Graphene exfoliation and analysis at a water-heptane interface

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Science in
Physics from the College of William and Mary in Virginia,

by

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Abstract

Literature review and calculations were performed at the Nanomaterials and Imaging Lab in the William & Mary Applied Science Department to explore a low-energy method for graphene exfoliation. Graphene's physical properties make it a desirable material for engineering and commercial applications. A reliable, scalable method for exfoliation and dispersion of graphene sheets is essential for the material to reach production areas. With experimentally-derived surface energy values for graphite, water, and heptane, the Dupre equation was used to understand an ideal liquid-liquid interface for graphene sheet production. Trapping powdered graphite at this interface enables sonication and centrifugation, disrupting planar interactions and organizing individual graphene flakes for deposition on a substrate. Solute samples are observed via optical microscopy. Early experimental results indicate limited efficacy of the production method.

Chapter 1

Introduction

Like silicon in decades past, graphene has been billed a "wonder material" by representatives of the scientific and engineering communities. Graphene is an allotrope of carbon, a unique physical configuration of the element's atoms. When arranged in indefinitely large hexagonal lattices, carbon atoms often form sheets that stack together like decks of playing cards. This tiered arrangement of planes, which we call "graphite", is owed to interplanar interactions called π bonds. Graphite can be found in everything from lubricants, to ashes in fireplaces, to pencil lead. However, when its sheets cleave apart into single or few-atom thick layers, they are referred to as graphene.

Graphene's interplanar π bonds facilitate electron mobility, granting it a low electrical resistivity comparable to silver's. This high electrical conductivity makes it a prime candidate for various electronic applications like ballistic transistors or supercapacitors. Even more notable are graphene's unmatched mechanical properties; tensile strength of 130 gigapascals (the highest of any known material), and greater ability to distribute impact forces than any material (ten times that of steel) make graphene ideal for applications stymied by wear cycles, such as prosthetics, aerospace research, and countless other technologies. To contextualize this immense strength,

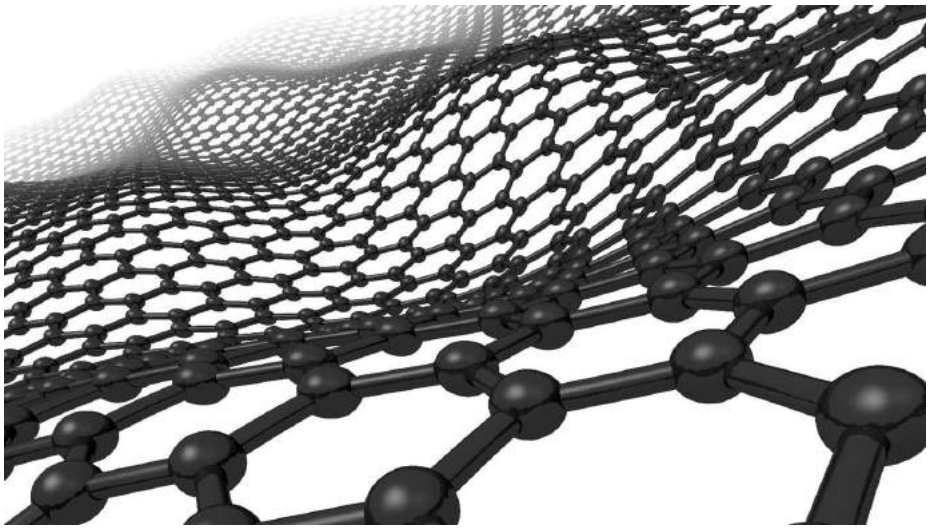

Figure 1.1: Artist's rendering of graphene monolayer.

consider a broad monolayer sheet of graphene, akin to a piece of cling wrap. Even at a macroscopic scale, a one-atom-thick piece of this material is so transluscent it would be incredibly difficult to see. This incredibly thin sheet of graphene could suspend the weight of a soccer ball in the air without fracturing.

Recognizing the immense potential a material with such properties presents for an array of technologies (capacitors, flexible screens, clothing, nanoscopic medical delivery devices, etc.), researchers have experimented with various means of graphene production. However, many of these methods are limited by their tedious nature, need for sophisticated equipment, use of environmentally insensitive chemicals, high input energy, or low yields of pristine graphene material. The Nobel laureates credited with successfully isolating graphene, Andre Geim and Konstantin Novoselov, used adhesive tape to remove particles of graphite from a larger lump, then repeatedly stuck and unstuck the tape from itself to obtain individual sheets of graphene [10]. Chemical vapor deposition [6], the most common means of modern graphene production, is plagued by these pitfalls. CVD requires substrates altered by chemicals

like hydrofluoric acid, as well as large, expensive equipment with strict maintenance schedules and massive energy demands. Ambitious progressive methods for graphene production, like acetylene combustion [7], can be subject to the same shortcomings, like yielding small chunks of graphene rather than broad sheets.

