Mathematical Modelling for Graphitic Nanostructures

Thomas Dyer
University of Wollongong

Recommended Citation
Mathematical Modelling for Graphitic Nanostructures

Thomas Dyer

This thesis is presented as required for the conferral of the degree:

Doctor of Philosophy

The University of Wollongong
School of Mathematics and Applied Statistics

2018
This work © copyright by Thomas Dyer, 2019. All Rights Reserved.

No part of this work may be reproduced, stored in a retrieval system, transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior permission of the author or the University of Wollongong.

This research has been conducted with the support of an Australian Government Research Training Program Scholarship.
Declaration

I, Thomas Dyer, declare that this thesis is submitted in fulfilment of the requirements for the conferral of the degree Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Thomas Dyer

May 12, 2019
Abstract

Graphitic nanomaterials have been some of the most widely studied materials of the last decade. The isolation of monolayer graphene in 2004 sparked attention from numerous researchers due to the sheer breadth of its exceptional properties. Thus, it is important that theoretical models keep up with the pace of experimental discovery.

Remarkably, macroscale modelling techniques translate well to nanoscale application. Treating graphitic structures as continuous surfaces allows the application of continuum mechanics and variational calculus amongst others. This thesis involves the formulation and subsequent analysis of three mathematical models relating to the conformation of graphitic structures.

Firstly, we study the interaction energy between sheets of graphene oxide, utilising a continuum model designed for carbon nanostructures. We model graphene oxide as a layered structure consisting of the central graphene sheet and attached functional groups. Varying the oxidation and hydration of these layers is shown to capture the nonstoichiometric nature of graphene oxide. We then model a single-walled carbon nanotube intercalated within the graphene oxide sheets and determine its equilibrium configuration. Molecular dynamics simulations are shown to agree with our analytical results.

Next, we investigate the conformation of the structure consisting of a single-walled carbon nanotube intercalated within a folded graphene sheet. Intercalation provides a potential enhancement of graphitic structures through surface functionalisation. Due to the isotropic nature of the fold, we can consider the problem as curves in two dimensions. The calculus of variations is employed to determine the minimum energy configuration from balancing the bending and adhesion energies. The results are shown to be in excellent
agreement with molecular dynamics simulations.

Finally, we examine wrinkle structures formed in a graphene sheet grown on a substrate. Understanding this process has the potential to assist with tuning the properties of the structure or simply eliminating undesirable effects. The calculus of variations is again used to calculate equilibrium wrinkle configurations. We observe several potential configurations of wrinkle depending on the choice of substrate.

Overall, this thesis employs analytical approaches to model graphitic structures, giving rise to explicit solutions that can provide insight into interactions between the nanostructures. The results are shown to agree well with molecular dynamics simulations and existing data in literature. The thesis demonstrates the power of mathematical modelling tools and techniques that can provide reliable predicting capability in the area of nanoscience and nanotechnology.
Acknowledgments

I would like to sincerely thank my supervisor, Professor Natalie Thamwattana, who has been continuously patient and supportive in her guidance. She always encouraged me to interact with the wider community. I also appreciate the invaluable help of my co-supervisor, Dr. Barry Cox. Additionally, I thank my external collaborators, Professor Wolfgang Basca and Dr Rouhollah Jalili, for providing and assisting me with interesting problems. Finally, I thank my friends and my family. I am truly grateful for their support which keep me from isolation.
Contents

Abstract iv

List of Figures x

List of Tables xiv

1 Introduction 1
  1.1 Structure and properties of graphene . . . . . . . . . . . . . . . . . . . 1
  1.2 Graphene production techniques . . . . . . . . . . . . . . . . . . . . . 3
  1.3 Applications of graphene . . . . . . . . . . . . . . . . . . . . . . . . . 5
  1.4 Thesis structure . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 7

2 Mathematical methodology 8
  2.1 Modelling molecular interaction . . . . . . . . . . . . . . . . . . . . . 8
    2.1.1 Lennard-Jones potential . . . . . . . . . . . . . . . . . . . . . . 10
    2.1.2 Coulombic potential . . . . . . . . . . . . . . . . . . . . . . . . 11
  2.2 Molecular dynamics . . . . . . . . . . . . . . . . . . . . . . . . . . . . 12
    2.2.1 Forcefields . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 13
    2.2.2 Numerical integration schemes . . . . . . . . . . . . . . . . . . . 15
  2.3 Calculus of variations . . . . . . . . . . . . . . . . . . . . . . . . . . . 16
    2.3.1 The Euler-Lagrange equation . . . . . . . . . . . . . . . . . . . . 18
    2.3.2 Variable Endpoints . . . . . . . . . . . . . . . . . . . . . . . . . 20

