mean shear rates ($\dot{\gamma}_m$), shear stresses ($\tau_m$) and strains ($\gamma_m$) given by

$$\dot{\gamma}_m = \frac{2}{3} \cdot \frac{\omega R}{H}$$

$$\tau_m = \frac{4}{3} \cdot \frac{M}{\pi R^3}$$

$$\gamma_m = \frac{2}{3} \cdot \frac{R \varphi}{H}$$

where $\omega$ is the angular velocity, $R$ is the plate radius, $H$ is the gap width, $M$ is the applied torque and $\varphi$ is the plate deflection angle. The PP50 measuring system is also equipped with a Peltier plate with a maximum temperature deviation of 0.2 °C which was used to maintain steady temperatures. The concentric cylinder measuring system has an inner diameter of 14.36 mm and an outer diameter of 14.36 mm providing a gap width of 100 μm and is capable of supplying shear rates of up to 45,000 s⁻¹.
The chief method of producing graphene, used throughout this thesis, is liquid phase exfoliation. As discussed in chapter 4, liquid phase exfoliation (LPE) of graphene has been shown to be effective, both solvent based\cite{66,71,72,152} and surfactant/water based\cite{76,77}. However, some serious issues are still present.

LPE is relatively slow, it can take over 100 hours of bath sonication to obtain a dispersion with a graphene concentration of 1 mg/ml\cite{72}. With high-power sonic tips the same concentration could require 2 hours\cite{84} as well as constant care to avoid heat-related solvent degradation or sonication-induced polymerization. Such long periods of sonication has been shown to reduce the quality of dispersed nanomaterials with sonication induced scission being observed in carbon nanotubes\cite{134,135} as well as extended sonication introducing defects into the basal plane of graphene flakes\cite{148}. Furthermore, the concentrations achievable using liquid phase exfoliation are simply too low to ship sizeable quantities of graphene. While concentrations up to 63 mg/ml have been reported\cite{84} using a method of recycling the dispersed material, these show limited stability above 26 mg/ml. Transporting significant quantities of graphene produced in this manner requires impractical quantities of solvent. Even with the highest concentrations reported, to ship a sample of graphene dispersion would require nearly forty times the graphene’s weight of solvent.

Ideally, a powder could be produced that was stable during storage and shipping and capable of being dispersed in solvents quickly and easily to yield graphene. This chapter outlines a proposed technique to produce such a powder and two solvents are compared using the method. A stabilizing solvent, NMP, and a known poor solvent
for graphene,[71] water, were both tested with the aim of investigating the importance of a stabilizing solvent being present during the exfoliation step of the pretreatment.

A route to further refine this method is then outlined allowing residual solvent to removed easily and effectively. Residual solvent and graphene quality is measured using thermo-gravimetric analysis coupled with mass spectroscopy (TGA-MS) and X-ray photo-spectroscopy (XPS) and material produced in the manner is compared to stock graphite in a solvent survey with the aim of reducing the scatter present in previous work.

5.2 OUTLINING AND TESTING THE PRETREATMENT TECHNIQUE

5.2.1 Experimental Procedure

The graphite used in these experiments was supplied by Sigma-Aldrich (Graphite Flakes product no. 33246) and used as supplied. NMP was purchased from Sigma-Aldrich and used as supplied. De-ionised water was obtained from an on-site in-line water deionizer (find make/model). All samples were sonicated using a VibraCell GEX750, solid flat head probe at 40% maximum amplitude.

Pretreatment consisted of adding graphite, at a concentration of 100 mg/ml, to 80 ml of solvent and sonicking the powder for various pretreatment times ($\tau_{PT}$): 4, 8 and 16 hours. This was done for both NMP and de-ionised water. The pretreated material was recovered via vacuum filtration through a nano-porous alumina membrane (Whatman Anodisk 47 mm, pore size 0.02 µm). The recovered powder was then rinsed with IPA and dried in a vacuum oven overnight at 60°C to remove residual solvent.

Sedimentation studies were performed on the pretreated dispersions immediately after switching off the sonic tip. This was done in a home-built apparatus which consists of a cuvette holder and an array of 4 pulsed lasers and photo-diodes measuring the absorbance as a function of time. A schematic of this apparatus can be found in section 4.2.3 on page 47. The data points from the laser 1 cm below the top of the cuvette taken for this study, with a baseline taken for each sample consisting of the
solvent (water or NMP) and cuvette used. TEM was also performed on the sedimenting samples by pipetting a few millilitres of the sedimenting dispersion onto holey carbon grids (Agar, 400 mesh copper). Images were obtained under bright field TEM (Jeol 2100 operating at 200 kV). After vacuum drying the powders were characterized using SEM (Zeiss Ultra Plus) and Raman spectroscopy was performed using a Witec Alpha 300 R, with an excitation wavelength of 532 nm and an 100x magnification optical lens.

The resulting powders were then studied by redispersing them in fresh NMP at a concentration of 100 mg/ml. These dispersions were sonicated for approximately 1 hour with 1 ml samples being withdrawn at fixed time intervals. These samples were diluted and centrifuged at 2000 rpm for 60 minutes (Hettich Mikro 22R). UV-Vis-IR measurements (Varian Cary 6000i with 10 mm quartz cuvettes) were then performed to determine concentration of the supernatant post centrifugation. An absorption coefficient of 3620 mg mL$^{-1}$ m$^{-1}$ was used to determine concentration. These dispersions were also further characterized using TEM. Finally thin films were prepared from them using vacuum filtration to be studied using Raman spectroscopy (Ten different spots were scanned, the baseline removed and the scans averaged).

5.2.2 Results and Discussion

5.2.2.1 TEM Analysis of Pretreated Dispersions

TEM grids were prepared from the pre-treated dispersions immediately after the tip was switched off with no centrifugation of the dispersions. A few drops were pipetted from the top of both NMP pretreated (NPT) and water pretreated (WPT) samples and dropped onto TEM grids. Shown in Figure 5.1 A and B are typical images of the flakes obtained from NPT and WPT samples respectively. What was seen in both cases is that the dispersions contained large, thick objects. This is indicative of unexfoliated or partially exfoliated graphite. However, in both samples there were large quantities of micrometer-length, electron-transparent flakes.

These flakes are consistent with the multilayer graphene nano-sheets seen in previous work.[69] In the case of NMP this is as would be expected. However, water would not
be expected to produce such a dispersion. The presence of exfoliated nano-sheets in a non stabilizing solvent gives some important insight into LPE. The observation that exfoliation can be achieved in the absence of stabilization would suggest that sonication is a brute-force technique. The high-energy process of cavitation creates shear rates sufficient to de-laminate the graphite flakes without the need for minimisation of surface energy cost through favourable graphene-solvent interactions.

![Figure 5.1: TEM images of objects found in dispersions immediately after pretreatment of graphite by sonication in NMP and water (τPT = 4 h). Also shown are images of objects remaining dispersed 25 hours after the end of sonication.](image)

To compliment the sedimentation analysis TEM samples were also prepared 25 hours after sonication had ceased. Typical TEM images for NPT and WPT are shown in Figure 5.1 C and D respectively. For both samples large quantities of nano-sheets were observed. While this is again unsurprising for NMP, it was not expected for WPT dispersions. As mentioned before graphene is not well stabilized in water. Dispersions produced in water will typically retain no graphitic material when centrifuged. Despite
this, it can be seen in the TEM images that quantities of graphene remain after 25 hours and furthermore that they remain relatively well exfoliated. It would be expected that aggregation of the sheets would occur due to the large mismatch of surface energies of graphene and water as the dispersion drives towards minimizing energy.\textsuperscript{[66, 71]}

5.2.2.2 Sedimentation Analysis

Using sedimentation measurements a more in depth analysis of the powders can be performed. These measurements monitor the optical absorbance of the dispersion as soon as the sonication was stopped without any centrifugation applied. The data obtained can be seen in Figure 5.2 for (A) NMP and (B) water. For NMP the absorbance decays rapidly, reaching a stable value of approximately 30\% of the starting absorbance after ~250 hours. This is seen for all pretreatment times and is consistent with a fraction of the larger dispersed material falling out under gravity until only the stably suspended material remains.

The sedimentation behaviour of the WPT samples is notably different. For each pretreatment time the absorbance falls steadily with time, at a different rate for each pretreatment time. Another notable difference is the presence of a “stability cliff”. After a well-defined time, referred to as the destabilization time $\tau_D$, the absorbance is seen to drop by an order of magnitude and furthermore, this destabilization time varies with pretreatment time. Regardless of pretreatment time however, water is clearly a poor stabilizing solvent for graphene, with a final absorbance dropping below the noise limit of the apparatus, or ~0.1\% of the starting absorbance.
5.2 OUTLINING AND TESTING THE PRETREATMENT TECHNIQUE

Figure 5.2: Sedimentation of pretreated dispersions post sonication for a number of pretreatment times. Inset in (A) shows a bi-exponential fit (16 h NPT). An example of a bi-exponential fit is also given in (B) (16 h water PT, dashed line). Arrow indicates destabilization time, $\tau_D$

These data can be analysed quantitatively. Unexfoliated graphite particles would be expected to rapidly settle out. Additionally, unstable exfoliated material would also sediment out, but more slowly due to its smaller size. As discussed in Section 4.2.3 on page 47, the concentration of a sedimenting phase should decrease approximately exponentially with time$^{[137]}$ with the time constants associated with the decay being correlated with the size of the particles. Broadly speaking, larger particles would be expected to sediment faster. It follows from this that a system consisting of a stable phase (phase 0) and two sedimenting phases (phases 1 and 2) of differing sizes, should have an optical absorbance varying with time as

$$A = A_0 + A_1e^{t/\tau_1} + A_2e^{t/\tau_2}$$  \hspace{1cm} (5.1)

with $A_0$ representing the absorbance of the stable phase and $A_1$ and $A_2$ represent the initial absorbance of unstable graphene and unexfoliated graphite, respectively. Similarly, $\tau_1$ and $\tau_2$ represent the sedimentation time constants of unstable graphene and unexfoliated graphite, respectively. Such an expression can be fitted to the data in Figure 5.2 and examples are shown in the inset of Figure 5.2A and as a dashed line in Figure 5.2B. This fitting has been applied to all six data sets and the fitting constants can be seen in Figure 5.3A through F. It is important to note that this fitting can only describe the WPT data up to the destabilization time however NPT samples could be described completely.
On applying this bi-exponential fitting, it can be clearly seen in Figure 5.3 B and D that \( \tau_1 \) and \( \tau_2 \) differ significantly in all cases, varying by a factor of \( \sim 10 \). This is strong evidence that two distinct sedimenting phases are present. The time constants associated with the larger graphite flakes, \( \tau_2 \), is also consistent with the TEM shown in Figure 5.1 which shows large graphitic objects at \( t = 0 \) which are absent at \( t = 25 \) hours.

From Figure 5.3 B \( \tau_2 \) is seen to be \( \sim 2 \) hours for WPT samples and \( \sim 8 \) hours for NPT samples. Large, unexfoliated platelets, settling exponentially with these time constants would be mostly settled out after 25 hours and this is reflected in the TEM images. Additionally the \( \tau_1 \) values of \( \sim 20 \) hours for WPT and 120 hours for NPT dispersions are consistent with time constants of between 10 and 220 hours observed for graphene nano-sheets.[70] Finally, the stable component, \( A_0 \), is close to 30\% for NMP and close to 0 for all WPT samples, entirely consistent with our understanding that graphene can only remain stably dispersed in the presence of a suitable solvent.

These sedimentation values were repeated to understand the variability of these measurements and it was found that for nominally identical samples there was limited reproducibility. The relative error associated with the fitting constants from Figure 5.3 is estimated from variability to be as high as 40\%. However despite this high degree of error some conclusions can be drawn. Shown in Figure 5.3 A are the \( A_2 \) values extracted from the fits. \( A_2 \) represents the absorbance arising from unexfoliated graphite at \( t = 0 \) and is proportional to the concentration of graphite remaining in the sample. It can be seen that \( A_2 \) remains approximately the same for both NMP and Water. If we assume sonication results in a fraction of the starting graphite being exfoliated into graphene, this implies that roughly the same amount of graphene is produced in NMP and water. This can be quickly checked by noting that \( A_0 \) and \( A_1 \) represent the absorbance of graphene, both stable (\( A_0 \)) and unstable (\( A_1 \)) against aggregation. For all samples the sum \( A_0 + A_1 \) is between 40\% and 65\%, suggesting again that the same quantity of graphene is produced in both solvents.
5.2 OUTLINING AND TESTING THE PRETREATMENT TECHNIQUE

Figure 5.3: Sedimentation fitting parameters for graphs shown in Figure 5.2 as a function of PT time, $\tau_{\text{PT}}$, in NMP and water: Image (F) shows destabilization time, $\tau_D$ plotted as a function of water pretreatment time with an empirical fit $\tau_D \propto \tau_{\text{PT}}^{-1/2}$. Inset: plot of total preparation time, $\tau_{\text{Prep}}$, as a function of $\tau_{\text{PT}}$.