The history of materials science demonstrates any progressive material (e.g. aluminum, silicon, carbon fiber) will not see widespread adoption unless production techniques strive for simplicity and maximum economic return. The intent of our experiment was to examine the mechanics of a low input energy, environmentally sensitive, scalable technique for graphene exfoliation at immiscible liquid interfaces. Unsophisticated production techniques such as these have been attempted in academic settings, as shown in the work of Adamson et.al.[1]. Calculations related to the mechanics of liquid-liquid interfacial exfoliation would confirm the efficacy of the Adamson group's technique, or suggest inconclusive evidence and areas for improvement. Replication of the Adamson group's exfoliation technique would also be attempted, as well as limited characterization via optical microscopy.

Chapter 2

Theory

2.1 Exfoliation

Graphene's characteristic single-plane configuration is not commonly found in nature. For example, though writing with a pencil may occasionally shear off a piece of the material, these pieces are very small. A researcher's natural inclination may be to turn to crystal synthesis for creating isolated 2D planes, as many levels of control are afforded over a *growth* process. However, Geim and Noveselov note this technique is not sustainable beyond small flake size, as phonon density increasing with crystal size forces the crystals to bend into a third dimension [10]. For various applications dependent on flat sheets of graphene, this is not a tenable approach. Instead, researchers and engineers typically resort to *exfoliation* techniques. From bulk graphitic material, sometimes oxidized first for the sake of diminishing interlayer interactions, graphene sheets can be cleaved via mechanical means (stirring, shaking, manual slicing/adhesion), exposure to high temperatures in a gaseous environment, or even electrochemical means (passing a potential through graphite in a conductive solvent) [11]. As seen in Fig. 2.1, the objective of any method is to break interplanar Van der Waals interactions stacking graphene sheets together, while preserving the integrity of the sheets themselves. With respect to mechanical means of exfoliation,

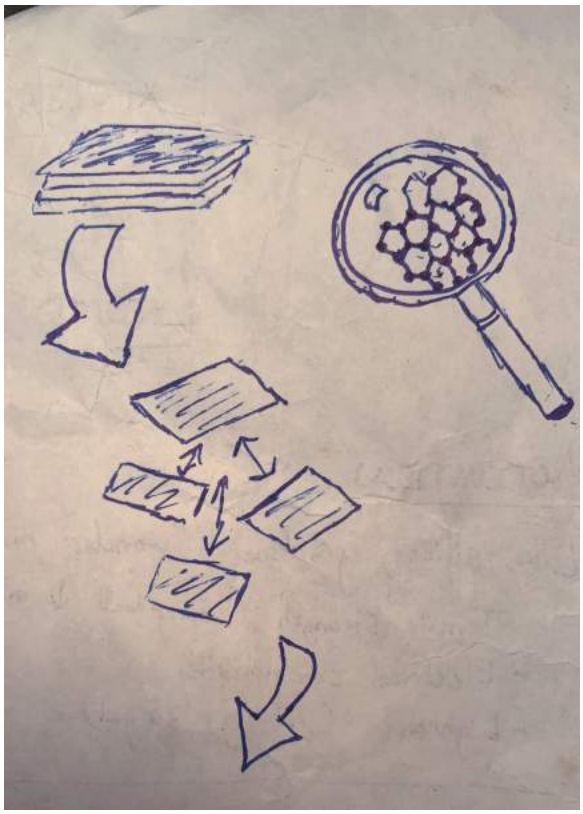

Figure 2.1: Illustration of stacked graphite exfoliating into graphene sheets, with detailed view of material's carbon lattice.

isolating graphite in a non-destructive environment like a liquid-liquid interface aids this objective. To create such an environment, an understanding of surface energy is required.

2.2 Surface Energy

The fundamental principle of physical chemistry supporting the experiment is surface energy. Denoted in formulae by the symbol γ, surface energy is excess energy at the outer layer of a material versus its bulk atoms, or the amount of work required to build an area of a given surface. In ideal practice, cutting a solid body in two increases the proportion of free energy in the system; energy expended in the cutting

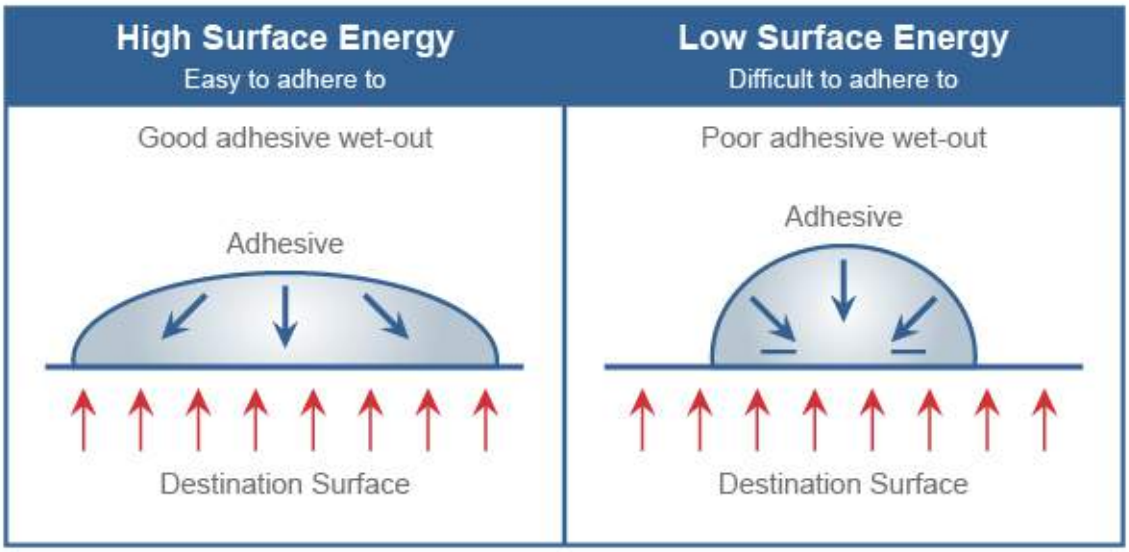

Figure 2.2: Comparison of high and low wetting of a liquid drop on a uniform solid surface.