3 Interaction of graphene oxide structures 23
### CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Graphene oxide background</td>
<td>23</td>
</tr>
<tr>
<td>3.2</td>
<td>Interaction energy between two sheets of graphene oxide</td>
<td>27</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Modelling approach</td>
<td>27</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Effects of oxidation levels on graphene oxide interlayer distance</td>
<td>35</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Effects of hydration levels on graphene oxide interlayer distance</td>
<td>37</td>
</tr>
<tr>
<td>3.3</td>
<td>Intercalation of a carbon nanotube between sheets of graphene oxide</td>
<td>40</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Modelling approach</td>
<td>40</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Results</td>
<td>47</td>
</tr>
<tr>
<td>4</td>
<td>Conformation of graphene folds around carbon nanotubes</td>
<td>50</td>
</tr>
<tr>
<td>4.1</td>
<td>Functionalisation and graphene folding</td>
<td>50</td>
</tr>
<tr>
<td>4.2</td>
<td>Modelling approach</td>
<td>51</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Circular cross-section nanotube</td>
<td>52</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Elliptical cross-section nanotube</td>
<td>59</td>
</tr>
<tr>
<td>4.3</td>
<td>Results</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>Conformation of graphene wrinkles on substrate</td>
<td>68</td>
</tr>
<tr>
<td>5.1</td>
<td>Wrinkles and chemical vapor deposition</td>
<td>68</td>
</tr>
<tr>
<td>5.2</td>
<td>Modelling approach</td>
<td>70</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Arch wrinkle structure</td>
<td>70</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Self-adhered wrinkle structure</td>
<td>80</td>
</tr>
<tr>
<td>5.3</td>
<td>Results</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>Conclusion</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>Bibliography</td>
<td>97</td>
</tr>
<tr>
<td>A</td>
<td>Additional mathematical details</td>
<td>107</td>
</tr>
<tr>
<td>A.1</td>
<td>Integration method required for deriving interaction energy</td>
<td>107</td>
</tr>
<tr>
<td>B</td>
<td>Selected LAMMPS molecular dynamics input code</td>
<td>109</td>
</tr>
<tr>
<td>B.1</td>
<td>Simulation of graphene oxide sheets</td>
<td>109</td>
</tr>
</tbody>
</table>
B.2 Simulation of graphene folds around nanotubes .......................... 111

Publications and presentations of the author ............................... 113
List of Figures

1.1 Graphitic materials such as fullerenes, nanotubes and graphite can be topologically constructed from graphene [1]....................... 2

1.2 The CVD process involves thermal decomposition of methane gas with carbon atoms forming a graphene sheet on a substrate [8]................. 4

2.1 The Lennard-Jones potential illustrating the van der Waals radius, \( \sigma \), and the well depth, \( \varepsilon \).......................... 10

2.2 A pair of bonded atoms \( i \) and \( j \), with a bond length of \( \rho_{ij} \)................................. 14

2.3 A bond angle of \( \theta_{ijk} \) between atoms \( i, j \) and \( k \)................................. 14

2.4 A dihedral bond angle of \( \phi_{ijkl} \) between the coplanar atoms \( i, j, k \) and the out-of-plane atom \( l \)................................. 14

2.5 The extremising curve, \( y \), for a given functional contrasted with a comparison function, \( Y \)................................. 18

3.1 The standard procedure for producing graphene oxide from bulk graphite. A graphite sample is oxidated and layers are exfoliated from the bulk. These layers are subsequently converted to reduced graphene oxide through a reduction process [26]................................. 24

3.2 The Lerf-Klinowski model for graphene oxide. Epoxy (C–O–C) and hydroxyl (C–OH) groups bond to the basal plane with carboxyl (CO\(_2\)H) groups decorating the edges [23]................................. 25

3.3 Geometric structure of an epoxy group on graphene oxide where carbon atoms are shown in black and oxygen atoms are shown in red. ......... 28
3.4 Geometric structure of a hydroxyl group on graphene oxide where carbon atoms are shown in black, oxygen atoms in red and hydrogen atoms in white. ................................................................. 29

3.5 A continuum model for a single graphene oxide sheet represented by a surface of graphene and two surfaces of mixed hydrogen and oxygen atoms. 30

3.6 Interaction between two graphene oxide sheets. Here, $z$ denotes the distance between sheets and $\delta$ denotes the distance separating C and OH layers. ................................................................. 30

3.7 The interaction energy between two graphene oxide sheets for varying degrees of oxidation (C:O). ................................................................. 36

3.8 a) A pair of 2nm $\times$ 2nm periodic sheets of graphene oxide shown after minimisation. b) The same sheets displayed after a 1000ps simulation. Both images are created using the Visual Molecular Dynamics (VMD) molecular visualization program [44]. ................................................................. 37

3.9 The interaction energy between two graphene oxide sheets of varied oxidation (C:O) given one (blue) and two (black) monolayers of water intercalated between the sheets. ................................................................. 39

3.10 a) A pair of 2nm $\times$ 2nm periodic sheets of graphene oxide separated with water molecules shown after minimisation. b) The same sheets displayed after a 1000ps simulation. ................................................................. 39

3.11 Construction process of a hybrid film consisting of layered sheets of graphene oxide and carbon nanotubes [53]. ................................................................. 40

3.12 A single-walled carbon nanotube lying between two sheets of graphene oxide. The distance from the centre of the tube to a lower sheet is given as $z$ Å. The angle of the nanotube from the horizontal plane is given by $\psi \in [0, \pi/2]$. ................................................................. 41

3.13 Interaction between a point and an infinite plane. ................................................................. 42

3.14 Interaction between a tilted circle and an infinite plane. ................................................................. 43

3.15 Interaction between a tilted cylinder and an infinite plane. ................................................................. 45
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.16</td>
<td>Interaction energy of a nanotube between sheets of graphene oxide separated by 100 Å. The distance from the lower sheet to the tube is given by $z$ and the angle of the tube to the horizontal is given by $\psi$.</td>
</tr>
<tr>
<td>3.17</td>
<td>The total van der Waals energy of a nanotube lying in the horizontal equilibrium position. The oxidation ratio, denoted as C/O, is the ratio of carbon (C) to oxygen (O) atoms in the graphene oxide sheets.</td>
</tr>
<tr>
<td>3.18</td>
<td>The angle, $\psi$, of a carbon nanotube at the equilibrium position situated halfway between a pair of graphene oxide sheets. Results are shown for varying separation distances, $Z$.</td>
</tr>
<tr>
<td>4.1</td>
<td>Representation of a graphene sheet wrapped around a carbon nanotube with a circular cross-section.</td>
</tr>
<tr>
<td>4.2</td>
<td>Representation of a graphene sheet wrapped around a carbon nanotube with an elliptical cross-section due to compressive force.</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for a circular cross-section of a (6,6) armchair nanotube.</td>
</tr>
<tr>
<td>4.4</td>
<td>Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for a circular cross-section of a (8,8) armchair nanotube.</td>
</tr>
<tr>
<td>4.5</td>
<td>Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for a circular cross-section of a (10,10) armchair nanotube.</td>
</tr>
<tr>
<td>4.6</td>
<td>Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for an elliptical cross-section of a (6,6) armchair nanotube.</td>
</tr>
<tr>
<td>4.7</td>
<td>Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for an elliptical cross-section of a (8,8) armchair nanotube.</td>
</tr>
</tbody>
</table>
4.8 Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for an elliptical cross-section of a (10,10) armchair nanotube.