The sedimentation time constants, however, differ significantly between the water and NMP. In Figure 5.3 B and D $\tau_1$ and $\tau_2$ are considerably longer for NPT samples compared to WPT samples. This difference is significant enough to be larger than the significant relative error and implies that, for both stable and unstable graphene flakes, the flakes present in NMP after sonication are smaller than those found in water. The observation that sonication in a good solvent produces smaller flakes may imply that sonic energy is transferred more effectively to the platelet in the presence of a good solvent and is contrary to the suggestion that the frictional constant felt by nano-objects during sonication is given by the product of the fluid viscosity times particle length.[134] Water and NMP having different viscosities (~1 mPa·s and ~1.7 mPa·s respectively) and while this is significant enough to cause the variation observed in $\tau_2$, the particle size generated by the pretreatment process in NMP differs by more than would be expected were viscosity the sole contributor to this variation.
It can be concluded from this that the frictional stress transfer must depend on the interaction between solvent and nano-object. This is consistent with observations of sonication induced scission of graphene being more effective in NMP[72] than in aqueous surfactant solutions.[75] These results would suggest that while simply supplying sonic energy is sufficient to exfoliate graphite, solvent-graphene interactions are important for efficient exfoliation as well as stabilization. It also suggests that the concentration of dispersed graphene may depend on solvent type in a way that depends on sonication effects and not just solvent–graphene interactions.

With the aim of optimizing this process Figure 5.3F shows the destabilization times, $\tau_D$, for WPT samples as a function of PT time. $\tau_D$ can be clearly seen to fall off smoothly with increasing $\tau_{PT}$. This is empirically fitted to $\tau_D \propto \tau_{PT}^{-1/2}$ as a dashed line. This is important from a processing perspective as a potential processing method would be to perform the sonication pretreatment and to simply let the material sediment out until $\tau_D$. At this point it is a simple matter of decanting the water to yield a wet powder which could be oven dried with the total time for this process simply being $\tau_{Prep} = \tau_{PT} + \tau_D$. As the destabilization time was seen to decrease with pretreatment time a minimum total preparation time, $\tau_{Prep}$, must exist. Plotting the empirical relationship between $\tau_D$ and $\tau_{PT}$ give $\tau_{Prep} = \tau_{PT} + 261 \tau_D^{-1/2}$. This is plotted in the insert of Figure 5.3F and gives a minimum processing time for $\tau_{PT} = 26$ hours. This is given as an example of how the pretreatment process could be optimized for industrial use.

5.2.2.3 Analysis of Pretreated Powders

While the dispersion was quick to sediment in water, NPT samples were stabilized for long times against aggregation. This meant that simply decanting the solvent to leave the powder behind was not possible for both samples and so for consistency both samples were separated from their pretreatment solvents by vacuum filtration. These powders were rinsed with IPA and dried in a vacuum oven to yield, for both solvents, a black powder which was visually reminiscent of graphite powder. These powders were analysed using SEM and Raman spectroscopy.

In Figure 5.4 SEM images can be seen for (A) the graphite starting material used, (B) WPT powder and (C) NPT powder. The starting material consists of large, well-defined
flakes with lateral size of the order of 500 μm. When we turn our attention to the pretreated powders however we can see large quantities of small poorly-defined flakes littering the surface of the samples. In the case of the WPT sample, the large 500 μm flakes are still present although they are covered in large numbers of smaller flakes, broken off the larger flakes by the pretreatment process. If we look to the NPT sample, we are greeted with a similar scene but the process appears to have occurred to a greater extent. While the underlying large starting material can be discerned, they are no longer clearly defined and appear to be dominated by smaller objects. It should be noted that SEM suggests the NPT sample contains a greater quantity of smaller material, in agreement with the sedimentation analyses outlined in the previous section.

Figure 5.4: SEM images of (A) starting graphite powder, (B) water pretreated powder (τPT = 16 h), and (C) NMP pretreated powder (τPT = 16 h). (D) Raman spectra of the starting graphite powder and the pretreated powders.

In Figure 5.4D, the Raman spectroscopy of the pretreated powders is seen alongside that of the starting material. All of these samples can be seen to show a well defined
G band (~1580 cm\(^{-1}\)), a small D band (~1350 cm\(^{-1}\)) and the 2D band can also be seen (~2700 cm\(^{-1}\)). All of these bands would be expected to be visible for graphitic material and the relatively low intensity of the D band suggests that the pretreatment has not resulted in large-scale introduction of defects into the basal plane of the graphite flakes. Both pretreated spectra show a D:G ratio larger than that of the starting material suggesting a smaller average particle size than the starting material which would be expected and is consistent with what was observed in the SEM images.

Analysing these data more closely, the 2D band of the starting material appears to have a “shoulder”, a characteristic trait of Bernal-stacked graphite, occurring at 2690 cm\(^{-1}\).[145] This shoulder is obscured in the pretreated samples as the 2D peak has shifted downwards from 2720 cm\(^{-1}\) to approximately 2700 cm\(^{-1}\). Instead a symmetrical peak is seen with the characteristic shoulder now absent, resembling those seen for few-layer graphene.[72, 145] These Raman spectra suggest that the pretreatment results in a high proportion of re-aggregated graphene indicating that the pretreatment is breaking apart the flakes.

5.2.2.4 Re-dispersion of Pretreated Powders

It has been shown that this pretreatment, both in water and NMP, yields a powder consisting mostly of graphite with considerable evidence of notable quantities of small, re-aggregated graphene flakes. These re-aggregated flakes would be expected to be more weakly bound to each other than the flakes in the starting material and so require less energy to re-exfoliate.[84] More simply, the pretreated powders are expected to exfoliate more easily to yield a dispersion. This was tested for both pretreatment solvents by sonicating them in NMP and removing small aliquots after various re-sonication times. These samples were centrifuged and the dispersed graphene concentration was measured.

The resulting concentration versus time data can be seen in Figure 5.5A for all pretreatment times and solvents. Concentration increases with sonication time for all samples as would be generally expected, however what is interesting is how rapidly concentration is seen to increase with time, with concentrations reaching 1 mg/ml in ~10 minutes for all NPT samples. Previous work using a similar sonic tip and
graphite as a starting powder shows times as long as 2 hours needed to reach the same concentration.[84] At any given re-sonication time it can be seen that NPT samples yield a significantly higher concentration, for all pretreatment times. From this graph it can be seen that, empirically, concentration increases as \( C = A(\tau_R)^{1/2} \), behaviour seen many times in liquid exfoliation of graphite.[70, 72, 84] This was plotted, indicated with the fitted lines seen in Figure 5.5.

![Graph showing concentration as a function of re-sonication time](image)

**Figure 5.5:** Re-dispersion of pretreated powders in NMP. (A) Dispersed concentration, \( C \), of graphene for pretreated powders re-sonicated for various times, \( \tau_R \), in NMP. (B) Fit constant, \( A \), and (C) time to reach 1 mg/mL, plotted versus \( \tau_{pt} \).

The fitting of the data in Figure 5.5A yields \( A \) for each pretreatment time and solvent. This value functions well as a metric to describe the rate of exfoliation and is plotted as a function of pretreatment time, \( \tau_{pt} \). In Figure 5.5B, \( A \) is seen to increase from 0.12 to 0.22 mg mL\(^{-1}\) min\(^{-1/2}\) for the WPT samples, as the PT time increased from 4 to 16 hours. While this increase is exponential, much higher values of \( A \) are found for NPT samples, also increasing exponentially from 0.42 to 1.0 mg mL\(^{-1}\) min\(^{-1/2}\) over the same \( \tau_{pt} \) range. This metric can be applied to previous work to extract \( A \) values and so
compare rate of exfoliation. A sonic bath,[72] for example, has shown A values of $\sim 0.01$ mg mL$^{-1}$ min$^{-1/2}$ with a sonic tip[84] yielding values of $\sim 0.1$ mg mL$^{-1}$ min$^{-1/2}$. Thus it can be clearly seen that the sonication-based pretreatment shown here can increase A, the rate of dispersion, 10-fold compared to sonication of untreated graphite. The rate of exfoliation observed here is also consistent with that seen for re-dispersion of re-aggregated graphene[84] attaining A $\sim 0.46$ mg mL$^{-1}$ min$^{-1/2}$, with this work surpassing that figure for longer pretreatment times in NMP.

This is presented in a more intuitive manner in Figure 5.5C which shows the time taken to reach 1 mg mL$^{-1}$, a reasonably high concentration for pristine graphene in solvent, and is presented as a function of pretreatment time. For both NPT and WPT powders this time falls exponentially with pretreatment time. The best time is seen for the 16 hour NPT sample for which a concentration of 1 mg mL was reached after only 1 minute of re-sonication time. This compares to approximately 90 minutes[84] of tip sonication being required to reach 1 mg mL$^{-1}$ using stock graphite powder in NMP.

![Figure 5.6](image)

Figure 5.6: (A, B) TEM images of graphene flakes prepared by re-sonicating pretreated powders. (C) Raman spectra of the thin films prepared from re-sonicated dispersions.
While this procedure has been shown to be highly effective at facilitating dispersion of graphene, particularly at high concentrations, it is important to confirm that the flakes produced are of similar quality to those produced from stock graphite. That is to say, of similar lateral size and absent of defects introduced into the basal plane of the platelets. Furthermore, particularly in the case of the WPT samples, the extent of aggregation/exfoliation of the flakes was of interest to ensure final dispersions prepared in the manner could be used without detriment. The final dispersions prepared by re-sonicating the pretreated powders were used to prepare TEM grids. Seen in Figure 5.6 A and B are representative flakes seen in these final dispersions. In both cases a large number of well exfoliated flakes could be seen, with the samples being indistinguishable from those prepared using graphite as a starting material.[66, 71, 72, 84]

To further assess the dispersion quality, and in particular the defect density, thin films were prepared using vacuum filtration and these films were studied using Raman spectroscopy. Seen in Figure 5.6C are the resulting data. Both films show a 2D band associated with few-layer graphene with no evidence of the shoulder associated with Bernal-stacked graphite, seen in the stock graphite sample in Figure 5.4D. The D bands of both samples are reasonably small, with mean $I_D/I_G$ ratios of 0.12 and 0.15 for the NPT and WPT films, respectively. While this value is larger than that seen for the pretreated powders, these samples have been centrifuged to remove the larger flakes and these values are completely consistent with micrometer-sized flakes, without basal plane defects having been introduced. This would suggest that the pretreatment has not introduced basal plane defects into the flakes and is consistent with the flakes observed during TEM.

In order to confirm no basal plane defects are being introduced via this process, the Raman spectra were studied in more detail. In order to provide evidence that no defects are introduced into the graphite basal plane during the pretreatments a method from Eckmann et al. is utilised[81, 147]. It was shown that the nature of defects in graphene can be ascertained by comparing the ratio of intensities of the D and D’ bands (the D’ band occurring at ~1620 cm$^{-1}$). The $I_D/I_{D’}$ ratio was characterised for edge defects as ~ 3.5, vacancy and basal plane point defects yielding a higher ratio.
at ~7 and finally sp\(^3\) defects higher again at ~13. All the sample spectra were fitted in order to separate the D’ peak from the larger G peak. This was done by fitting a Lorentzian peak to both the G and D’ peak at 1580 cm\(^{-1}\) and 1620 cm\(^{-1}\) respectively. The resulting data can be seen in figure 5.7, with the outlined regions for defect types plotted. As can be seen, the spectra arising from this pre-treatment method are entirely consistent with edge-type defects, providing evidence that no additional basal plane defects are introduced by this method. Furthermore, the observation that additional basal plane defects are not being introduced is consistent with observations in other studies utilising sonication.[72, 153]

![Graph showing Raman peak intensity ratios](image)

Figure 5.7: Plotting the Raman peak intensity ratios for the pretreated powder (hollow) and final dispersion films (solid) for water and NMP (blue and red respectively)

5.3 FURTHER REFINING THE TECHNIQUE

From the SEM images of the pretreated powders it is clear to see that a large quantity of unexfoliated graphite platelets still remain. Previous work has shown that the removal of these platelets is beneficial when producing extremely high concentration dispersions.[84] In previous work this was achieved using centrifugation, a method that is impractical if one wishes to produce large quantities of material. This was
addressed by means of coarse filtration of the pretreated slurry which yields a black dispersion. The reaggregated graphene powder can then be retrieved using fine-pore vacuum filtration as was used previously. The powder obtained in this manner is closer in appearance to thin films made from filtering graphene dispersions than the starting graphite powder.

The concentration versus time plots shown in Figure 5.5 indicate that the pretreatment procedure is more effective using NMP than water. This however is problematic as NMP is a highly toxic, high boiling point solvent and, due to its affinity for graphene, it is notoriously difficult to remove NMP from graphene layers[154]. This residual solvent makes the material incompatible with many applications and furthermore causes difficulties when evaluating the graphene quality using methods such as XPS.[66, 81]

To extend the applications of the method outlined in this chapter, a facile method to remove residual solvent is needed. In this section one such method to achieve this is outlined allowing production of reaggregated graphene powders with minimal residual solvent. This allows the final powder to be assessed more fully using XPS as well as use of the material without solvent contamination arising from the starting material.