process is equal to the combined energies of the new surfaces. As depicted in Fig. 2.2, surface energies of liquids may be explained through wetting phenomena, whether a solid surface's energy changes upon addition of a liquid drop. Depending on the respective surface energies of the liquid and solid, the drop may remain stable (low wetting), partially disperse (high wetting), or completely disperse (perfect wetting).

The liquid interface exfoliation technique described in this thesis uses immiscible liquids (i.e. water and heptane). Though solid surfaces do not play a direct role in the production technique explored by the Adamson group, liquid surface energies and their role in the manifestation of an interfacial energy do. The stable barrier created between two liquids of significantly different surface energies can hold graphene sheets in place; capillary forces overwhelm the weight of the sheets, as long as the film is thinner than the corresponding capillary length. This phenomenon provides a space for graphene sheets to cleave from bulk graphitic material via mechanical agitation

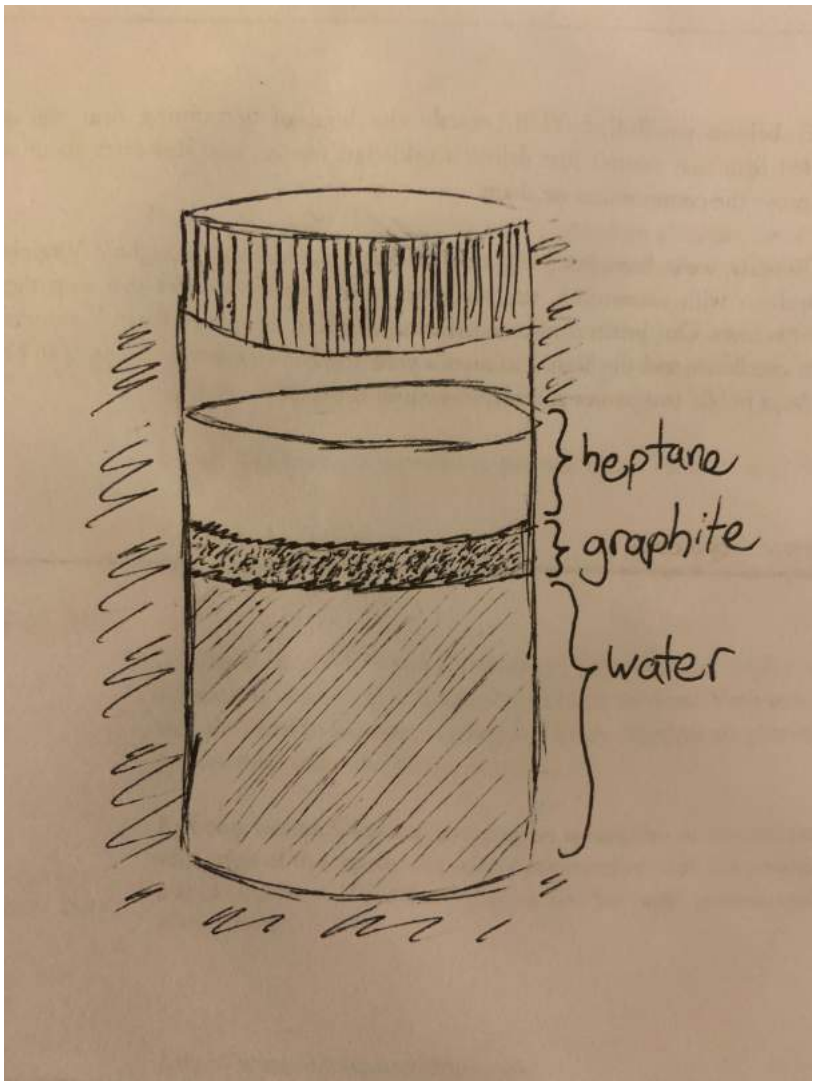

Figure 2.3: Illustration of graphite at heptane-water interface during exfoliation process.

(exfoliate), akin to jostling a sheaf of transparency sheets stuck together by static electricity. Through random agitation of graphite at the interface of the two liquids, stacked graphene sheets would be exposed to forces in lateral and axial dimensions that would overwhelm the strength of the Van der Waals interactions keeping the planes together. Additionally, the low tension between the two participant liquids would, theoretically, allow graphene sheets to disperse across the interface into a

single or few-layer film. This film could be recovered via a lift-off method (e.g. slide climbing)

Experimental results from the Adamson group indicate strong hydrophilic traits of single and few-layer graphene at a heptane-water interface. Recent experiments in the Schniepp group considered gallium as a substitute for water due to its larger γ, but rapid surface oxidization after graphene sheet exfoliation rendered the material difficult to process. Graphite in heptane-water presents the greatest potential for further research, as long as time-sensitive production techniques are observed. More advanced characterization techniques (e.g. SEM) will enable substantial analysis of experimental results, including returned quantitative data.