5.1 A top-down SEM image displaying graphene wrinkles formed by the CVD process [84].

5.2 Representation of an arch-shaped graphene wrinkle partially attached to a substrate, separated by an equilibrium distance, \( \delta \), measured from the \( x \)-axis. This graph is symmetrical under reflection over the \( y \)-axis.

5.3 Representation of an arch-shaped graphene wrinkle with an s-shaped structure.

5.4 Representation of an self-adhered graphene wrinkle partially attached to a substrate, separated by an equilibrium distance, \( \delta_1 \), measured from the \( x \)-axis. The wrinkle adheres to itself at an equilibrium distance \( 2\delta_0 \). This graph is symmetrical under reflection over the \( y \)-axis.

5.5 The curve shown in Fig. 5.1 decomposed into two segments, \( A \) and \( B \). Segment \( A \) has been rotated anticlockwise by \( \pi \) radians and translated such that the left endpoint is at the origin.

5.6 The total energy of an arch-shaped graphene wrinkle on copper substrate for selected bending rigidities, \( \gamma \).

5.7 The total energy of a self-adhered graphene wrinkle on copper substrate for selected bending rigidities, \( \gamma \).

5.8 The total energy of an arch-shaped graphene wrinkle on nickel substrate for selected bending rigidities, \( \gamma \).

5.9 The total energy of a self-adhered graphene wrinkle on nickel substrate for selected bending rigidities, \( \gamma \).
# List of Tables

1.1 The relationship between graphene production methods and the resultant structure of the graphene sheet [5, 6] ......... 3

3.1 Lennard-Jones constants ........................................ 31

3.2 The electrostatic potential of charged groups on graphene oxide. .... 31

4.1 Numerical solutions for the endpoint $x_0$ and root mean square comparison for (6,6), (8,8) and (10,10) circular cross-section nanotubes with different values of the bending rigidity, $\gamma$. .......................... 65

4.2 Numerical solutions for the endpoint $x_0$ and root mean square comparison for (6,6), (8,8) and (10,10) elliptical cross-section nanotubes with different values of the bending rigidity, $\gamma$. .......................... 66

5.1 Interfacial properties between graphene and selected substrates obtained from DFT calculations [86]. Interaction between graphene layers is taken from [72]. ......................................................... 89

5.2 The critical compression, $l$, associated to selected bending rigidities, $\gamma$, of a graphene sheet on copper and nickel substrates. This compression represents the transition point where the self-adhered wrinkle becomes more energetically favourable than the arch wrinkle. ............... 90

5.3 The dimensions of graphene wrinkles on copper and nickel substrates where $\gamma = 1.2$. The transition between models occurs after a compression of 20 Å in both cases. ................................. 91
Chapter 1

Introduction

The study of graphene has gathered increasing interest in recent years with graphitic materials encompassing a significant section of current materials research. Despite its relatively recent discovery, the outstanding properties of graphene have attracted researchers from a wide range of areas. One of the current challenges involves mass-producing graphene of sufficient quality to create a commercially viable product. Successful application of graphitic materials requires a strong understanding of the relationship between the properties of graphene and its structural configurations. In this thesis, we model various forms of graphitic structures with the ultimate goal of providing theoretical insight into their equilibrium configurations.

1.1 Structure and properties of graphene

Graphene is considered as one of the most promising nanomaterials currently studied. A sheet of graphene consists of a single monolayer of carbon atoms arranged in a hexagonal lattice. Graphene was first assumed to be a theoretical material of only an academic interest. Such two-dimensional materials were considered thermodynamically unstable and of no practical concern [1]. This was proved incorrect in 2004, when monolayer graphene was isolated using the aptly named “scotch tape” method. The technique involved the repeated exfoliation of small graphite flakes using an adhesive tape. Researchers were then able to analyse the unique properties of graphene for the first time. The pioneers
of this research, Andre Geim and Konstantin Novoselov, received the 2010 Nobel Prize in Physics for this achievement. Graphene is often viewed as the building block for a plethora of graphitic materials encompassing a variety of geometric structures. Geim’s seminal review paper [1] shows in Fig. 1.1 how graphene can be folded into “zero-dimensional” fullerenes, rolled into “one-dimensional” carbon nanotubes, and restacked to recover three-dimensional graphite.

The atomic structure of graphene consists of a two-dimensional hexagonal network of carbon atoms. Pristine graphene structure has a carbon-carbon bond length of 1.42 Å with an angle of 120 degrees between these bonds. Each carbon atom forms three covalent $\sigma$-bonds with its neighbours via three $sp^2$ hybrid orbitals. The remaining $p$-orbital forms a conjugated system with contiguous atoms forming $\pi$-bonds [2]. These weakly-bonded electrons provide metal-like properties. In fact, graphene occupies a unique state between metal and semi-conductor with an absent band-gap. Additional properties of graphene include its large surface area ($\sim 2600 \text{ m}^2/\text{g}$) [2, 3], extraordinary mechanical strength (Young’s Modulus $\sim 1100\text{GPa}$) [4] measured at 10 times greater than steel and unparalleled thermal conductivity ($\sim 5000 \text{W/m/K}$) [2, 4]. Graphene exhibits a high inte-
ger quantum hall effect at room temperature [4], has a charge carrier (electron) mobility at room temperature of 200,000 cm² V⁻¹ s⁻¹ and is completely impermeable to any gases. Graphene also offers high optical transparency of up to 97.7%. The combination of so many exceptional properties in a single material makes graphene incredibly versatile. However, for such properties to flourish, pristine sheets of graphene lacking both grain boundaries and defects are required [5]. Current graphene production methods still involve a trade-off between these ideals.