5.3.1 Experimental Procedure

NMP was purchased from Sigma-Aldrich and used as received. Graphite flakes were obtained from the Henglide Qingdao Graphite Company. Reaggregated graphene powder was produced by shearing graphite in NMP at a starting concentration of 100 mg/ml for 90 minutes at 4500 r.p.m. using a Silverson high-shear mixer model L5M fitted with the small square perforated stator. The resulting dispersion was coarse filtered through lab paper to remove large unexfoliated particles before the remaining dispersion was vacuum-filtered through 0.2 micron nylon filter membranes and washed with IPA to yield a re-aggregated powder.
A portion of this powder was then placed in Millipore water and heated to ~70 °C for 4 hours. The powder was again vacuum-filtered to remove the water, washed with IPA and vacuum dried alongside the remaining re-aggregated powder that had not been heat treated in water. The starting graphite, re-aggregated graphene and “water treated” re-aggregated graphene were then all analysed using TGA-MS and XPS.

Mass spectrometer coupled to thermo-gravimetric analysis (TGA-MS) was carried out in collaboration with Kathrin C. Knirsch from the Hirsch group based in FAU Erlangen-Nürnberg using a Netzsch STA 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (MS/EI) with the following programmed time-dependent temperature profile: 30-500 °C with 10 °C/min gradient. The initial sample weights were about ~10 mg, and the experiments were performed under inert gas atmosphere with a He gas flow of 80 mL/min.

X-ray Photoelectron Spectroscopy was performed in collaboration with Dr. Nina Berner from the Duesberg group in Trinity college and was carried out under ultra-high vacuum conditions (< 5x10⁻¹⁰ mbar), using monochromated Al Kα X-rays (1486.6 eV) from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. The starting graphite, pre-treated powder and pre-treated refluxed powder were dried in vacuum at 70 °C for 5 h before insertion into the vacuum chamber. An Omicron CN10 electron flood gun was used for charge compensation and the binding energy scale was referenced to the adventitious carbon 1s core-level in the survey spectra at 284.8 eV. C1s core-level regions were recorded at an analyser pass energy of 15 eV and with slit widths of 6 mm (entry) and 3 mm x 10 mm (exit), resulting in an instrumental resolution of 0.49 eV. After subtraction of a Shirley background, the core-level spectra were fitted with Gaussian-Lorentzian line shapes and using Marquardt’s algorithm.

5.3.2 Results and Discussion

5.3.2.1 Thermogravimetric Analysis - Mass Spectroscopy

In order to evaluate the purity of the reaggregated graphene samples, TGA-MS was performed on the starting material, the material after pretreatment and the material
after pretreatment and water treatment. TGA-MS is a particularly useful tool to analyse residual material in a sample as the weight loss of the TGA can be directly linked to the mass fragments detected using mass spectroscopy. Furthermore the mass fragments are characteristic for the material removed using TGA. Some typical mass fragments of NMP that were detected are shown in Figure 5.8. The only other significant mass fragments detected had a mass/charge (m/z) ratio of 17 and 18 and can be attributed to water.

![Figure 5.8: Detected mass fragments associated with NMP](image)

The TGA traces can be seen in Figure 5.9 in black for the starting graphite (A, B) the reaggregated graphene powder (C, D) and the reaggregated and water treated graphene (E, F). The panels on the left show mass fragments associated with NMP and the panels on the right show those attributed to water. For the starting material no significant weight loss is observed for either, indicating the source graphite is high quality and purity.

The reaggregated graphene however shows a significant, sharp weight loss at 90 °C and a more gradual weight loss for temperatures > 130 °C. The mass spectrometry observed predominantly mass fragments associated with NMP (with the exception of some m/z = 18 at 100 °C) in the temperature range of 50 - 130 °C. The weight loss over this temperature range is ~ 15 % which clearly indicates that NMP is not completely removed by simply filtering and washing the material. The weight loss of 5 % associated with temperatures > 130 °C can be attributed to water from the washing cycles during filtration. While it might seem counter intuitive that water is detached at a higher temperature than NMP this can be explained by the fact that water molecules are comparatively small and are easily trapped between reaggregating
nanosheets. Molecules trapped in this manner have been observed to have higher desorption temperatures.[155]

In contrast to this is the reaggregated graphene sample after the water treatment seen in Figure 5.9 E where the weight loss is much smaller ~ 10 % and, importantly only traces of NMP mass fragments remain. Additionally these fragments are detected at higher temperatures (120 - 250 °C) suggesting that this residual NMP is also trapped between reaggregated nano-platelets and therefore was not removed by the treatment in water. Unfortunately, it is not possible to precisely quantify the residual NMP due to a much higher relative ion current from the water mass fragments. These mass fragments of m/z = 17 and 18 can be seen in Figure 5.9 F overlapping the temperature range where detached residual NMP is detected. Regardless, it is clear that the water treatment has removed the overwhelming majority of the residual NMP from the sample.
To illustrate this, we can analyse intensity ratios of the maximum ion current of the most intense NMP fragment (m/z = 42) and the most intense water fragment (m/z = 18). Before the water treatment the peak ion current with m/z = 42 is a factor of ~3.6 higher than the m/z = 18 fragment of water. Whereas after the water treatment the same mass fragment associated with NMP is just ~0.1 times that of the m/z = 18 water fragment. This further stresses that the total weight loss that occurs in the water treated reaggregated graphene sample is due to water desorption rather than residual NMP.

Figure 5.9: TGA weight loss (black line) with coloured lines indicating mass fragments associated with (left) NMP and (right) water for (A-B) The starting graphite, (C-D) The reaggregated graphene and (E-F) The reaggreagated graphene after water treatment.
### 5.3.2.2 X-Ray Photo-spectroscopy

In order to ascertain the structural quality and integrity of the starting graphite as well as the pretreated graphite samples before and after water treatment, the samples were analysed using XPS. It should be noted that quantitative analysis of the C1s core level spectra is challenging for samples that have been exposed to atmospheric conditions due to adventitious carbon. Furthermore the main sp² component is asymmetric due to energy losses of the photoelectrons emitted from the conjugated carbon network which typically gives rise to a “tail” at higher binding energies. The extent of this asymmetry is strongly dependent on the number of defects in the graphite. In this case however as the stock graphite is known to be of high quality, the same calibration and peak fitting procedure is used as described for HOPG.[156] This validity of this approach is confirmed by the appearance of \( \pi - \pi^* \) shake-up peaks at 291 eV which further confirms the high structural quality of the graphite starting material.

<table>
<thead>
<tr>
<th></th>
<th>C = C</th>
<th>C - C</th>
<th>C - O</th>
<th>C = O</th>
<th>COOH</th>
<th>C - N</th>
<th>C = N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting Graphite</td>
<td>90.8</td>
<td>0</td>
<td>7.37</td>
<td>0.47</td>
<td>0.37</td>
<td>0.53</td>
<td>0.46</td>
</tr>
<tr>
<td>Before Water Treatment</td>
<td>90.64</td>
<td>0.46</td>
<td>4.98</td>
<td>1.53</td>
<td>1.68</td>
<td>0.12</td>
<td>0.59</td>
</tr>
<tr>
<td>After Water Treatment</td>
<td>92.69</td>
<td>0</td>
<td>4.6</td>
<td>0.83</td>
<td>0.73</td>
<td>1.15</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5.1: Relative areas of the fit components of the XPS C 1s core level spectra of the parent graphite and the reaggregated graphene before and after heat treatment in water.
In addition to the main sp² carbon component in the c1s core level spectra, traces were found of C-O, C=O, COOH, C-N and C=N in all spectra including the untreated starting graphite (see Table 5.1 and Figure 5.10). It should be noted that the C-C component is potentially unreliable due to the comparatively high level of asymmetry of the C=C carbon fit component which could partially mask minor contributions.
from C-C. In a somewhat unexpected outcome, the highest content of C=C fitting component was found for the water treated reaggregated material, indicating its high purity. While many of the non C=C fit components can be attributed to NMP for the treated graphite samples, no definite conclusions can be made as they are also found in the starting graphite. The most striking result from the core level spectra is that the C-O component is significantly reduced for both the treated graphene (with and without water treatment) samples compared to the starting graphite. This suggests that, not only has the exfoliation not given rise to more defects in the sp² carbon framework, but that it has in fact partially purified the material.

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>O 1s</th>
<th>F 1s</th>
<th>Cl 1s</th>
<th>Na 1s</th>
<th>N 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting Graphite</td>
<td>97.37</td>
<td>2.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before Water Treatment</td>
<td>91.85</td>
<td>3.89</td>
<td>2.66</td>
<td>0.16</td>
<td>0.44</td>
<td>1</td>
</tr>
<tr>
<td>After Water Treatment</td>
<td>88.74</td>
<td>5.03</td>
<td>4.89</td>
<td>0.58</td>
<td>0.4</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 5.2: Atomic percentages of the elements detected in the XPS survey spectra of the parent graphite and the reaggregated graphene before and after heat treatment in water.

5.4 USING PRETREATED GRAPHITE TO REDUCE SCATTER IN SOLVENT SURVEY

Having outlined a method of pre-treating graphite in order to ease its redispersion and a further method of removing the residual solvent, it was of interest to see how this material compared to previous studies performed using raw graphite. Previous studies have shown the material is largely in agreement with solubility theory which has been used successfully to describe liquid exfoliated samples as well as to predict stabilising solvents for the material being dispersed.[66–68, 71]

The material obtained from pretreatment is demonstrably easier to exfoliate. It is hoped that this might reduce experimental variability associated with sonication and the resultant sample concentration might be more reproducible. Furthermore it is hoped that this might reduce the scatter seen when these surveys have previously been studied using solubility theory. The further step of “refluxing” the pretreated powders
is of importance here as it reliably reduces residual NMP, ruling out a stabilising effect associated with a “good” solvent and it is hoped this too will reduce the scatter seen in this solvent survey. It is hoped that this will further cement the validity of using solubility theory to describe these dispersions as well as allowing more conclusions to be drawn from the resulting fittings.

5.4.1 Experimental Procedure

Graphite was sourced from Sigma-Aldrich (Graphite Flakes product no. 33246) and pre-treated before use. All solvents (≥99% purity) were purchased from Sigma-Aldrich and used as supplied. De-ionised water was obtained from an on-site in-line water deionizer (ELGA LabWater Vision 250). All samples were sonicated using a GEX600, tapered tip probe at 20% maximum amplitude. The sonic tip was set to stop once 5 kJ had been delivered to the samples while being careful to ensure that the energy was delivered to the samples steadily without excessive heating. Centrifugation was performed at 4000 rpm for 120 minutes using a Hettich Mikro 220R, a centrifugation regime that was selected due to the concentration saturation of the most viscous solvent.

Pre-treatment was performed by shearing the graphite at 100 mg/ml in 2.5 L of NMP at 6000 rpm for 90 minutes. The samples were then coarse filtered to remove large unexfoliated aggregates and the powder was then placed in deionised water at approximately 70 °C for 4 hours. This work was carried out in collaboration with Ivan Caffrey and Auren Ferguson in Prof. Bergin’s group in Trinity College Dublin. Solvents were selected from the 2010 study by Hernandez et al.\cite{71} This list of solvents was vetted for solvents known for instability, extremely high viscosity (>5 mPa s), and highly toxic solvents. This was done in order to reduce the scatter caused by solvent degradation and inadequate centrifugation for high viscosity solvents. The full list of solvents used and their respective properties can be found in a table in the appendix for this section.
5.4.2 Results and Discussion

We firstly look at the dispersed graphene concentration as a function of solvent surface energy, as has been studied previously\cite{66,67}.

![Graph showing dispersed graphene concentration versus solvent surface energy.](image)

This is very similar to what has been seen previously for graphene and other layered materials; a broad peak centred at approximately 70 mJ/m² with significant scatter occurring throughout. A number of solvent blends were attempted however the samples produced had very poor reproducibility and no information could be obtained from the resulting plots.

As has been done previously,\cite{68,71} these dispersions can be studied using Hansen solubility parameters. This separates Figure 5.11 into three separate graphs of concentration versus solvent dispersive, polar and hydrogen bonding parameter seen in the following Figure.
These graphs do not show significant improvement on those seen in previous solvent studies as much scatter is still present in the data. However, it is important to note that the theory predicts that all 3 parameters must be taken into account, explaining why many samples are found below their expected value for the parameters taken on their own. In order to combine the parameters, we combine them into a single term, $R^2$

$$R^2 = (\delta_{D,S} - \delta_{D,G})^2 + (\delta_{P,S} - \delta_{P,G})^2 + (\delta_{H,S} - \delta_{H,G})^2$$

where $\delta_D$, $\delta_P$, $\delta_H$ are the Hansen dispersive, polar and hydrogen bonding parameters with the subscripts $S$ and $G$ denoting those for solvent and graphene flake respectively. The Hansen solubility parameters have been predicted to scale\cite{119,120} as follows

$$\phi_N \propto e^{\left(-\frac{v_N}{3RT}(R^2)\right)}$$

where $\phi_N$ is the volume fraction of the dispersed phase, $v_N$ is the molar volume of the dispersed phase, $R$ is the gas constant and $T$ is the temperature.