2.3 Surface Energy Calculations

Graphene film formation occurs via reassembly of sheets at the liquid interface, as interfacial free energy in a system tends to be minimized. Consider the following surface energies: $\gamma_{\text{water}} = 72.9$ mN/m [1], γ_{heptane}, 20.1 mN/m [1], $\gamma_{\text{graphene}} = 54.8$ mN/m [3]. Graphene-water and graphene-heptane interfacial surface energies were not readily available after extensive literature review, from contemporary or historical sources. $\gamma_{\text{graphene-water}}$ and $\gamma_{\text{graphene-heptane}}$ were estimated using a dispersion force-dependent derivation of the Dupre equation (Eq. 2.1), a formula representing the free energy change when two immiscible liquids are brought in contact. From these values, a spreading parameter S (Eq. 2.2) predictive of distribution of graphene material was derived, which bore resemblance to the positive spreading parameter of the system provided in the Adamson group's paper:

$$W_{12} = \sqrt{W_{11}W_{12}} = 2\sqrt{\gamma_1\gamma_2} \tag{2.1}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2} \tag{2.2}$$

$$S = W_{132} = W_{12} + W_{33} - W_{13} - W_{23} = \gamma_{13} + \gamma_{23} - \gamma_{12} \tag{2.3}$$

Heptane-water (12)

$$W_{heptane-water} = 2\sqrt{(20.1mN/m)(72.9mN/m)} = 76.6mN/m \tag{2.4}$$

Graphene-graphene (33)

$$W_{graphene-graphene} = 2\sqrt{(54.8mN/m)(54.8mN/m)} = 109.6mN/m \tag{2.5}$$

Heptane-graphene (13)

$$W_{heptane-graphene} = 2\sqrt{(20.1mN/m)(54.8mN/m)} = 66.4mN/m \tag{2.6}$$

Water-graphene (23)

$$W_{water-graphene} = 2\sqrt{(72.9mN/m)(54.8mN/m} = 126.4mN/m \tag{2.7}$$

With these calculated interface energies, the spreading parameter S should be [76.6 + 109.6 - 66.4 - 126.4)]mN/m, which returns **S = 6.6 mN/m**. This small positive value indicates water will spread across an interface with heptane, presumably guiding adhering graphene sheets with it. This dispersion would be an essential mechanism for consistent graphene film formation.

Though a convenient method for understanding surface energies in three-phase systems, Young's equation is subject to a critical flaw. Young's equation relies on surface energy values with high precision, as a slight shift of one number can give a wildly inaccurate impression of a system. The only possible way to predict these systems

was using experimentally-derived surface energy values from the same experiments, as we do not have adequate resources/experience to test surface energies ourselves. Additionally, many papers disagreed on the surface energy value for a given material. These calculated spreading parameters are intended to be predictive, not precise.

Early in the experimental process, gallium was a subject of interest for its exceptionally high independent surface energy (γ_{gallium} = 708 mN/m). A strong influence of gallium on its interface with water is a logical conclusion. When added to heptane, graphite/graphene sheets will presumably spread even more efficiently across this interface than water, as S parameter values will be increasingly positive.

Heptane-gallium (12)

$$W_{heptane-gallium} = 2\sqrt{(20.1mN/m)(708mN/m)} = 238.6mN/m \tag{2.8}$$

Gallium-graphene (23)

$$W_{gallium-graphene} = 2\sqrt{(708mN/m)(54.8mN/m} = 393.9mN/m \tag{2.9}$$

Substituting these newly-calculated interface energies with gallium, the spreading parameter S would become [238.6 + 109.6 - 66.4 - 393.9)]mN/m, which returns **S = 112.1 mN/m**. This far larger positive value indicates gallium will spread far more efficiently across heptane, but strong adhesion forces between gallium and graphene could present difficulty when trying to process the film. Use of a strong surfactant could violate the non-toxic aspirations of the experimental method.

The experimentally-demonstrated oxidation of the gallium-graphene surface renders this system undesirable. Any viable production technique would need to have no element of graphene functionalization, as that can be added to the process later.

Chapter 3

Experimental Methods

3.1 Samples

Interfaces produced by immiscible liquids with different γ values allow suspension of a substance like graphite while subjecting it to external forces (i.e. bath sonication, centrifugation). Considering the weak nature of graphite's inter-planar π bonds, mild agitation of the powder at the interface of two immiscible liquids produces a uniform film that remains temporarily stable. If either participant liquid is allowed to evaporate, graphene will precipitate at the bottom of a scintillation vial.