1.2 Graphene production techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Crystallite size (µm)</th>
<th>Sample size (mm)</th>
<th>Cost</th>
<th>Electronic quality</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical exfoliation</td>
<td>&gt;1,000</td>
<td>&gt;1</td>
<td>Low</td>
<td>Very High</td>
<td>Research</td>
</tr>
<tr>
<td>Chemical exfoliation</td>
<td>≤ 0.1</td>
<td>Infinite as thin film</td>
<td>Low</td>
<td>Low</td>
<td>Coatings, paint/ink, composites, transparent conductive layers, energy storage, bioapplications</td>
</tr>
<tr>
<td>Chemical exfoliation via graphene oxide</td>
<td>~100</td>
<td>Infinite as thin film</td>
<td>Low</td>
<td>Low</td>
<td>Coatings, paint/ink, composites, transparent conductive layers, energy storage, bioapplications</td>
</tr>
<tr>
<td>CVD</td>
<td>1,000</td>
<td>~1,000</td>
<td>High</td>
<td>High</td>
<td>Photonics, nanoelectronics, transparent conductive layers, sensors, bioapplications</td>
</tr>
<tr>
<td>SiC</td>
<td>50</td>
<td>100</td>
<td>High</td>
<td>High</td>
<td>High-frequency transistors and other electronic devices</td>
</tr>
</tbody>
</table>

The production of graphene typically involves a trade-off between sample quality and manufacturing costs. Graphene fabrication techniques can be classified into either top-down or bottom-up approaches. Large-scale graphene productions are based on top-down approaches which largely follow the mechanical, physical and chemical exfoliation of graphene from a graphite sample [7]. Conversely, the bottom-up approach generally involves constructing a graphene sheet atom-by-atom on some substrate. This approach often results in fewer defects and subsequently improved electronic properties. However, the costs tend to be high and do not scale up well for applications requiring macroscopic quantities of graphene. Some details are provided in Table 1.1.

Exfoliation of graphene involves the separation of a single graphene sheet from graphite. Graphite is composed of layered sheets of graphene weakly-connected by intermolecular
forces. However, the large surface area of graphene renders these forces non-trivial. Successful exfoliation requires overcoming these forces while introducing a minimal amount of defects. The traditional method of solving this problem was devised by Hummer in the late 1950s. Hummer’s method utilises powerful oxidising agents to produce graphite oxide which has a marked increase in interlayer distances weakening the van der Waals bonding and hence permitting easier exfoliation [7]. The resulting oxidated form of graphene is known as graphene oxide. A variety of thermal or chemical reduction processes can be employed to strip these oxidated groups from the surface of the molecule, producing reduced graphene oxide (rGO). This material retains more defects due to the harsh oxidation conditions [7]. Subsequently, there is a marked loss in electronic quality. Further details of the structure and properties of graphene oxide are discussed in Chapter 3.

![Figure 1.2: The CVD process involves thermal decomposition of methane gas with carbon atoms forming a graphene sheet on a substrate [8].](image)

Smaller, higher quality sheets can be formed using chemical vapor deposition (CVD). The CVD process is a method of depositing gaseous reactants onto a substrate. The substrate is annealed in a reactor at high temperatures of \( \sim 1000^\circ C \) to increase grain size. A mixture of hydrogen and methane gases is then introduced. The high temperature causes the gas to decompose and resulting carbon atoms diffuse into the substrate as shown in Fig. 1.2. Finally, the reactor is cooled in a neutral environment. Carbon atoms precipitate
CHAPTER 1. INTRODUCTION

on the surface of the substrate forming graphene layers. Depending on the cooling rate, substrate and reactants, the number of layers and general quality of the final structure can be regulated. Copper substrate has been shown the best choice for uniform, monolayer growth due to low carbon solubility. Alternatively, multilayer growth can be achieved with a nickel substrate. Despite the relatively pristine lattice structure, the CVD process is not perfect. Graphene tends to form in “islands” which merge forming a polycrystalline structure. That is, the differing lattice orientations form grains, negatively impacting the electron transport and mechanical properties. Additionally, during the cooling process, wrinkles may be formed in graphene as a result of the difference in thermal expansion coefficients of the substrate and graphene sheet. Further details of wrinkle formation are discussed in Chapter 5.

1.3 Applications of graphene

Graphene has proven to have potential applications in a variety of disparate areas including drug delivery, solar cells, electronic and biological sensors, transparent conductive coatings and energy storage.

Graphene can act as a carrier for targeted and controlled drug delivery. Selective modifications can be engineered allowing a direct attraction to diseased cells. The large surface area, low toxicity and biocompatibility of graphene make it useful for this purpose [2]. While graphitic materials can cause cell damage and other side effects, they can be treated or wrapped with biocompatible polymers, such as polyethylene glycol (PEG), to increase biocompatibility and reduce significant threat. However, the study of graphene toxicity is still an ongoing area of research [2, 7]. The large planar surface and $\pi$-conjugated structure of graphene is an ideal platform for immobilising a wide variety of substances including drugs and biomolecules [2, 7, 9]. Drug molecules bind to the surface and reactive edges of graphene sheets. Molecules may also covalently bond to polymers on the surface which is considered a more stable, if less efficient route [3, 4]. These carriers can then be controlled with stimulus from external fields [2].