However the parameter values for $D,P,H$ for graphene are unoptimised and we have largely been limited to the assumption that the best solvent has the same parameters as graphene. Using all the solvents tested we can refine these by using a simple script to run through all the possible parameter combinations in order to find the the three parameters that agree most closely with the theory, in that the returned plot is the most linear and this is shown in Figure 5.13.
This script returns $\delta_D = 19 \text{ MPa}^{0.5}$, $\delta_P = 9.1 \text{ MPa}^{0.5}$, $\delta_H = 3 \text{ MPa}^{0.5}$ for graphene, which differ significantly from the values assigned previously ($\delta_D = 18 \text{ MPa}^{0.5}$, $\delta_P = 9.3 \text{ MPa}^{0.5}$, $\delta_H = 7.7 \text{ MPa}^{0.5}$). While again, much scatter is present, the theory is followed returning a linear graph with a negative slope of $m = -0.09491$. If we look to equation 5.3, we see $m \sim -\frac{v_N}{3RT}$ and solving for $v_N$ we get $v_N = 693.63 \text{ m}^3\text{mol}^{-1}$. This value is at the very least, of the correct order of magnitude to the expected value; if we assume a flake of 1 micron in lateral size and a mean thickness of 3 layers we get a molar volume of $\sim 602 \text{ m}^3\text{mol}^{-1}$ showing the samples are consistent with solubility theory.

5.5 Conclusions

In this chapter a facile pretreatment has been outlined capable of producing graphite powder that can redispersed at higher concentrations and in less time, using less energy to redisperse. This technique involves sonication in solvents and has been demonstrated to be effective using water, a known poor solvent for graphene, in addition to being effective using known stabilising solvents for graphene. However,
the resulting material is dependant on the solvent used, in that the size distribution of
the resultant dispersion varies significantly between NMP and water. Curiously it was
observed that while the majority of material sedimented out of the water pretreatments,
aggregation and sedimentation was below expected levels when considering energy
minimisation within the dispersion.

The powder produced in this manner was demonstrably easier to redisperse, reaching
a concentration of 1 mg/ml in just 1 minute, a concentration that normally would
take ~ 90 minutes to reach using untreated graphite. While this level of redispersibility
is not seen using water, water presents considerable advantages from a processing
standpoint in that the pretreated graphene may be collected using simple sedimentation
in addition to water being non-toxic and significantly cheaper. That this pretreatment
is effective using water allows the solvent used in the process to be chosen depending
on the final application. This pretreatment technique is potentially valuable for prepar-
ation, transport and sale of graphitic material with the aim of producing and using
graphene in a final application.

We have further refined this technique to show that NMP may be largely removed
by an additional, simple processing step, consisting of placing the material in hot
water for a period of four hours. The final material was studied using TGA-MS and
XPS showing that not only was the majority of residual NMP removed but the final
purity and defect density of the material was not affected negatively and was, in some
ways, improved over the starting material. This pretreatment and solvent removal
technique was then used to reduce scatter in a solvent survey and was shown to
follow the expected solubility theory closely. While no significant improvement was
noted and experimentation into using this material to study solvent blends was largely
unsuccessful, this pretreatment technique was, again, not seen to negatively affect the
expected behaviour when dispersing the material in a variety of solvents.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_D$ (MPa$^{0.5}$)</th>
<th>$\delta_P$ (MPa$^{0.5}$)</th>
<th>$\delta_H$ (MPa$^{0.5}$)</th>
<th>Surface Energy (mJ m$^{-1}$)</th>
<th>Average Dispersed Concentration (mg/ml)</th>
<th>Standard Deviation (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone</td>
<td>17.8</td>
<td>8.4</td>
<td>5.1</td>
<td>63</td>
<td>(mg/ml) 0.03709</td>
<td>0.00519</td>
</tr>
<tr>
<td>N-methyl-pyrrolidone (NMP)</td>
<td>18</td>
<td>12.3</td>
<td>7.2</td>
<td>73.2</td>
<td>0.03365</td>
<td>7.77817x10$^{-4}$</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>18.8</td>
<td>12</td>
<td>3.3</td>
<td>63.7</td>
<td>0.02681</td>
<td>0.00625</td>
</tr>
<tr>
<td>Ethanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>51.39</td>
<td>0</td>
<td>4.0695x10$^{-4}$</td>
</tr>
<tr>
<td>Water</td>
<td>15.5</td>
<td>16</td>
<td>42.3</td>
<td>102.5</td>
<td>0.00407</td>
<td>3.99686x10$^{-4}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>18</td>
<td>1.4</td>
<td>2</td>
<td>57.52</td>
<td>1.17205x10$^{-4}$</td>
<td>4.03266x10$^{-4}$</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>15.8</td>
<td>5.3</td>
<td>7.2</td>
<td>53</td>
<td>0.00229</td>
<td>0.00243</td>
</tr>
<tr>
<td>Heptane</td>
<td>15.3</td>
<td>0</td>
<td>0</td>
<td>49.14</td>
<td>0</td>
<td>3.44651x10$^{-4}$</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7</td>
<td>52.7</td>
<td>9.37182x10$^{-4}$</td>
<td>7.74098x10$^{-4}$</td>
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<tr>
<td>Hexane</td>
<td>14.9</td>
<td>0</td>
<td>0</td>
<td>47.4</td>
<td>0</td>
<td>0.00278</td>
</tr>
<tr>
<td>Dibenzyl ether</td>
<td>19.6</td>
<td>3.4</td>
<td>5.2</td>
<td>68.8</td>
<td>0</td>
<td>0.00458</td>
</tr>
<tr>
<td>N-ethyl-pyrrolidone (NEP)</td>
<td>18</td>
<td>12</td>
<td>7</td>
<td>-</td>
<td>0.00168</td>
<td>3.95774x10$^{-4}$</td>
</tr>
<tr>
<td>N-formyl piperidine (NFP)</td>
<td>18.7</td>
<td>10.6</td>
<td>7.8</td>
<td>-</td>
<td>0.00148</td>
<td>0.00125</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>16</td>
<td>7.2</td>
<td>5.9</td>
<td>52.8</td>
<td>0</td>
<td>2.52522x10$^{-4}$</td>
</tr>
<tr>
<td>Vinyl pyrrolidone (NVP)</td>
<td>16.4</td>
<td>9.3</td>
<td>5.9</td>
<td>71.6</td>
<td>0.01565</td>
<td>0.00157</td>
</tr>
</tbody>
</table>

Table 5.3: List of solvents employed showing solvent parameters and measured dispersed concentration
RHEOLOGICAL BEHAVIOUR OF LIQUID PHASE EXFOLIATED GRAPHENE DISPERSIONS

6.1 INTRODUCTION

During the course of this work, liquid phase exfoliation (LPE) using high-shear mixing was demonstrated by Paton et al.\cite{Paton2011} However, the exact mechanism of this process and the underlying flow requirements were not well understood. Understanding the behaviour of platelets during the delamination process, under precisely controlled conditions, is required to gain further insight into this process. A rheometer equipped with a Couette geometry is particularly useful as the shear conditions within the gap are almost perfectly uniform allowing high shear rates to be applied to graphene/solvent mixtures in a highly controlled environment. The exfoliation of graphite in NMP was studied using this method to investigate the shear rate dependence of graphene exfoliation with a particular focus on the onset of turbulence and its necessity for exfoliation.

Of further interest are the properties of the dispersions themselves. LPE to produce and process materials for conductive inks,\cite{Bartlett2010} coatings, composites and energy storage,\cite{Huang2010} a robust understanding of the rheological properties of the dispersions is required. In general, the rheological properties of extremely high concentration dispersions is controlled by the microstructure of the stress-bearing network that is formed by the particles in the dispersion and the nature of the inter-particle interactions. Unlike carbon nanotubes (CNTs),\cite{Gomez2008, Andriotis2008} the relationship between the microstructure and rheology of suspensions of graphene platelets beyond the rigidity percolation, the point at which this network forms, has not yet been investigated. While comparisons could be made between the high-aspect ratio pristine graphene flakes and graphene oxide (GO) or clay dispersions, the resulting structures and rheology of clay and GO
are highly sensitive to surface charges present on the platelets.\cite{44, 47, 123, 160} Pristine graphene platelets on the other hand, interact predominantly through Van der Waals interactions and, as a result, provide a well defined model system to study stress bearing networks of high aspect ratio, weakly interacting platelets.

In this chapter, high concentration graphene dispersions in 1-methyl-2-pyrolidone (NMP) are produced using the pretreatment procedure presented in detail in Chapter 5. These dispersions form microstructures which exhibit a soft, glassy rheological response\cite{161} and this can be probed using rheological measurements.

6.2 **Experimental Procedure**

NMP and graphite were both purchased from Sigma Aldrich. All shear measurements were performed using an Anton Paar MCR 301 rheometer. Shear exfoliation was investigated using a cc28.7 concentric cylinder setup. The Couette geometry has a gap width of 0.1 mm and is capable of shear rates of up to 45,270 s$^{-1}$. Samples were prepared by placing 1.8 g of sieved graphite in 25 ml of NMP in the Couette cell cup and setting the rheometer to a well-defined speed (and so shear rate). This allowed two sets of measurements to be performed; concentration as function of time at a fixed shear rate (45,270 s$^{-1}$) and concentration as a function of shear rate for a fixed time (60 minutes). The resulting dispersions were centrifuged at 2000 rpm for 45 minutes (Hettich Mikro 220R) and the supernatant (generally dark, indicating dispersed material) was collected. Concentrations were measured using absorption spectroscopy (Varian Cary 50) using an extinction coefficient of 3620 mg mL$^{-1}$ m$^{-1}$.\cite{72} Raman was performed on films made from these dispersions and TEM grids were prepared to characterise the extent of exfoliation of the dispersed material.

The graphene suspensions were prepared via LPE in NMP, for which a viscosity of $2.2 \pm 0.1$ mPa s was measured for the solvent used in this work. This is somewhat larger than the literature value of 1.8 mPa s, likely due to water absorption during sample preparation. To study the effects of interparticle interactions, highly concentrated dispersions of graphene were required. To make sufficient quantities of these
high concentration suspensions to test using the rheometer, the method described in the previous chapter was employed. Graphite was first exfoliated in NMP using shear exfoliation in a Silverson high-shear mixer model fitted with the small square perforated stator. The unexfoliated material was removed using coarse filtration with the exfoliated material collected via vacuum filtration. This reaggregated exfoliated material is then redispersed in fresh NMP using tapered tip sonication (Vibracell, GEX750) at 40% amplitude for 20 minutes.

The dimensions of the exfoliated graphene flakes were measured using TEM-based statistics. We found a typical a length of $D = 1 \pm 0.5 \, \mu m$ with a sample size of $>50$ flakes. Flakes produced in this manner have been shown to have a mean thickness of between 3 and 8 layers,[71, 72, 84] corresponding to a thickness of $h = 1 - 3 \, nm$ (see Figure 6.1 on page 112 in the appendix of this chapter). The final graphene concentration in our samples ranged from 1 to 39 mg ml$^{-1}$, which corresponds to volume fractions between $4.8 \times 10^{-4}$ and 0.019.

The viscoelastic measurements are performed in a plate–plate geometry. The diameter of the plate and the gap size are 50 mm and 0.5 mm, respectively, allowing oscillation measurements down to shear stresses of $0.1 \, mPa$. The samples were bath-sonicated for 60 minutes prior to loading in the rheometer to ensure a well-dispersed suspension. To avoid shear alignment, the samples were not pre-stressed. To check that the samples have settled into an equilibrium, we performed consecutive oscillatory strain sweeps which were highly reproducible. The suspensions were stable on the order of days and, while phase separation was observed after 1 week, the samples were considered stable over experimental time-scales. We used the same geometry to measure the viscosity up to strain rates of $\dot{\gamma} = 200 \, s^{-1}$. For concentrations below 4 mg/ml, we use a Couette geometry to measure the viscosities.
6.3 RESULTS AND DISCUSSION

6.3.1 Investigation of Shear Exfoliation

When considering the main method of LPE, sonication, the expectation was that localised, turbulent regions were responsible for exfoliation. However, initial results using the high-shear mixer indicated that turbulent energy dissipation might not be necessary[81] and so this was investigated using the rheometer. Shown in Figure 6.1 is the dispersed concentration after centrifugation of graphene as a function of time with the rheometer supplying the maximum shear rate (45,270 s\(^{-1}\)). The material is dispersed with concentration increasing as \(~ t^{0.69}\) which closely compares to that seen using the high shear mixer of \(t^{0.66}\).[81] This maximum shear rate corresponds to a Taylor number of ~ 440 which is well below the critical value of 1700 where Taylor instability appears, corresponding to a Reynolds number (Re) of \(Re_{\text{Couette}} = 275\). This critical point represents the transition from purely laminar flow to periodic secondary flow in a couette.[162] One report suggests a Taylor-like instability above \(Re_{\text{Couette}} = 128\)[163] (corresponding to a shear rates above \(2.1 \times 10^4\) s\(^{-1}\)), meaning that the presence of any secondary flow cannot be excluded completely. However, exfoliation is nonetheless observed at shear rates far below that required for fully developed turbulence. The dispersed material was confirmed to be exfoliated few-layer graphene through TEM and Raman performed on films produced from the dispersions. The sediment produced by centrifugation was also studied for various shear rates using SEM. These are presented in the appendix for this chapter.