To prepare samples, 1 and 2 mg samples of bulk pristine graphite are first measured on a digital scale, with attention to the potential health risks posed by airborne nanoparticles. Afterwards 1 and 2 mg of bulk pristine graphite are placed in a 20 mL glass scintillation vial with 5.0 mL of n-heptane and millipore water. This vial is placed in a dry beaker within a Fisher Scientific FS30D Ultrasonic Cleaner (see Fig. 3.1). Using a Thermo-Scientific tabletop orbital shaker, the vials are then centrifuged at 2000 rpm for 60 seconds to exfoliate the graphite and disperse it across the interface. After centrifugation, visual analysis for climbing behavior on the sides of the vial and presence of material at the interface is carried out. Samples can be taken with a micro-pipette at the interface and deposited on a glass slide. Adamson

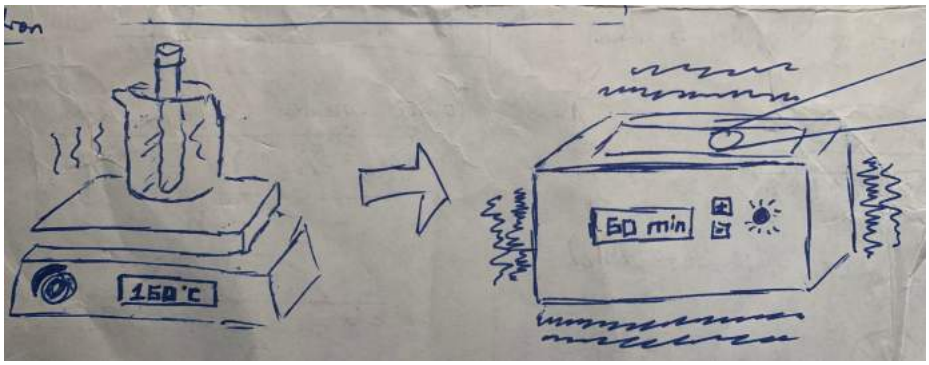

Figure 3.1: An illustration of the heated plate and ultrasonic cleaner used for sonication of samples and phase change of gallium.

et. al. note graphene films will climb the hydrophilic walls of a glass scintillation vial; a vial treated with trimethylsilyl chloride will render the walls hydrophobic, allowing the film to climb a hydrophilic untreated glass slide.

In early stages of the experiment, production of graphene at a gallium-heptane interface was attempted. Vials of gallium were warmed in beakers of water beyond the element's melting point. 5.0 mL of gallium were pipetted into scintillation vials in the same fashion as heptane in the method described below. Gallium was eventually abandoned due to time constraints, as well as surface oxidation of the graphene-gallium mixture, but resolving exposure to air and exploration of surfactant techniques could make it a viable candidate once more.

3.2 Characterization

Characterization of the samples was performed with an Olympus darkfield optical microscope at x5 and x40 power. Optical microscopy gives an impression of how much graphene versus aggregate is present at the sample interfaces, but is limited by the workable distance of the microscope to the slide. Electron or atomic force

microscopy may provide necessary corroboration of results; in the Adamson group's experiments, individual graphene flakes had diameters on the order of hundreds of nanometers, far too small to observe via optical microscopy.

Chapter 4

Results and Discussion

Returned data from experiments was limited and entirely qualitative in nature, due to unsuccessful recovery of graphene material for characterization (adhesion to gallium), limitations of optical microscopy, minimal experience with more advanced characterization techniques, and unforseen time constraints. However, visual inspection of generated samples and analysis under optical microscope gave an impression of experimental efficacy, via comparison to results from the Adamson group.

As denoted in the previous chapter, gallium has a tendency to partially resolidify after sonication and centrifugation, trapping any useful graphitic material via strong adhesion forces; Fig. 4.1 illustrates this phenomenon. Exposure to air would have oxidized the surface of this colloid, and characterization was not pursued. However, research attempting to isolate any graphene from the gallium surface, while immersed in another liquid or otherwise, is rife with potential.

Visual inspection of water-heptane samples indicated similar behavior to samples generated by the Adamson group. The liquid interface showed a clear capillary boundary, with apparent organization of graphitic material at the interface after agitation. Film climbing on a slide was not attempted, but the characteristic climbing behavior of the glass vial walls was observed, as seen in Fig. 4.2. Graphitic mate-

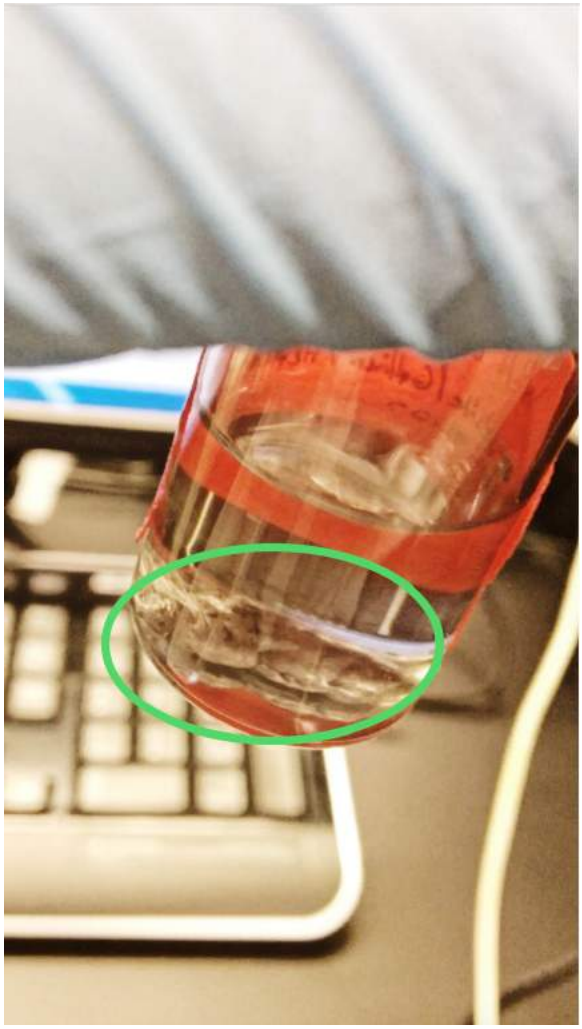

Figure 4.1: A graphite in gallium-heptane sample. Note the gallium has cooled to a semisolid state, with any usable graphene or graphite aggregate adhering to its surface.