Graphene has applications in a variety of electronic sensors including chemical, me-
CHAPTER 1. INTRODUCTION

Mechanical and biological sensors. Graphene is an ideal material for sensors due to its thin, flexible, stretchable surface [9, 10] that is highly sensitive to small changes in many physical parameters such as strain, pressure, carrier density and temperature [11]. Combinations of these parameters can be exploited to produce multifunctional sensors. However, this sensitivity can also be negative due to the competition between so many parameters [12]. There are also issues with stability and repeatability as many changes are not easily reversible [12].

The high carrier mobility of graphene suggests a use in electronic devices. However, pristine graphene is not considered ideal for logic circuits due to the absence of a bandgap making it unable to trigger an off-state [5, 9]. Researchers have attempted to circumvent this issue through doping and working with graphene nanoribbons [9].

Graphene has the potential for use in flexible and stretchable transparent conductive coatings for use in devices such as touchscreens, solar cells and light-emitting diodes (LEDs) [5, 9]. Graphene is mechanically stronger, more flexible and much more readily available than the usual choice of indium titanium oxide. One of the greatest barriers to commercial use is the production of highly conductive graphene sheets which maintain their mechanical properties [13, 14].

Graphene also has potential application in energy storage. Graphene has been considered for use as an advanced electrode material in supercapacitors as its high surface area and conductivity allows for better charge storage and an improvement in energy density. Hydrogen storage often depends on solid state materials such as Metal Organic Frameworks (MOFs) which often rely on temperature and pressure changes to absorb and release hydrogen molecules [6, 15]. Graphene offers a more stable alternative. Its surface is efficient for binding hydrogen atoms and these binding forces can be modulated by curvature changes [15, 16]. Certain combinations of graphitic nanomaterials consisting of varying shapes and properties can also offer novel properties and enhanced performance [6].
1.4 Thesis structure

This thesis is structured into five chapters as detailed here.

The first chapter provides a brief overview of the structure, properties and some important applications of graphene. We also discuss various graphene production methods which inherently affect its properties.

The second chapter introduces the mathematical and computational techniques employed in this thesis. We review discrete atomic techniques for modelling molecular interactions using potential functions. A continuum model is also introduced as an alternative approach to modelling these interactions. This approach simplifies the often infeasible computational problems encountered in the discrete modelling. We additionally cover some essential background of molecular dynamics simulation. These simulation techniques are employed throughout this thesis as a comparison to analytical results. Finally, we provide some background for variational calculus which is used extensively in the latter half of this thesis.

The third chapter proposes an analytical model for graphene oxide, graphene with attached oxidated groups. We demonstrate the effects of different parameters on the equilibrium structure of graphene oxide. We further expand this model, incorporating the encapsulation of a carbon nanotube between graphene oxide sheets and determining its natural equilibrium.

The fourth chapter employs calculus of variations to analyse the morphology of folded graphene. We examine the implication of intercalating carbon nanotubes into these folds to produce a novel form of functionalisation. We formulate two alternative models based on the eccentricity of the intercalated tube.

Finally, the fifth chapter investigates the formation of graphene wrinkles on a metallic substrate during chemical vapour deposition. We use calculus of variations to examine the conformation of these wrinkles under various choices of parameters.
Chapter 2

Mathematical methodology

In this chapter, we outline various mathematical techniques and algorithms employed in this thesis. We first discuss the interaction between molecules as defined through potential functions. These are instrumental in determining analytical solutions for intermolecular interaction. Following this, we examine molecular dynamics simulation, a numerical technique popularly employed in modelling complex interaction behaviours. Finally, we provide a background to variational calculus which is utilised in predicting minimum energy conformations of folded graphene and wrinkle structures formed during graphene growth.

2.1 Modelling molecular interaction

This thesis utilises a continuum approximation formulated by Girifalco [17] and subsequently extended by Cox et. al. [18, 19] for calculating intermolecular interaction. Before introducing this approach, we provide a brief overview of the nature of intermolecular forces and the typical methods for modelling this interaction. Intermolecular forces are the interaction forces between discrete particles, including molecules, atoms and ions. These forces are significantly weaker than intramolecular forces, which bind the molecule together. However, the physical properties of molecular materials including friction, surface tension and viscosity are all driven by intermolecular forces. The interaction between molecules can be decomposed into attractive and repulsive forces. The
attractive forces between charge-neutral molecules such as pure graphene are denoted the van der Waals attractive forces. Charged, or polar, molecules including graphene oxide are additionally affected by electrostatic forces. The repulsive forces are generally short-ranged in nature and are comprised of the interaction between negatively charged electron shells and Pauli’s exclusion principle. These details are important components of forcefields in molecular mechanics and ultimately one of the most complex aspects of any molecular simulation.

Given a pair of distinct molecular structures, the intermolecular energy is typically calculated by a sum of interatomic potentials. A potential function describes how the potential energy of an atomic system depends on the spatial coordinates of the atoms. Interaction between pairs of atoms, or pair potentials, tend to be the most popular due to their relative computational cheapness. However, many-body effects also have an important impact on the system and many potential functions implicitly incorporate these effects into their structure.