The shear-rate dependence of exfoliation is of particular interest as it has the potential to reveal information about the exfoliation mechanism. This is shown in Figure 6.2 for a range of shear rates between \(~ 200\) s\(^{-1}\) and \(45,000\) s\(^{-1}\). The most striking result is that material was only successfully dispersed at shear rates above \(~ 10^4\) s\(^{-1}\). This minimum shear rate is low enough that exfoliation can occur within the laminar flow regime \((10^4\text{ s}^{-1} \leq \dot{\gamma} \leq 2.1 \times 10^4\text{s}^{-1})\), indicating that turbulence is unnecessary for successful exfoliation. This “shear min” was found to agree with that found using the high shear
mixer,[81] suggesting the exfoliation mechanism is similar for both methods. Above this shear min. the concentration increases rapidly with increasing shear rate with a factor of 10 increase in dispersed concentration when increasing the shear rate from $10^4$ to $4 \times 10^4$.

Having gained an insight into the exfoliation of graphite to form graphene under shear conditions, we focus our attention on studying the rheological behaviour of the graphene dispersions themselves. Low concentration dispersions would be expected to be a good analogue for LPE samples as they are being produced and high concentration samples might allow us to understand the energetics of these dispersions with regards to inter-flake interactions leading to aggregation.

### 6.3.2 Yielding and Flow of Graphene Dispersions

#### 6.3.2.1 Sample Properties

At first, the low concentration regime was investigated. However, this proved problematic as the sample viscosity in the low concentration regime is dominated by the
solvent viscosity and the viscosity of NMP was seen to vary significantly with the water content absorbed from the atmosphere. The resulting scatter (as can be seen in the low concentration measurements in Figure 6.3) made measurement in the Einsteinian regime impossible using NMP and so the study moved focus to higher concentrations where inter-particle forces contribute significantly to the measured viscosity.

When measuring high concentration samples, the first aim was to determine the critical concentration $c_c$ at which the rigidity percolation occurs (Figure 6.3 on the next page). At this point the effective viscosity of the suspensions increases dramatically and the storage modulus $G'$ becomes non-zero. The dispersion viscosity increased very little up to 4 mg ml$^{-1}$ at which point it increases dramatically as $\sim c^{2.2}$. This critical concentration $c_c$ and the corresponding critical volume fraction $\phi_c$ can be determined more accurately by measuring the storage modulus plateau ($G'_0$) in the linear response regime of a strain sweep. An example of this appears in the inset of Figure 6.4. The strain sweep measurements were obtained at a constant frequency of 1 Hz and were measured for all concentrations above $c_c$. In the linear, low-strain regime a steady storage modulus ($G'$) is exhibited, greater than the loss modulus ($G''$). At a certain strain value (the yield strain) $G'$ decreases until eventually the sample is fluidized as
Figure 6.3: Viscosity vs graphene concentration measured at $\dot{\gamma} = 200 \text{ s}^{-1}$. Horizontal and vertical lines denote solvent viscosity (2.2 mPa s) and critical concentration (4.2 mg ml$^{-1}$) respectively. Inset shows representative TEM image of graphene flake from the dispersions being tested.

G"$>$G'. This is a viscoelastic behaviour typically seen in soft, glassy materials. The variation of this plateau was measured and is plotted as a function of volume fraction minus the critical volume fraction and in Figure 6.4. The storage modulus plateau is expected to scale as $G'_0 \propto (\phi - \phi_c)^\alpha$ beyond the percolation threshold, where $\alpha$ is the percolation exponent. This power law was fitted to the data, yielding $\alpha = 3 \pm 0.1$, $\phi_c = 2 \pm 0.005 \times 10^{-3}$, or $c_c = 4.2 \pm 0.1 \text{ mg ml}^{-1}$.

As discussed in Section 3.3 on page 31, the onset of rigidity is strongly dependent on the dimensions of the particles in a suspension. This has been studied for conduction percolation[164] as well the onset of solid-like behaviour for silicate nanocomposites.[165, 166] The sample dispersions can be modelled as randomly oriented disc-shaped platelets allowing the percolation threshold to be estimated once the platelet dimensions (diameter, $D$ and thickness, $h$) are known. These disks exist in hypothetical spheres of the disc’s diameter. Although the discs are free to rotate within this sphere below percolation, as the concentration increases the dispersed spheres will eventually touch and form a percolating network. The critical volume fraction at
which the spheres begin to overlap ($\phi_0$) is therefore the ratio of the disc volume to the embedding sphere with a pre-factor ($\phi_j$) to account for interstices between spheres giving $\phi_c = \phi_j 1.5h/D$.

Ren et al. have argued\cite{165} that $\phi_j$ is simply the percolation threshold for overlapping spheres (0.30). However, with the system being studied in the liquid phase, a higher packing fraction such as random close packing (0.64) might be more appropriate. With an aspect ratio ($h/D$) of the order of $10^{-3}$, $\phi_j = 0.64$ returns a value approximately a factor of two smaller than the value we obtained experimentally. It is likely that these estimates are a lower bound, as simulations of overlapping, monodisperse ellipsoids in the extreme oblate limit ($h/D \sim 10^{-3}$), a close approximation for discs, have shown that the percolation threshold for conduction is somewhat higher at $1.27 h/D$\cite{130}. Further experiments on the conduction percolation threshold of graphite platelets\cite{164} have found critical concentrations in the range of $1.3 h/D$ to $1.7 h/D$. Furthermore, conductivity percolation is not indicative of mechanical stability in the network. Mechanical stability, which is required for a finite yield stress, requires the platelets have a minimum number of contacts on average. Recent work on jammed

Figure 6.4: Storage modulus plateau vs relative packing fraction measured at 1 Hz. Line indicates fitting to power law $G'_0 \propto (\phi - \phi_c)^3$, inset shows typical strain sweep with $G'(\text{squares})$ and $G''(\text{circles})$.
packings of frictional ellipsoids have shown that, on average, each particle must have 4 contacts in three dimensions.[167] It would therefore be expected that the onset of rigidity would occur at somewhat higher volume fractions than $\phi_0$. Finally, this value will be higher if the platelets become partially aligned at higher concentrations, meaning that modelling the dispersed particles as spheres becomes less valid.

While values obtained for $\phi_j$ range from 0.3 to 1.13, there is agreement in the literature that the critical concentration for rigidity percolation scales with the aspect ratio $h/D$. For simplicity we will set $\phi_j = 1$ which will yield $\phi_0 = 1.5h/D = 1.5 \times 10^{-3}$, while noting that small deviations from this value reflect the details of the network structure and are beyond the scope of this study. This is valid as the exact prefactor in $\phi_0$, which is of order 1, isn’t crucial for modeling the yield strain in Equation 6.1.

The measured percolation exponent, $\alpha = 3.0 \pm 0.1$, is close to what has been found for graphene oxide composites.[160] In these GO/PMMA composites the value for $\alpha$ was found to be sensitive to the extent of oxidation of the platelet, ranging from 2.4 to 3.1 as the surface oxidation was reduced. Other studies have investigated clays, such as Laponite, and carbon nanotubes, both of which exhibit lower exponents, with $\alpha = 2.35$[123] observed for laponite and CNT suspensions exhibiting $\alpha = 2.3 \pm 0.1$[158].

These results can be compared to rigidity percolation simulations that incorporate both central and bond bending forces.[168, 169] For example, in the absence of bond bending forces, with bonds only stretching and contracting, the percolation exponent is $\alpha = 2.1 \pm 0.2$. This compares well to CNT suspensions implying they correspond to central force networks. For systems that resist bond bending as well, this exponent is predicted to be $\alpha = 3.75 \pm 0.1$. The value obtained from our graphene samples, $\alpha = 3.0 \pm 0.1$, is clearly larger than those for purely central force systems suggesting the presence of bending forces. Intuitively, graphene platelets may form spatially extended contacts compared to the point like contacts formed by rods. However $\alpha$ is also not close to 3.75 either, which suggests that a significant fraction of the bonds are point-like. This can be understood as a platelet forming a bond with either its edge or corner, where the latter corresponds to a point-like bond.

The non-linear rheological response of the samples were measured as seen in the inset of Figure 6.4 showing a typical shear sweep. At low strain, the response is linear
and mostly elastic ($G' >> G''$) as indicated by the plateau of the moduli. At larger strains the sample fluidizes as the structure yields and the yield strain ($\gamma_c$) is defined here as the point at which $G'$ has decreased by a factor of 10. This is illustrated in Figure 6.5 where the storage moduli, normalised by the storage modulus plateau value, collapse onto a master curve for various $\phi$ when plotted vs $\gamma / \gamma_c$. In the inset of Figure 6.5 it can be seen that $\gamma_c$ is inversely proportional to $\phi$ which is analogous to what has been seen with CNTs$^{[158]}$. Close to $\phi_c$ however, the yield strain appears to plateau around 0.5.

6.3.2.2 A Simple Model to Understand Sample Behaviour

The yield strain of a sample depends on the internal microstructure which in turn depends on the particle volume fraction. Below the yield strain, the bonds between particles respond elastically and the response is determined by the energetics of bond bending/stretching and potentially the flake stiffness. At larger strains however, these bonds are broken and the response becomes non-linear. For the sample to become fluidised, the flakes must rotate through angles large enough to disentangle them from...
the bond network. To understand why the yield strain varies with packing fraction, a model is employed that is analogous to that proposed by Hough et al. for CNT’s.\[158\]

![Diagram showing the graphical illustration of a disc representing a graphene platelet, embedded in an ellipsoid to estimate pore size.](image)

Figure 6.6: (a) Graphical illustration of disc representing graphene platelet, embedded in an ellipsoid to estimate pore size. (b) Side view of graphene platelet rotated by an angle $\theta_{\text{max}}$.

The flakes in the dispersion will assemble into some disordered network with an average mesh size $\xi$. The mesh size can be related to the packing fraction $\phi$ by embedding the flakes into a packing of oblate ellipsoids with semi-axes $D/2$, $D/2$, and $\xi/2$ as can be seen in Figure 6.6 (a). At the rigidity transition, the packing fraction corresponds to the flakes being embedded in spheres. If we apply the approximate flake dimensions from earlier, discs of diameter $D$ and thickness $h$, the packing fraction becomes $\phi = 3h/2\xi$, where, at $\phi_c$, $\xi = D$ which gives $\phi_c = 3h/2D = 1.5 \times 10^{-3}$ as before.

To understand the yield strain, we must estimate the maximum angle of rotation required to separate the platelets in order for fluidization to occur. For CNT’s it has been shown\[158\] that the arc length of the maximum angle, $\theta_{\text{max}}$, corresponds to the mesh size assuming an affine deformation and stiff particles. Applying this assumption, the maximum angle can be estimated as follows

$$\gamma_c = \tan \theta_{\text{max}} \approx \frac{\xi}{\sqrt{D^2 - \xi^2}} = \frac{3h}{2D \sqrt{(\phi^2 - \phi_c^2)}}$$

as $\xi = 3h/2\phi$ and $D = 3h/2\phi_c$ and this is illustrated in Figure 6.6 (b). Although this equation fits the data remarkably well, it is important to note that the divergence of
the yield strain as $\phi \rightarrow \phi_c$ is obviously unphysical. Regardless, this simple, local model captures the behaviour of the yield strain very well for $\phi$ far from $\phi_c$.

Turning our attention to the shear stress measured as a function of strain amplitude at a constant frequency (1 Hz). In Figure 6.7 the oscillatory strain sweeps for various volume fractions are shown. At low strains, the stress increases linearly up to the yield point and then starts to plateau. This yield strain corresponds to rigidity loss due to bond breaking as the sample is sheared. Therefore the corresponding yield stress $\sigma_y$ could be used to estimate the bond energy, $E_b$, between the flakes, assuming this quantity is $\phi$ independent. This analysis has previously been performed to obtain the interaction energy between CNT’s\cite{158} and colloidal spheres\cite{170}. The $\phi$ dependence of $\sigma_y$ can be inferred from the elastic response of the samples. This elastic response continues up to the yield point and so the yield stress scales as $\sigma_y \sim G'_{0}\gamma_c$. However, as previously shown, $G'_{0} \propto (\phi - \phi_c)^3$ and $\gamma_c \propto 1/\sqrt{\phi_2 - \phi_c^2}$ so we can write $\sigma_y \propto (\phi - \phi_c)^3(\phi^2 - \phi_c^2)^{-0.5}$.