rial also appeared to re-organize at the interface after long periods of settling (Fig. 4.3), upon agitation. These data give no indication of how much graphene material was generated by the experiments, flake diameter, or any other quantitative product. However, the similarities borne to samples generated by the Adamson group are an indication that the technique is replicable.

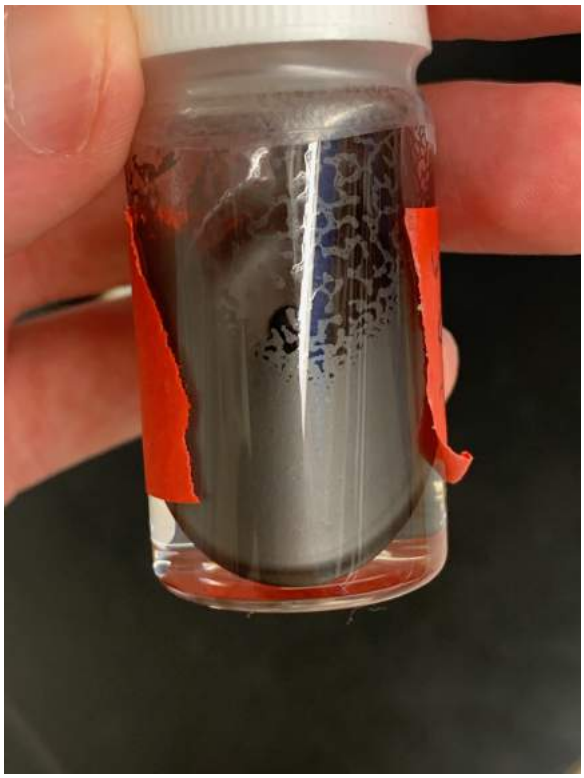

Figure 4.2: This graphite in heptane-water solution shows clear evidence of climbing behavior.

Observation of samples using an Olympus darkfield optical microscope indicated clear distribution of graphitic material, as seen in Fig. 4.5 and 4.7, with x5 images of both samples showing dense population of material and the 2 mg solution showing presence of large aggregate not seen in the 1 mg solution. This may be an indication that lower concentrations of graphite powder are favorable for liquid-liquid interface exfoliation.

As seen in Fig. 4.6 and 4.8, x40 images of both the low and high graphite concentration samples show broad variance in reflected light, indicating a lack of uniform topography in the samples and uneven distribution of material. Much of this may be owed to the presence of liquid on the slide, which could have created

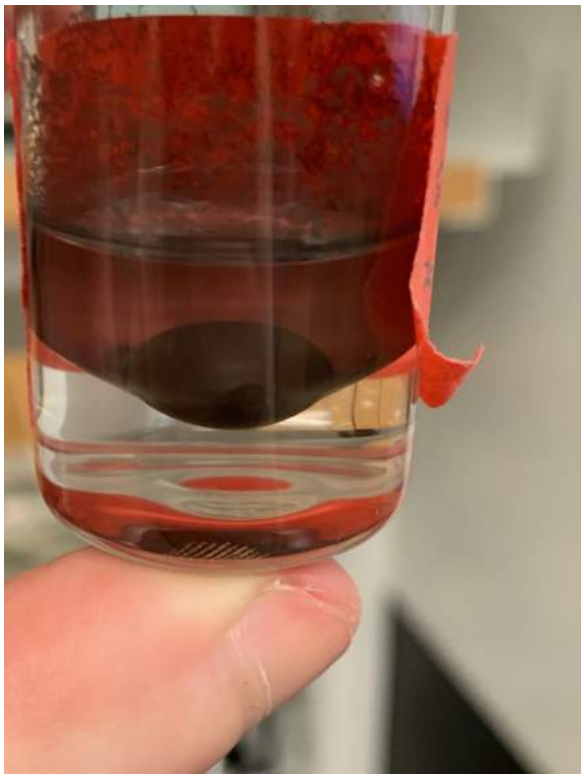

Figure 4.3: This graphite in heptane-water solution shows re-accumulation of graphitic material after a long settling period.

a suspending effect, but variance in grain size is evident as well. We can get an impression of distribution of material from the image–at x40, the image depicts an area approximately 2mm square. Counting approximately 30 similarly-sized grains of material per millimeter, average grain diameter could be extrapolated as 70 micrometers. Dry deposition of these samples on a silicon substrate and characterization at far greater magnification would provide the opportunity to corroborate results, confirm the presence of actual graphene, and measure grain size. In these images, we see roughly uniform deposits of large-scale graphitic material, with optical characteristics far too reflective to be graphene. As seen in Fig. 4.9, any graphene sheets viewed at higher magnification would have a consistent hue (flat) and be nearly transparent. It's difficult to conclude any effective production of *graphene* from these results.