We can calculate the intermolecular energy between a pair of molecules as

$$E = \sum_i \sum_j \phi(\rho_{ij}),$$  \hspace{1cm} (2.1)

where we denote $\phi(\rho_{ij})$ as the potential function for atoms $i$ and $j$, each on distinct molecules, separated by a distance $\rho_{ij}$. Such summations are commonly employed in molecular simulation. However the computational cost, especially when working with large molecules, makes large scale simulation infeasible. An alternative is to construct a continuum approximation to calculate the interaction energy [18, 19]. This approximation follows the assumption that atoms are uniformly distributed or “smeared” over each molecule. Subsequently (2.1) may be replaced by

$$E = \eta_1 \eta_2 \int \int \phi(\rho) \, dS_1 \, dS_2,$$  \hspace{1cm} (2.2)

where $\eta_1$ and $\eta_2$ are the mean surface density of atoms over each molecule and $\rho$ is the distance between two typical surface elements $dS_1$ and $dS_2$ located on the two interacting
molecules. In general, the mean surface density can be found from dividing the number of atoms on the molecule by the surface area.

Due to its symmetrical lattice structure, the mean surface density of a graphene sheet is fairly elementary to derive. Consider a unit surface of graphene comprising of a hexagonal lattice with the vertices representing carbon atoms and the edges representing bonds with each atom adjacent to three hexagonal faces. As the carbon-carbon bond length in pristine graphene is given as 1.421 Å, the surface area of the hexagon is given by 5.246 Å². Thus, the mean surface density of graphene is given by \( \eta = \frac{(6/3)}{\text{surface area of hexagon}} \). As such, we find the mean surface density of graphene to be 0.3812 Å⁻².

2.1.1 Lennard-Jones potential

![Figure 2.1: The Lennard-Jones potential illustrating the van der Waals radius, \( \sigma \), and the well depth, \( \epsilon \).](image)

The 6-12 Lennard-Jones potential, initially proposed by Sir John Lennard-Jones in 1924, is the most commonly used model for intermolecular interaction. The Lennard-Jones potential is used to calculate the interaction between atoms on different, non-polar molecules, or even the same molecule provided the atoms are separated by sufficiently
many bonds. The Lennard-Jones potential is given by

\[ \phi(\rho) = 4\varepsilon \left[ -\left( \frac{\sigma}{\rho}\right)^6 + \left( \frac{\sigma}{\rho}\right)^{12} \right], \]

where \( \rho \) represents the distance between atoms, \( \varepsilon \) indicates the potential well depth or the strength of interaction between the atoms and \( \sigma \) is the van der Waals radius, the distance at which the potential is zero. These parameters are visually displayed in Fig. 2.1. In this thesis, we use the more mathematically convenient form,

\[ \phi(\rho) = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}}, \quad (2.3) \]

where the attractive and repulsive parameters are respectively given by \( A = 4\varepsilon\sigma^6 \) and \( B = 4\varepsilon\sigma^{12} \). It should be noted that these parameters only apply to interactions between identical types of atom. When calculating the Lennard-Jones potential for a pair of atoms with differing type, we derive new parameters from the Lorentz-Berthelot mixing rules defined as

\[ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \]
\[ \varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{1/2}. \]

Other commonly used interatomic pair potentials including the Buckingham and Morse potentials provide a more accurate, exponential model for the repulsive component. The Lennard-Jones potential is often preferable due to its more convenient mathematical structure and comparative computational cheapness.

### 2.1.2 Coulombic potential

In the case where an atom is located on a polar molecule, it may be associated with a charge. The long-range potential energy between charged particles is known as the electrostatic potential energy. The electrostatic potential between two particles is typically
represented by the pairwise Coulombic potential which is defined as

$$\phi(\rho) = \frac{Q_i Q_j}{4\pi\varepsilon_0 \rho_{ij}},$$  \hspace{1cm} (2.4)$$

where $Q_i$ and $Q_j$ are the charges on atoms $i$ and $j$ respectively, $\rho_{ij}$ is the distance separating the atoms and $\varepsilon_0$ is the permittivity of free space.

2.2 Molecular dynamics

The aim of computational simulations is to understand and predict the properties and behaviour of materials. In particular, we use molecular dynamics simulations in this thesis as a comparison to our analytic models. Simulations behave in much the same way as conventional experiments, however they are able to run tests in situations that may be otherwise impossible or prohibitively expensive to the experimentalist. While simple systems can be modelled exactly, scaling up these systems with high number of interacting bodies rapidly renders the system analytically unsolvable. However, by using computational simulations to solve these problems numerically, highly accurate results can be achieved. These models may be tested by comparing simulated data with appropriate experimental results.

Molecular dynamics (MD) simulation is a computational simulation technique for computing the equilibrium and transport properties of a many-body system. The classical approach to molecular dynamics is the “ball-and-stick” model where atoms, here denoted as particles, are represented by soft balls and bonds are represented by elastic sticks. It is also possible to describe matter in a higher and less detailed level which is known as coarse-graining of the model. This technique involves smoothing out extraneous detail to minimise computational time.

A typical simulation involves constructing a system with a fixed number of particles. The force on each particle is calculated and Newton’s equations of motion are used to determine the time-evolution of the system. When equilibrium is reached, measurements of the system can be made.
This basic procedure of a simple molecular dynamics simulation is detailed as follows:

1. Read in the parameters of the system. This includes such variables as the initial temperature, time step, number of particles and density.

2. Initialise the system by selecting the initial positions and velocities of each particle.

3. While the system is not in equilibrium, we repeat the following steps:

   (a) Compute the forces affecting each particle.

   (b) Compute the resultant time evolution of the system.

4. Calculate the system’s properties.

The initial positions of each particle are chosen such that each pair is sufficiently far apart as to avoid overlapping. This can be achieved by placing our particles on a cubic lattice or otherwise placing our particles in the shape of the system we are attempting to simulate. The most computationally expensive part of an MD simulation is calculating the forces on each particle in the system. As shown in Fig. 2.1, van der Waals interaction energy between particles rapidly diminishes as the separating distance increases. Computational cost can then be reduced by introducing a cutoff distance, only comparing nearby particles. These particles are often stored in neighbour lists to further reduce this cost. The force between particles is calculated using forcefields.