The elastic energy density stored at the yield point is $E = 0.5G\gamma_c^2 = 0.5\sigma_c\gamma_c$. This can be used to extract a bond energy $E_b$, assuming all bonds (or a fixed fraction thereof) are broken at the yield point. If we assume a bond density $n_b$ then we can write $E_b = E/n_b$ and this can be expanded to

$$E_b = \frac{\sigma_y\gamma_c}{2n_b} \quad (6.2)$$

For $E_b$ to be $\phi$ independent the bond density must scale as $\sigma_y\gamma_c \propto (\phi - \phi_c)^3/\sqrt{\phi_2 - \phi_c^2})$. In order to obtain the prefactor $n_b$ the bond density can be expressed as the product of the number density $n_n$ and the average number of bonds per particle $z$. The number density is simply $n_n = \phi/V_g$, where $V_g$ is the platelet volume $D^2h$. Therefore, the excess bond density (beyond $\phi_c$) scales as $(\phi - \phi_c)/D^2h$. It follows that $z$ scales as $(\phi - \phi_c)/(\phi + \phi_c)$ with some unknown prefactor. However, simulations of other disordered jammed systems have shown that this prefactor is of order 1.\cite{171} Combining this, and substituting equation 6.1 into equation 6.2 yields

$$E_b = \sigma_y \frac{3Dh^2(\phi + \phi_c)^{0.5}}{4(\phi - \phi_c)^{2.5}} \quad (6.3)$$
Interestingly, if the yield strain is fitted using an empirical power law, $\gamma_c \propto (\phi - \phi_c)^{-0.8}$, instead of equation 6.1, then $z \propto (\phi - \phi_c)^{0.4}$. The exponent is close to 0.5, such as is found in sphere packings.\[167, 171\] As before, it is important to note that these equations only hold for large $\phi$ as one would expect a finite bond density and yield strain at $\phi = \phi_c$.

This can be used to obtain an estimate for the bond energy in terms of $k_B T$ by rescaling the shear stress, $\sigma 3Dh^2(\phi + \phi)^{0.5} / 4k_B T(\phi - \phi_c)^{2.5}$ and plotting it versus the strain normalised by the yield strain. This can be seen in Figure 6.7 (b) and shows an excellent collapse of the data onto a master curve. A plateau develops at approximately 20 $k_B T$. This energy may be compared to estimates of the van der Waals bonding energy between bonding graphene flakes which have been shown to have a surface energy of $\sim 70$ mJ m$^{-2}$. The bond energy is dependent on the geometry of the bond as
bonds along an edge will have a greater surface area and so ultimately greater energy. Bonds across an edge will have an area of \( \sim hD \) yielding a bond energy of \( 1.7 \times 10^4 k_B T \) whereas a point-like contact will have an area of \( \sim h^2 \) giving a bond energy of \( 17 k_B T \). The bond energy measured is close in magnitude to the latter and so we conclude that the bonds are point-like with a limited spatial extent. However, they are not purely central force in nature as indicated by the percolation exponent.

Finally the rheological behaviour for our samples under steady-shear can be measured as a function of strain rate. These can be seen in Figure 6.8. Shear thinning is observed for all concentrations, as might be expected. However, a small plateau is seen around \( \dot{\gamma} = 10 \text{ s}^{-1} \), with the exception of the 5 mg ml\(^{-1}\) sample where the plateau is seen at 1 s\(^{-1}\). At high shear rates the measured viscosity tends towards the solvent viscosity [172] which is likely due to shear alignment of the platelets.

This can be understood by utilising a relaxation ansatz to calculate the steady shear viscosity at low shear rates using the storage modulus and yield strain. This method approximates steady shear as a sequence of elastic deformations that dissipate their stored energy in irreversible microscopic processes on a characteristic timescale \( t_r \) [173] In the case of the graphene dispersions being studied, this refers to the inter-flake bonds breaking at the yield strain. After the flakes are separated, the bonds quickly reform due to thermal motion, assuming that the thermal timescale \( \tau \) is much shorter than the deformation timescale \( \dot{\gamma}^{-1} \), i.e. \( Pe = \dot{\gamma} \tau \ll 1 \). For high aspect ratio graphene flakes the most relevant timescale is that of rotational diffusion [174] where \( \tau = 4\eta_s D^3/3k_B T = 0.7 \text{ s} \), again approximating the flakes as discs of diameter \( D \).

The apparent viscosity, that is to say the shear-rate dependant viscosity, of the graphene dispersions can be represented by \( \eta \approx G_0 t_r \). In this instance, \( t_r \) is the time between consecutive yielding events and so is simply \( t_r = \gamma_c / \dot{\gamma} \). Therefore the viscosity becomes \( \eta \approx G_0 \gamma_c / \dot{\gamma} \) where we can use an earlier substitution \( \sigma_y \sim G_0 \gamma_c \) and substitute equation 6.3 value for the yield strain giving

\[
\eta \approx \frac{4E_b(\phi - \phi_c)^{2.5}}{3h^2D(\phi - \phi_c)^{0.5}} \frac{1}{\dot{\gamma}}
\]  

(6.4)
6.3 Results and Discussion

Figure 6.8: (a) Apparent viscosity versus Peclet number for various graphene concentrations: (note; legend applies to both figures). (b) Rescaled viscosity from (a) vs strain rate with fitting showing $1/\dot{\gamma}$ behaviour predicted by relaxation ansatz.

and this is tested in Figure 6.8 (b) by rescaling the measured viscosity plotted versus the strain rate. The rescaled viscosity can be seen to scale well with the predicted $1/\dot{\gamma}$ behaviour with the exception of the 5 mg ml$^{-1}$ sample which is very close to $\phi_c$ where the scaling is likely to break down as noted before. It is also worth noting that this scaling continues beyond $\text{Pe} \gg 1$, where dissipation is mainly viscous and not simply bond breakage within the sample microstructure, for samples far above the critical volume fraction $\phi_c$. 
6.4 CONCLUSIONS

A new method of producing exfoliated graphene in the liquid phase, high-shear exfoliation, has been demonstrated and investigated using a rheometer. This method of exfoliation has been demonstrated to be possible without turbulence being necessary. The exfoliation was found to progress with time as $t^{0.69}$, very close to the $t^{0.66}$ observed using a high shear mixer, implying that the kinetics of exfoliation is similar in both cases. A minimum shear rate required for exfoliation was observed using the rheometer and was found to occur at shear rates above $10^4 \text{s}^{-1}$, this minimum shear rate was again in agreement with that seen for the high shear mixer, suggesting that the underlying physics involved in exfoliation is similar in both cases.

Using a rheometer we have also probed the microstructure of high concentration graphene dispersions, beyond the rigidity percolation. The results are consistent with an elastic network of stiff platelets held together by bonds with an energy of the order of $20 \text{k_B}T$, consistent with van der Waals interactions that would be expected in these samples. These bonds have a limited spatial extent of the order of the width of the platelets and are not purely central force in nature. The yield strain of these dispersions was found to decrease with increasing concentration due to the decreasing volume allocated for each platelet as the mesh size of the network decreases.

The steady shear viscosity beyond the rigidity percolation is well described by a relaxation ansatz for $\text{Pe} < 10$ and can be expressed in terms of the platelet dimensions, bonding energy and volume fraction. This work is an important step towards understanding the microstructure and mechanical response of graphene suspensions, particularly at high concentrations. Furthermore, the basic measurements of these systems are of particular interest to printing and spray coating applications where understanding sample viscosity and behaviour under shear is paramount.
Figure 6.9: Raman spectra of graphite sediment produced after shearing at (a) 40 rpm and (b) 3000 rpm in the rheometer couette cell. Inset SEM images show graphite surface, where an increased amount of sub 15 μm flakes were visible for the high rpm sample.
Figure 6.10: TEM micrographs demonstrating exfoliation of graphite into graphene using a rheometer.
Figure 6.11: Histogram showing length statistics from TEM measurements for the graphene/NMP dispersions used in the rheological study, inset shows representative TEM image of a few layer graphene flake.
TESTING OUR UNDERSTANDING OF THE SHEAR EXFOLIATION MECHANISM

7.1 INTRODUCTION

High shear exfoliation is a much lower energy process compared to sonication and its discovery led to a mechanism being developed to describe how the exfoliation progresses. This mechanism was briefly described in Section 2.2.2.4 on page 13. The theory arising from this mechanism has been seen to match closely\[81] with the data obtained for the exfoliation of graphite in NMP, aqueous surfactant solution and to a lesser extent CHP, however the broad range of properties have not been tested extensively. In this chapter the theory used to describe shear exfoliation will be tested in order to further understand this scalable and industrially relevant graphene production method.

\[
\gamma_{\text{min}} = \left[ \sqrt{\frac{E_{S,G}}{\eta L}} - \sqrt{\frac{E_{S,L}}{\eta L}} \right]^2
\]  

(7.1)

While this minimum shear rate has been measured for graphene, it has not yet been observed for other materials and it is unclear how it might change with material choice. This has implications when considering shear exfoliation for other materials, in particular in surfactant solution, where extremely high shear rates can become impractical to apply using the same processing methods. Furthermore it is important to known precisely if and how the theory applies to other materials in order to facilitate the scaling up of production of these materials.

While equation 7.1 describes the minimum shear for exfoliation it can also be rearranged for L, describing a lower limit of exfoliable platelets; \( L_{\text{min}} = \left[ \frac{\sqrt{E_{S,G}} - \sqrt{E_{S,L}}}{\eta \gamma} \right]^2 \). This can be further extended to take into account the mean flake length which is
defined by the centrifugation regime after exfoliation. At a given centrifugation rate, flakes above a certain length, \( L_{cf} \), should be largely removed. This can be used to crudely obtain a value for the mean dispersed flake length as roughly the average of \( L_{\text{min}} \) and \( L_{cf} \). This assumes a regular, symmetrical population of flake lengths and, while it can be shown that length distributions are log-normal this is considered a reasonable approximation for our samples. The length distributions for the materials studied are shown in the appendix of this chapter.

\[
< L > \approx \left[ \frac{\sqrt{E_{SL}} - \sqrt{E_{SG}}}{2\eta\dot{\gamma}} \right]^2 + \frac{L_{cf}^2}{2}
\]  

(7.2)

Looking more closely at Equation 7.1, the equation states that the minimum shear required for exfoliation is dependant on the difference between the solvent and material surface energies. This implies that shear min is potentially solvent dependent and this is tested in this chapter. This could provide a route to optimise the shear exfoliation process by minimising the required shear rate, thus making a greater degree of exfoliation easier to achieve.

Turning our attention to Equation 7.2, we can investigate how platelet length varies with applied shear rate. While this has been observed for graphene,[81] we investigate the relationship again and for two other materials, MoS\(_2\) and WS\(_2\), using a metric based on UV-Vis absorption spectra. It has been demonstrated that the mean nanosheet length for these materials affect the spectral profile due to the nanosheet edges which can be expressed as peak intensity ratios in order to yield the flake length. Additionally, quantum confinement effects result in predictable shifts in A-exciton position, allowing the flake thickness to be measured.[132] Using these, the flake length and thickness can be measured as a function of shear rate, allowing us to further test the shear model as well as to define shear min in a more concrete manner.

7.2 EXPERIMENTAL PROCEDURE

Graphite, grade 3763, was supplied by Asbury Carbons. Tungsten sulphide (WS\(_2\)) powder (~2 \( \mu \)m) and molybdenum sulphide (MoS\(_2\)) powder (~6 \( \mu \)m) and all solvents
(purity >99%) were all purchased from Sigma Aldrich and used as supplied. Shear mixing was performed in a Silverson high-shear mixer, model L5M using the 32 mm diameter rotor and square hole mesh screen for MoS2 and WS2 as higher shear rates were required. The 12 mm rotor “tubular” mixing head, as described in section 4.2.2 on page 45, was used for the solvent survey using graphene to reduce necessary solvent required for sample processing as a greater variety of solvents were tested.

Before testing, all materials were batch treated by shearing them at 50 g/L in IPA in order to remove impurities present in the raw materials, in particular MoS2. The starting powders were sheared for 3 hours at 4500 rpm using the 32 mm rotor and then filtered through a fine pore nylon filter (0.045 μm pore size) membrane and dried in a vacuum oven at 50 °C overnight. Samples were then prepared in various solvents at a starting concentration of 50 g/L sheared at various fixed shear rates for 60 minutes. When varying solvent choice, all samples were sheared at 4500 rpm. All samples were then centrifuged at 2000 rpm for 5 hours and 45 minutes in the Thermo Scientific Heraeus Megafuge.