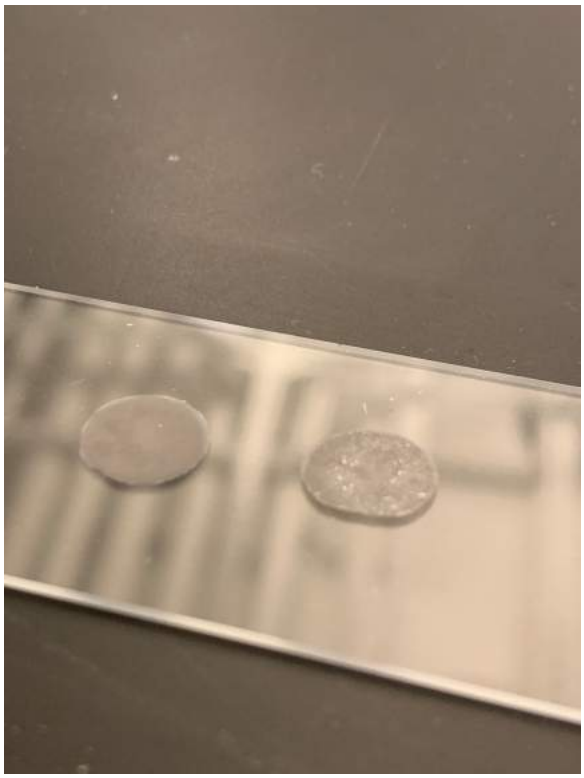

Figure 4.4: A slide of dry sample from graphite in heptane-water solutions, the liquid reactants having evaporated away. Note apparent visual differences owed to lower (left) and higher (right) concentrations of graphite powder.

Even under ideal circumstances, a replication of the Adamson group's results would yield graphene flake diameter on the order of hundreds of nanometers, as seen in Fig. 4.9. Ability to characterize samples aside, consider the nanoscopic lateral dimensions of these sheets. Assuming the given production technique scales linerarly, a room-sized operation may generate enough material for macroscopic applications, but whether such a technique would be consistently successful is unknown.

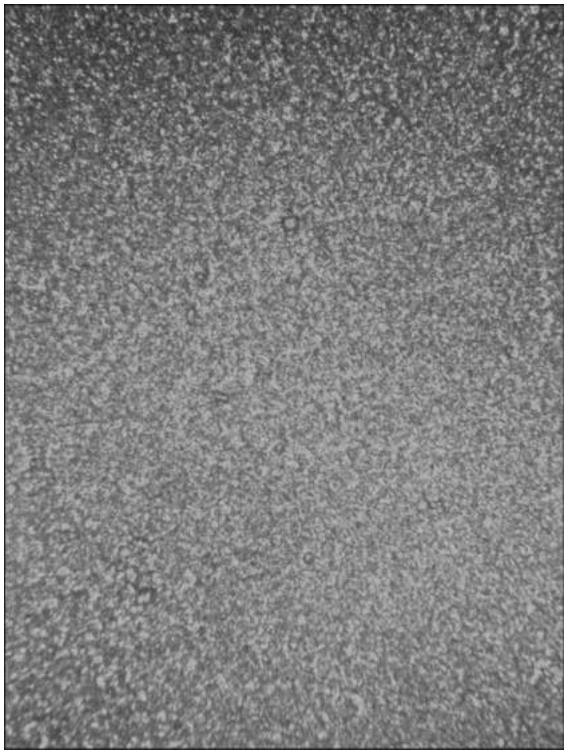

Figure 4.5: This is a x5 image of a droplet from a 1 mg graphite in heptane-water sample under an optical microscope.

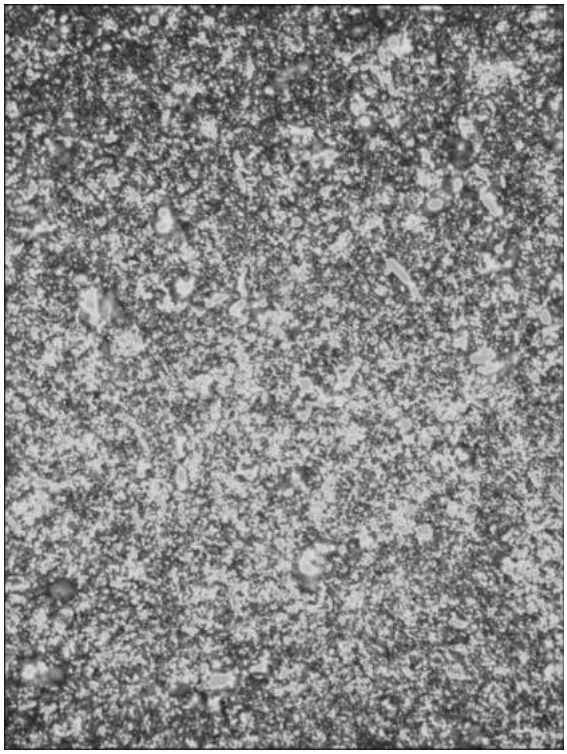

Figure 4.6: This is a x40 image of a droplet from a 1 mg graphite in heptane-water sample under an optical microscope.