### 2.2.1 Forcefields

A forcefield is a collection of equations and constraints designed to reproduce molecular geometry and selected properties of tested structures. Some of the most well-known forcefields include AMBER, CHARMM and OPLS. The atomic force field model describes physical systems as collections of atoms held together by interatomic forces. We typically define this as a potential function in terms of the $N$ atoms in the system where $U(r_i), i \in \{1, ..., N\}$ with the position vector $\mathbf{r}_i(t) = (x_i(t), y_i(t), z_i(t))$. The forces are
determined from the gradient of this potential. A typical forcefield has the form

\[
U(r_1, r_2, \ldots, r_N) = E_{\text{bonded}} + E_{\text{unbonded}}
\]

\[
= E_{\text{bonds}} + E_{\text{angles}} + E_{\text{dihedrals}}
\]

\[
+ \sum_{\text{vdW}} \left( -\frac{A}{\rho_{ij}^6} + \frac{B}{\rho_{ij}^{12}} \right) + \sum_{\text{electrostatic}} \frac{Q_i Q_j}{4\pi\varepsilon_0 \rho_{ij}},
\]

where the non-bonded terms are defined in Section 2.1. The bonded terms describe the in-

Figure 2.2: A pair of bonded atoms \(i\) and \(j\), with a bond length of \(\rho_{ij}\).

Figure 2.3: A bond angle of \(\theta_{ijk}\) between atoms \(i, j\) and \(k\).

Figure 2.4: A dihedral bond angle of \(\phi_{ijkl}\) between the coplanar atoms \(i, j, k\) and the out-of-plane atom \(l\).
tramolecular structure whereas the non-bonded terms define the forces between unbonded atoms. The exact details of the bonded terms may vary depending on the chosen force-field. The simulations conducted in this thesis employ commonly used Hookean forms for these terms. The first of the bonded terms, $E_{\text{bonds}}$, describes the stretching of bonds as shown in Fig. 2.2 and can be expressed as

$$E_{\text{bonds}} = k_{ij}(\rho_{ij} - \rho_0)^2,$$

where $k_{ij}$ is the force constant, $\rho_{ij}$ is the current bond length and $\rho_0$ is the equilibrium bond length. The second term describes the bending of bonds as shown in Fig. 2.3. The Hookean form for the stretching or bending of the bonds is

$$E_{\text{angles}} = k_{ijk}(\theta_{ijk} - \theta_0)^2,$$

where $k_{ijk}$ is the force constant, $\theta_{ijk}$ is the current bond angle and $\theta_0$ is the equilibrium bond angle. The third term accounts for the torsion rotation of bonds as shown in Fig. 2.4. The harmonic form of this expression is expressed as

$$E_{\text{dihedrals}} = k_{ijk}(1 + d \cos(n\phi_{ijk} - \phi_0))$$

where $k_{ijk}$ is the force constant, $n$ is the multiplicity or number of minima, $\phi_{ijk}$ is the out-of-plane dihedral angle and $\phi_0$ is the phase shift.

### 2.2.2 Numerical integration schemes

The potential energy is a function of the position of all atoms in the system. Due to the typical complexity of this function, the dynamics of the resulting system must be solved numerically. Verlet-style algorithms are the most popular used in molecular dynamics as they are reasonably stable over the long time period necessary to run a simulation. These algorithms are based on a simple truncation, of the order $O(\Delta t^4)$, of the Taylor expansion of the particle’s coordinates. Here, $\Delta t$ is our time-step which is required to be very small.
The simulations conducted for this thesis have a timestep of magnitude $10^{-15}$ seconds.

Calculating the kinetic energy of the system, necessary for maintaining stability, requires knowledge of the velocity at every timestep. However, the simple Verlet algorithm only provides the velocity up to $O(\Delta t^2)$. More advanced modifications, including the leap-frog algorithm, the Beeman algorithm and the velocity-Verlet algorithm allow the calculation of the velocity at $O(\Delta t^4)$, equivalent to that of the position. Of these options, the velocity-Verlet algorithm is mostly used as it is computationally cheap, stable and time-reversible.

Recall that the position vector for a given particle $i$ at a given time $t$ is defined as $\mathbf{r}_i(t) = (x_i(t), y_i(t), z_i(t))$. We additionally define the first derivative of the position vector, the velocity vector, as $\mathbf{v}_i(t)$ and the second derivative, the acceleration vector, as $\mathbf{a}_i(t)$. The basic steps in the velocity-Verlet algorithm are given as

$$
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2,
$$
$$
\mathbf{a}_i(t + \Delta t) = \frac{\mathbf{F}_i(t + \Delta t)}{m_i},
$$
$$
\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2}(\mathbf{a}_i(t) + \mathbf{a}_i(t + \Delta t))\Delta t,
$$

where $m_i$ represent the mass of our particle. The force on the particle, $\mathbf{F}_i(t)$, is derived from the potential function. Further details can be found in [20].

### 2.3 Calculus of variations

Many physical problems, whether at the microscale, macroscale or the nebulous mesoscale, involve finding the equilibrium states of a mechanical system. This can be shown to be equivalent to finding the minimal energy states, a concept commonly known as the principle of least action. One technique for determining these states is through a field of mathematical analysis known as the calculus of variations. Variational calculus involves finding the extremum of functionals, a mapping from a set of functions to the real numbers. This has proven to be an exceptionally versatile method of studying optimisation.
problems. Applications of the theory include determining minimal surfaces, geodesics and optimal control problems.