MoS2 and WS2 samples were then transferred from NMP into aqueous surfactant solution before being characterised using UV-Vis spectroscopy. This was done to avoid the potential impact of different solvents on the optical spectra, as size and thickness metrics were quantified using sodium cholate as a surfactant. This was achieved through high speed centrifugation of 3 ml of each sample at 16,000 rpm using a Hettich Mikro 220R equipped with the high speed 24 sample rotor. This crashed the material into a pellet and the solvent could be pipetted leaving the pellet behind to be redispersed in half the volume (1.5 ml) using bath sonication in sodium cholate (NaCho) in water (2 mg/ml) in order to raise the concentration to facilitate UV-Vis measurement. UV-Vis measurements were performed in 4 mm quartz cuvettes using a Cary 50 UV-Vis Spectrophotometer with 2 mg/ml NaCho solution as the baseline. TEM grids were prepared by drop casting a few ml of dispersion onto holey carbon grids and drying the samples under vacuum as well as in the pre-vac chamber in the TEM. TEM micrographs were obtained using a Jeol 2100 TEM.
In this chapter two metrics, devised by Dr. Claudia Backes, are employed to yield the platelet dimensions. For the TMD samples the metrics utilize the UV-Vis-obtained extinction spectra and specific peak intensities in order to gain insight into the length and thickness of the flakes. Looking at the spectra in Figure 7.1 A obtained for MoS₂, it can be seen that the optical density at 345 nm appears to be a local minimum and, when the spectra are normalised to this minimum as seen in Figure 7.1 B, the labelled A and B excitons can be seen to vary as a function of the applied shear rate.

Firstly, the local minimum at 345 nm can be used to obtain concentration with an extinction coefficient of $6820 \text{ l g}^{-1} \text{ m}^{-1}$[113] and it has been demonstrated by Backes et al that this is largely invariant with respect to flake length for flakes of $L > 60 \text{ nm}$[132]. Meanwhile the B exciton, normalised to the local minimum, can be used to obtain flake length in microns, using

$$L_{\text{MoS}_2} = \frac{3.5 \text{ Ext}_B / \text{ Ext}_{345\text{ nm}} - 0.14}{11.5 - \text{ Ext}_B / \text{ Ext}_{345\text{ nm}}}$$

Characterising the shift in the A exciton is more complex however, as the peak is relatively broad and so we take the smoothed second derivatives of the spectra, which can be seen in Figure 7.2. By noting the peak position, $\lambda_A$, the flake thickness (in layers) can be determined by the following empirical equation
\[ N_{\text{MoS}_2} = 2.3 \times 10^{36} e^{(-54,888/\lambda_A)} \] (7.4)

Figure 7.2: (A) Close up of A and B excitons from Figure 7.1 (B), straight line is to emphasise shift in A exciton. (B) Showing smoothed, 2nd order differential of (A), focused on the A exciton, for all shear rates to allow more precise determination of \( \lambda_A \), arrow indicates direction of increasing shear rate. Legend applies to both figures.

This process can be applied similarly to WS\textsubscript{2}[175] whereby the length metric uses the ratio of the A exciton (the variation in WS\textsubscript{2} spectra as a function of wavelength can be seen in Figure 7.3 with excitons labelled) intensity to the local minimum at 290 nm and the empirical equation becomes

\[ L_{\text{WS}_2} = \frac{E_{A} / E_{290\text{nm}} - 0.00763}{0.00283} \] (7.5)
The equivalent empirical equation for thickness is again analogous using the A-exciton peak position where again the second derivative of the spectra is used to obtain the peak position. The following equation can then be used to obtain the flake thickness.

$$N_{WS_2} = 6.35 \times 10^{-32} e^{(\lambda_A/8.51)}$$

(7.6)

An issue arises when determining the WS$_2$ concentration however, as the most simplistic metric relies on the Abs value at 235 nm, where the extinction coefficient is largely size invariant. Residual NMP in the samples studied here renders this wavelength inaccessible and so a size dependant extinction coefficient must be used. This can be done by relating the extinction coefficient, for example at the A exciton, to a the peak intensity ratio $A/290$ which is related to the nanosheet size as described above according to equation 7.6.

$$\epsilon = -6.5012 + 48.855 \left( \frac{Ext_A}{Ext_{290\text{nm}}} \right)^{0.84297}$$

(7.7)

Once the extinction coefficient is obtained the concentration can be calculated as normal using the optical density at the A exciton.

However, the same metric cannot be applied to graphene as these excitons do not exist in the extinction spectra for graphene. Because of this, in order to obtain
information about the platelet dimensions, we turn to Raman spectroscopy. The Raman spectra, seen normalised to the G peak in Figure 7.4 can be seen to vary as the exfoliating shear rate is varied, in particular the D band.

![Figure 7.4: Average Raman spectra for graphene films produced from dispersions exfoliated at various shear rates](image)

It has been shown that the ratio of the D band height to the G band height in LPE samples is largely dependant on the size of graphite platelets.\[70\] This is due to the lack of introduction of basal plane defects into the graphene lattice during the exfoliation process. Furthermore, it has been shown that the 2D band height varies strongly with the flake thickness.\[145\] Using this information, a metric was devised by Dr. Claudia Backes et al. to empirically determine the flake dimensions using Raman spectra of films formed from the exfoliated dispersions.\[176\]

\[
< L >_{\text{graphene}} = \frac{0.094}{(I_D/I_G)_{\text{graphene}} - (I_D/I_G)_{\text{graphite}}} \quad (7.8)
\]

This metric takes into account the D:G ratio of the parent graphite in order to account for the defect density of the starting material and, using this, the D:G ratio of the exfoliated graphene samples can be used to obtain a measure of the flake length. This has been fitted empirically to equation 7.8 seen above. In order to obtain flake thickness,
the 2D peak is analysed, for both the parent graphite and the exfoliated graphene film, at two wavenumbers; $\omega_1 = 2720 \text{ cm}^{-1}$ and $\omega_2 = 2690 \text{ cm}^{-1}$. The intensity at these two points are used to form the metric as

$$M = \frac{I_{\omega_1}/I_{\omega_2}\text{graphene}}{I_{\omega_1}/I_{\omega_2}\text{graphite}}$$

(7.9)

The value for “$M$” can subsequently be used to obtain thickness in number of layers in the empirical formula

$$N_{\text{graphene}} = 10^{0.84M + 0.45M^2}$$

(7.10)

7.4 RESULTS AND DISCUSSION

As seen in the previous chapter, in order to exfoliate graphite to form graphene one must apply a shear rate greater than a threshold value, measured to be approximately $10^4 \text{ s}^{-1}$. In order to investigate if this exists for solvent dispersions of other materials, graphene, MoS$_2$ and WS$_2$ were prepared in NMP at various fixed shear rates while keeping centrifugation and processing parameters the same. The concentrations of each are determined by first characterising the samples using UV-Vis spectroscopy using the metrics described in the previous section. The results can be seen in Figure 7.5.
As might be expected, 3 distinct shear rates are observed in order to exfoliate graphite, MoS$_2$ and WS$_2$ at appreciable quantities, with the required shear rate increasing from $\sim 10,000$ s$^{-1}$ to $\sim 30,000$ s$^{-1}$ and $34,000$ s$^{-1}$ for the three materials respectively. However, it is dangerous to assume this is in any way a reflection on the inter-flake bonding, as the dispersed concentration in one solvent at fixed centrifugation conditions does not give us sufficient information to gain insight into the energetics between the flakes of the material.

While it might appear that WS$_2$, requiring the highest shear rate to exfoliate, therefore has stronger inter-flake bonds, we have not directly measured the surface energy of these materials. Furthermore, this assumes that all other variables in the shear exfoliation mechanism remain the same. These materials were all exfoliated in the same solvent, NMP, and the materials each having a distinct surface energy is but one possibility. In order to observe the effects of variation in the surface energy term...
directly, we can vary the solvent used, and hence the solvent surface energy, while keeping the material the same and so this was tested using graphene. This can be seen in Figure 7.6.

![Concentration versus shear rate for various solvents investigating minimum shear required for exfoliation](image)

Figure 7.6: Concentration versus shear rate for various solvents investigating minimum shear required for exfoliation

Curiously, shear min was observed to remain largely invariant for graphene for all the solvents tested. This is despite a notable variation in the solvent surface energy for example DMSO and DMF and in viscosity in the case of CHP, all of which are predicted to affect the minimum shear required for exfoliation. This means that clearly something else is varying within the sample with the solvent choice. Looking to equation 7.2 on page 114 once more, further characterisation of the samples were performed to observe if any variation in mean platelet length was occurring.

In this set of experiments, steps were taken to ensure consistent lengths between samples by way of keeping the centrifugation regime constant. It should be noted that the sedimentation velocities are expected to be strongly dependent on solvent viscosity. However, with the exception of CHP, viscosities are similar. In addition, the centrifugation time of 5 hours 45 minutes should be long enough to minimise effects of the solvent viscosity on the sedimentation velocities. Hence, potentially
varying graphene sizes cannot be attributed to the post-exfoliation centrifugation, which defines the upper limit of flake size in the dispersions. The mean flake size, on the other hand, is dependant on the term describing the minimum shear for exfoliation and this may explain the observed invariance. In order to investigate this, dispersions were prepared in various solvents and then characterised using TEM.

Figure 7.7: (A) Mean flake length for six different solvents plotted versus solvent surface energy.

(B) Flake length plotted as outlined in Equation 7.11

As seen in Figure 7.7 A, there is a significant variance seen in mean flake length as we vary the solvent in which the shear exfoliation is performed. This is despite the fact that these sample were prepared at identical shear rates and centrifuge conditions. The length histograms can be seen in the appendix of this chapter. This somewhat explains why shear min was not seen to vary predictably with solvent choice as particle size could not be controlled between samples simply using centrifugation regimes. It should be feasible to plot this mean size variation using equation 7.2 which can be rearranged to form

\[
(2 < L > L_{cf}) \eta = \frac{[\sqrt{E_{pp}} - \sqrt{E_{ss}}]^2}{\dot{\gamma}}
\]  

(7.11)

and this is plotted in Figure 7.7 B. The predicted linear trend can roughly be observed and is proportional to the inverse of the supplied shear rate as shown by the straight line fitting. In this fitting \(L_{cf} = 0.5 \mu m\) and \(E_{graphene} = 71.68 \text{ mJ/m}^2\). There is a significant amount of scatter which can be expected and is rationalised as follows. This is partially due to the TEM length statistics having a degree of variability. Furthermore, it should
be noted that the selection of $L_{cf}$ here is not optimised, but selected due to the best fitting achieved in Figure 7.9 discussed later on in this chapter. This leaves it lower than the mean flake size measured in certain solvents and so this value needs to be set in a more concrete manner for each solvent sample. However, we do not have a a more theoretically robust method of selecting $L_{cf}$ and so this must be left for future work.

Having observed shear min. for 3 materials and tested the effects of variation in the surface energy term of the mechanism, we turn our attention to the effects of variation of the applied shear rate. It has been shown previously that platelet length and thickness vary with the applied shear rate and so the platelet dimensions must be monitored. However, TEM statistics are also a slow and labour intensive process and extremely challenging in the case of poly-disperse samples containing broad distributions of nanosheet lengths, as is the case here. This can lead to an under representation of the small nanosheets, for example, which cannot be resolved sufficiently when images are taken to capture the larger nanosheets. In addition, thickness determination is not practical in most cases. In the following, the quantitative length and thickness metrics as described above for graphene, MoS$_2$ and WS$_2$ were applied to gain an insight into the nanosheet size and thickness as a function of shear rate. This can be seen in Figure 7.8.

All three materials exhibit a steady decline in thickness and length as shear rate is increased and, frustratingly, the length and thickness decrease in unison. A plateau can be seen for graphene at approximately the minimum shear for exfoliation, something that is not seen for either MoS$_2$ or WS$_2$ although, for all materials, the sharpest decline in thickness occurs around the minimum shear for exfoliation observed in Figure 7.5. The thickness versus shear rate plot can be fit exponentially as shown in Figure 7.8. This shows quite clearly that as the shear rate is increased, the exfoliation efficiency of the process also increases. Furthermore, it allows us to define the minimum shear rate as the shear rate at which the mean flake thickness drops below 10 layers yielding minimum shear values of 11,000 s$^{-1}$, 30,500 s$^{-1}$ and 34,000 s$^{-1}$ for graphene, MoS$_2$ and WS$_2$ respectively. These values coincide with the shear rate required for appreciable dispersed concentrations for all materials as well as being in close agreement with the values obtained for the exfoliation of graphite measured previously.
Figure 7.8: Length and thickness plotted against shear rate for graphene, MoS$_2$ and WS$_2$.