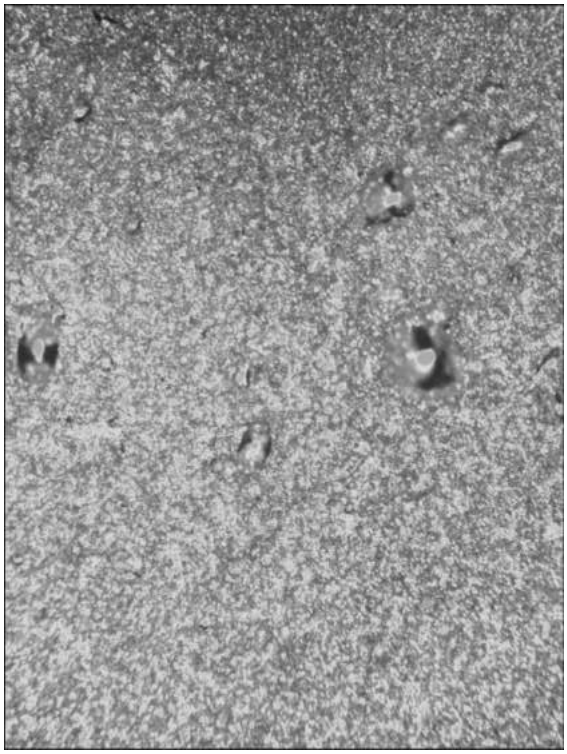

Figure 4.7: This is a x5 image of a droplet from a 2 mg graphite in heptane-water sample under an optical microscope.

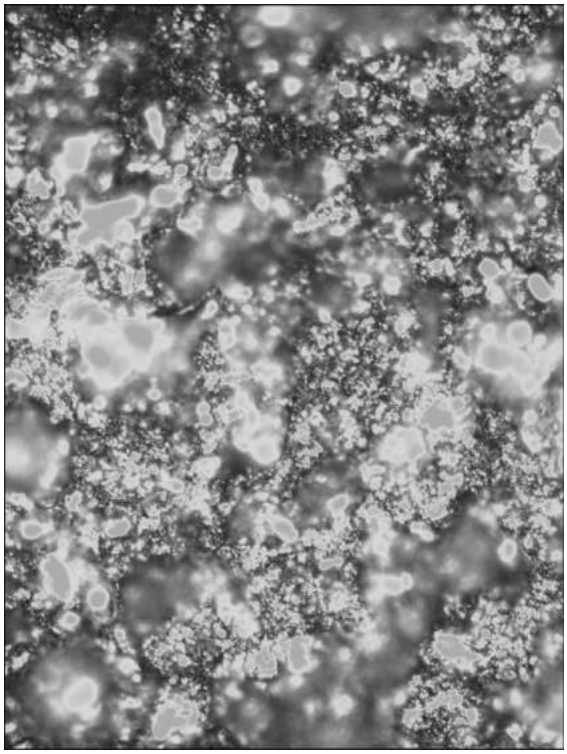

Figure 4.8: This is a x40 image of a droplet from a 2 mg graphite in heptane-water sample under an optical microscope.

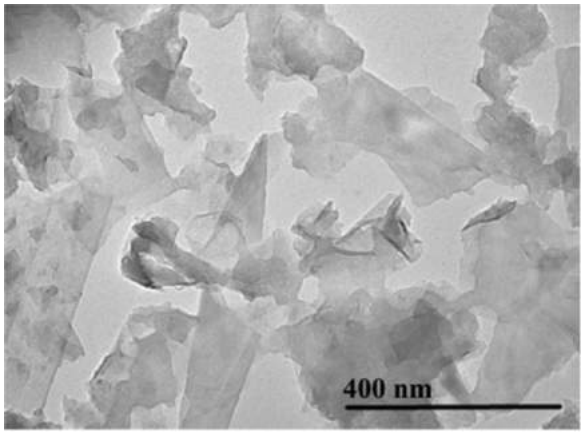

Figure 4.9: From [1], this is a TEM image of graphene sheets exfoliated at a liquid-liquid interface.

Chapter 5

Conclusions

From current experiments and theoretical calculations, graphite in a water-heptane solution shows inconclusive promise for low input energy production of graphene sheets on an industrial scale. Considering the abundance of water and limited environmental impact of n-heptane, this infrequently explored production technique has potential for laboratory use; minimal equipment and no exotic resources are required. However, attention will have to be paid to the sensitive nature of this production method–without extraction of graphene sheets in a timely manner, the solution may reach an unsalvageable state. In addition, the generation of substantial graphene material has yet to be determined, with the use of advanced characterization techniques like electron or atomic force microscopy. The small scale of these liquid interfacial experiments is notable. Whether such a method could be adapted to commercial use in a more effective way than extant production techniques is questionable, depending on the scalability of these phenomena.

Future experiments will enable confirmation of sample production on larger scales, manipulation of timescales and other experimental parameters, and detailed characterization of graphene samples. Attention should be paid to surface energy values; techniques like Wilhelmy slide testing should be used whenever possible. Sig-

nificant production of single and few-layer material via this liquid interface mechanism will confirm whether its environmental and economic benefits are complemented by meaningful generation of product.

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