The mean flake length is predicted in equation 7.2 to decrease as a function of shear rate and it should be seen to vary with a similar form. This is plotted in Figure 7.9 for all materials where the fitting agrees very well with the data with the exception of graphene, which stands out somewhat exhibiting a sort of plateau. The fittings yield values of $E_{\text{graphene}} = 71.9$ mJ m$^{-2}$, $L_{cf} = 500$ nm, $E_{\text{MoS}_2} = 72.2$ mJ m$^{-2}$, $L_{cf} = 300$ nm and $E_{\text{WS}_2} = 72.2$ mJ m$^{-2}$, $L_{cf} = 170$ nm.
Figure 7.9: Plotting the platelet length as a function of shear rate for the three materials according to equation 7.2

The surface energies yielded from these fittings are broadly similar varying only slightly between the graphite and the two TMDs which is in agreement with what has been reported previously with solvent studies on exfoliation of these materials.[177] However, the maximum flake length as allowed by centrifugation appears to vary significantly. This is as we might expect as the value for \( L_{cf} \) appears to decrease as the density of the material increases, with the densities of graphite, MoS\(_2\) and WS\(_2\) being; 2.26 g/cm\(^3\), 5.06 g/cm\(^3\) and 7.5 g/cm\(^3\) respectively from their respective material data sheets. This would suggest that the shear min variation between these materials is largely due to the mean platelet length variation between the materials caused by the effects of density variation on the centrifugation regime, as the theory predicts smaller flakes requiring higher shear rates to be exfoliated. This is consistent with recent work on shear exfoliation of black phosphorous,[178] which has a density similar to that of graphite, at 2.69 g/cm\(^3\), reporting a minimum shear rate for exfoliation of \( 1.25 \times 10^4 \) s\(^{-1}\) compared to graphene, with a density of \( \sim 2.26 \) g/cm\(^3\) having a minimum shear rate for exfoliation of \( \sim 1 \times 10^4 \) s\(^{-1}\).[81]
Nacken et al. have shown that the value for $L_{cf}$, referred to as the “cut size”, can be described by the centrifugation conditions and sample/solvent densities using the following relation:[179]

$$L_{cf} = \sqrt{\frac{18\eta}{(\rho_p - \rho_l) \times \omega^2 t \times \ln\left(\frac{r_2}{r_1}\right)}} \quad (7.12)$$

where $\eta$ is the sample viscosity, $\rho_p$ and $\rho_l$ are the platelet and solvent densities, respectively, $t$ is the centrifugation time, $\omega$ is the centrifugation speed and $r_1$ and $r_2$ are, respectively, the minimum and maximum radius of the sample when within the centrifuge. To investigate this we plot $(L_{cf})^2$ against the inverse of the sample material density minus the solvent density, in this case NMP (1028 kg/m$^3$). This is shown in Figure 7.10 where a linear trend can be observed. This fitting returns a slope of $\sim 3 \times 10^{-10}$ and we can compare this to what would be expected using the sample viscosity and centrifugation parameters. For the Megafuge $r_1$ and $r_2$ are 0.042 m and 0.168 m respectively and NMP has a quoted viscosity of $\eta = 1.7 \times 10^{-3}$ Pa s. Using these values with the experimental centrifugation regime (2000 RPM for 345 minutes) the expected slope is approximately $1 \times 10^{-9}$. While the values disagree by a factor of 3, this is nonetheless a significant level of agreement showing the shear exfoliation theory to be consistent with established work. This further demonstrates the validity of this simple theory and justifies its application to shear exfoliation of 2D materials other than graphite, for which it was developed.

Figure 7.10: Plot showing $L_{cf}$ versus inverse of material density minus solvent density for graphite, MoS$_2$ and WS$_2$ in NMP. Fitting shows linear fit intercepting the origin.
7.5 CONCLUSIONS

We have investigated the theory put forward to describe high-shear liquid-phase exfoliation in a number of manners using 3 different materials; Graphene, MoS\(_2\) and WS\(_2\). We have shown that the theory can be used to describe the exfoliation of other layered materials, namely MoS\(_2\) and WS\(_2\) expanding the use of the model. This allowed the minimum shear rate required for exfoliation to be determined for these materials as 30,500 s\(^{-1}\) and 34,000 s\(^{-1}\) for MoS\(_2\) and WS\(_2\) respectively.

The potential for optimising the process through solvent selection was also investigated and, while no improvement in the shear min was found, it yielded an unexpected route towards controlling the material platelet length. This variation in lateral size was found to be broadly in agreement with theory, though more work needs to be done in order to fully characterise the parameters involved and this must be left to future work.

Finally, new metrics using Raman and UV-Vis spectroscopy allowed the length and thickness of the three materials to be monitored as a function of applied shear rate. Flake thickness was seen to decrease with increasing shear rate and this was successfully fitted to an exponential function. Monitoring flake thickness allows us to define the minimum shear rate required for exfoliation to be defined in a more robust manner as the shear rate at which the mean flake thickness drops below 10 layers thick.

The length of the three materials was found to decrease as a function of shear rate and this was successfully fitted to the shear exfoliation model, with the fittings yielding broadly similar surface energies for the materials which are in close agreement with previous values obtained. The maximum flake length obtained from the fittings was seen to scale roughly with the material density indicating that the difference in shear min may depend on the difference in flake size in the final dispersions, which again is in agreement with the shear theory.

The observations from this work would suggest that in order to successfully exfoliate a layered material, a high shear rate is required in order to obtain the thinnest flakes. However, this is counterbalanced by the obtained material having a smaller lateral size
as both the thickness and length were seen to decrease most rapidly about the shear rate required for a significant quantity of material to be dispersed. Finally, the shear exfoliation differences between materials appear to be correlated with the material density, with denser materials requiring a higher shear rate in order to be successfully dispersed. This is consistent with higher shear rates being required to delaminate the smaller flakes that would remain after the centrifugation regime was applied to a sample of a denser material.
8.1 Conclusions

This thesis sought to further our understanding of liquid phase exfoliation (LPE) of two-dimensional layered nanomaterials to facilitate the production and application of these novel materials. This has been achieved to some extent in a number of ways but, as will always be the case in research, many questions still remain and some of these are addressed in the next section discussing future work.

Firstly, we have demonstrated an effective pre-treatment procedure for producing a reaggregated graphene powder that can be redispersed using liquid phase exfoliation techniques at higher concentrations in less time than the parent, untreated graphite. This is of particular importance to liquid phase exfoliated materials due to their typically very low concentration. This means that large volumes of liquid to be necessary to yield significant quantities of material; a fact most detrimental for transporting/shipping material. Using this pre-treatment, a dry powder can be produced which subsequently may be redispersed at its destination at high concentration using very little energy, circumventing the need to ship large quantities of solvent. The resulting material, made up of reaggregated few-layer graphene platelets, can be dispersed at concentrations of 1 mg/ml in times as low as 1 minute. The pretreatment time was investigated in order to optimise total processing time to produce the pretreated powder yielding an optimal time of ~26 hours. Furthermore, while NMP was found to be more effective, this pretreatment was shown to be possible in water and all without introducing basal plane defects into the platelets or reducing the quality of the final dispersions produced from this material.

During the course of this work a new method of LPE was demonstrated in the form of exfoliation using a high shear mixer. This was used for the exfoliative step
in this process and coarse filtration was employed to remove the remaining unexfoliated graphite as a potential route to scaling up this pretreatment method. This was subsequently expanded upon by demonstrating that the vast majority of the residual NMP introduced in the pretreatment procedure may be removed by an additional “reflux” step. This involves submerging the powder in Millipore water and heating it to 70 °C for a period of 4 hours. It was shown using TGA-MS that the NMP can be effectively removed, while noting that a smaller quantity of water is introduced into the samples. Using XPS to further characterise the samples, this treatment step was not seen to introduce any additional impurities or defects into the material.

Through removing the residual stabilising solvent it was hoped that we could test the solubility energetics of this pretreated material without concerns of the residual solvent skewing our results. This was taken as an opportunity to reduce the scatter seen in previous solvent surveys used to investigate the solubility parameters describing graphene dispersions and steps were taken to account for total energy input to the samples, centrifugation and solvent viscosity variations and, by using the pretreated material, it was hoped that variability inherent in the sonication process could be removed. While a large amount of scatter was still found to be present in these samples, the material was found to fit the theory very closely which is encouraging for future work in this area.

The newly demonstrated exfoliation technique was of particular interest to this work as shear exfoliation is a much lower energy process and so is a more predictable system to study and model. This prompted a study of graphene exfoliation using very precisely controlled shear conditions by utilising a concentric cylinder rheometer, capable of very high shear rates. Graphene exfoliation was demonstrated using this setup allowing the minimum shear rate required for exfoliation to be determined very precisely, which was found to occur at approximately $1 \times 10^4 \text{ s}^{-1}$, in agreement with work performed using the high shear mixers. That graphene can be exfoliated at these low shear rates confirms that turbulence is not required for exfoliation to occur, as the onset of secondary flow is predicted to occur at shear rates of $2.1 \times 10^4 \text{ s}^{-1}$.

In order to further understand graphene dispersions and the energetics of dispersion aggregation the rheological properties of high concentration graphene dispersions
were probed. The resulting behaviour is typical of soft glassy viscoelastic fluids, with the onset of sample rigidity occurring at a critical concentration of $4.2 \pm 0.1 \text{ mg ml}^{-1}$. This concentration was shown to be consistent with that expected for high aspect ratio ellipsoidal disks to overlap in suspension. These dispersions were also seen to be shear thinning, as might be expected for such a dispersion due to alignment of the graphene platelets under shear. The viscoelastic behaviour of these dispersions was successfully described through application of a simple model, with the data falling onto a master curve. The data obtained from the stress/strain plots allows us to infer an inter-flake bond energy of approximately $20 \text{k}_B \text{T}$. This is consistent predominantly point-like bonds with limited spatial extent with a platelet surface energy of $70 \text{ mJ m}^{-2}$, which is in agreement with what has been previously seen for dispersions of graphene platelets. The onset of viscoelastic behaviour as well as the concentration this occurs at is of particular importance with regards to applications such as screen printing and ink-jet printing of LPE 2D nanomaterials as is the shear thinning behaviour and the extent to which it occurs. The ability to model and predict these properties is an important step forwards in our understanding of these liquid exfoliated materials.

Finally, the theory put forward to describe the shear exfoliation was further explored in order to test its validity and explore potential routes to utilise its properties to control the final dispersion of exfoliated material. This was achieved by attempting to apply the theory to two alternative 2D-layered materials in addition to graphene. The three materials were found to have three distinct minimum shear rates required for exfoliation to occur in significant quantities, as one might expect, with shear rates of approximately $11,000 \text{ s}^{-1}$, $30,500 \text{ s}^{-1}$ and $34,000 \text{ s}^{-1}$ required for exfoliation of graphite, MoS$_2$ and WS$_2$ respectively. Additionally, the theory was tested by observing the effects of varying the exfoliating solvent surface energy for graphene. This was seen to have no measurable effect on the value of shear min however significant variation in the mean platelet length was seen as the solvent surface energy was varied. This could be largely described by the theory, though it was noted that the parameters used in the fitting are not optimised. The variation in flake length and thickness was investigated as a function of shear rate for all three materials and was seen to fit the theory very closely. Both flake length and thickness was seen to vary most strongly about the
minimum shear value, allowing this value to be defined in a more robust manner
as the shear rate at which the dispersed platelets are on average below 10 layers in
thickness. It is considered likely that this variation in shear min value is related to the
material density as, using a constant centrifugation regime, the denser material will
consist of smaller platelets which the theory predicts require higher shear rates to be
successfully delaminated. This is consistent with all three materials, with the densest
material having the smallest mean length as well as the highest observed shear min
value.

8.2 future work

While the pretreatment technique has been demonstrated using NMP and water, it
would be interesting to replicate the method using surfactant/water solutions. This
might have the beneficial effect of residual surfactant further increasing the interlayer
spacing of the reaggregated platelets, facilitating their redispersion. If proven effective
this method of pretreatment might replace NMP which is of particular interest due
to the toxicity of NMP and its incompatibility with many materials. A potential
experimentation route is to replicate the pretreatment time study and compare the
results to those observed for NMP and water with scope to further investigate the
effects of different length surfactant chains.

As a logical addendum to this work, it would be beneficial for many industries
to demonstrate a reliable method to easily remove the residual surfactant from the
dry powder, as was performed for NMP. Using similar characterisation methods of
TGA-MS and XPS the level of residual surfactant can be measured and furthermore
the effect of removing this residual surfactant on the efficiency of redispersion of
the pretreated and cleaned powder could be studied to understand if the residual
surfactant plays an important role.

The Rheological study was consistent with the mean flake length observed in
the dispersions but the theory states that flake length plays an important role in
determining the critical concentration at which the viscoelastic behaviour begins to
become apparent. This could be further tested by controlling mean particle size using controlled centrifugation to create high concentration dispersions of more controlled and less polydisperse lateral sizes. How mono-disperse flakes at larger length scales might behave, for example, is of particular importance as, for many applications, longer flakes with less polydispersity are preferable. With potential phenomena such as liquid crystalinity, this could be a very interesting avenue for a research project. The rheological study might also be replicated using surfactant/water stabilisation methods as this would allow the Einsteinian regime at low concentrations to be reliably measured. Furthermore the effects of surfactant on the interflake bonding energy and how it might compare to NMP stabilised dispersions is important to further understand the energetics of the dispersion stabilisation.

For the work performed in Chapter 7, it would be interesting to observe the how the mean platelet length varies as a function of shear rate for different solvents. As it has been observed that for many solvents the shear min remains largely invariant and the platelet length varies, how the platelet length varies as a function of shear rate is an important factor to consider to complete this study. Furthermore the platelet thickness as a function of shear rate in various solvents might reveal certain solvents to be more practical for particular applications in addition to revealing information about the specific interaction between the solvent and platelet.
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