This thesis includes finding optimal graphene conformations under the effect of molecular interaction, bending and possible external forces. A graphene sheet has an intrinsic hexagonal symmetry and the elastic properties of a hexagonal structure are known to be isotropic [21]. This remarkable property allows us to utilise continuum elastic methods as would be typical in the macroscale case. Consequently, a two-dimensional cross-section of a graphene sheet, under the assumption of perfect elasticity, can be represented as an elastica. That is, we deal with minimising the total energy along an inextensible plane curve \( y \in C^2[x_0, x_1] \). This requires functionals of the form \( J : C^2[x_0, x_1] \to \mathbb{R} \) such that,

\[
J(y) = \int_{x_0}^{x_1} F(x, y(x), y'(x), y''(x)) \, dx.
\]

Our functional \( J \), represents the total energy of the system while the integrand \( F \) describes how the relationship between the energy and the curve structure. The bending energy of an elastica was shown by Euler to be

\[
E = \gamma \int_C \kappa^2 \, ds,
\]

where \( \gamma \) is the bending rigidity of the material, \( s \) is the arclength along the curve \( C \) and \( \kappa \) is the signed curvature defined as

\[
\kappa = \frac{y''}{(1 + y'^2)^{3/2}}.
\]

Finding the minimum energy to such a problem requires finding the solution to the second-order Euler-Lagrange equation. The Euler-Lagrange equation, in its various forms, is fundamental to solving variational problems.
2.3.1 The Euler-Lagrange equation

Any variational problem can be reduced to boundary value problems connected to associated differential equations known as the Euler-Lagrange equations. We include the following derivation of the Euler-Lagrange equation as it will be used in Chapters 4 and 5. Firstly, we assume the existence of a continuous, twice-differential function \( y = y(x) \) with endpoints defined as \( y(x_0) = y_0 \) and \( y(x_1) = y_1 \) such that \( y \) extremises the functional

\[
J(y) = \int_{x_0}^{x_1} F(x, y(x), y'(x), y''(x)) \, dx.
\]  

(2.5)

Figure 2.5: The extremising curve, \( y \), for a given functional contrasted with a comparison function, \( Y \).

It should be noted that for the problems encountered in this thesis, \( y \) will act as a minimiser for the functional. We next denote a family of comparison functions, each permitted to differ slightly from \( y \), as

\[
Y(x) = y(x) + \epsilon \eta(x),
\]
where \( \eta(x) \) is an arbitrary differentiable function for which

\[
\eta(x_0) = \eta(x_1) = 0, \\
\eta'(x_0) = \eta'(x_1) = 0,
\]

(2.6)

for some given non-negative parameter \( \varepsilon \). One such comparison is shown in Fig. 2.5. We see that regardless of our choice of \( \eta(x) \), each member of this family of curves is extremised when \( \varepsilon \) is chosen to be zero. It naturally follows that

\[
Y'(x) = y'(x) + \varepsilon \eta'(x), \\
Y''(x) = y''(x) + \varepsilon \eta''(x).
\]

We now express (2.5) as

\[
J(\varepsilon) = \int_{x_0}^{x_1} F(x, Y(x), Y'(x), Y''(x)) \, dx.
\]

(2.7)

This redefinition allows us to find the extremum using standard techniques as we know \( J'(0) = 0 \). Taking the derivative with respect to \( \varepsilon \), we find

\[
J'(\varepsilon) = \frac{d}{d\varepsilon} \int_{x_0}^{x_1} F(x, Y(x), Y'(x), Y''(x)) \, dx
\]

\[
= \int_{x_0}^{x_1} \left( \frac{\partial F}{\partial Y} \eta + \frac{\partial F}{\partial Y'} \eta' + \frac{\partial F}{\partial Y''} \eta'' \right) \, dx
\]

\[
= \int_{x_0}^{x_1} \left( \frac{\partial F}{\partial y} \eta(x) + \frac{\partial F}{\partial y'} \eta'(x) + \frac{\partial F}{\partial y''} \eta''(x) \right) \, dx.
\]

Evaluating at the point \( \varepsilon = 0 \), we find

\[
J'(0) = \int_{x_0}^{x_1} \left( \frac{\partial F}{\partial y} \eta(x) + \frac{\partial F}{\partial y'} \eta'(x) + \frac{\partial F}{\partial y''} \eta''(x) \right) \, dx.
\]

Finally, we integrate by parts twice to eliminate \( \eta'(x) \) and \( \eta''(x) \) from the integrand. After
some routine calculation, we find the result

\[ J'(0) = \left[ \left( \frac{\partial F}{\partial y'} - \frac{d}{dx} \left( \frac{\partial F}{\partial y''} \right) \right) \eta(x) + \frac{\partial F}{\partial y''} \eta'(x) \right] \bigg|_{x_0}^{x_1} \]

\[ + \int_{x_0}^{x_1} \left[ \frac{\partial F}{\partial y'} - \frac{d}{dx} \left( \frac{\partial F}{\partial y''} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial y''} \right) \right] \eta(x) \, dx \]

\[ = \int_{x_0}^{x_1} \left[ \frac{\partial F}{\partial y'} - \frac{d}{dx} \left( \frac{\partial F}{\partial y''} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial y''} \right) \right] \eta(x) \, dx = 0. \quad (2.8) \]

As \( \eta(x) \) is taken to be arbitrary over our curve, the remainder of the integrand, known as the Euler-Lagrange equation, must satisfy

\[ \frac{\partial F}{\partial y'} - \frac{d}{dx} \left( \frac{\partial F}{\partial y''} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial y''} \right) = 0. \]

### 2.3.2 Variable Endpoints

We are often presented with variational problems not accompanied by the appropriate number of boundary conditions. For example, this occurs when the endpoints of a minimising curve are permitted to vary. Fortunately, this requires a slight change in the derivation which implicitly generates the missing conditions, termed natural boundary conditions. The key change with this derivation is that we can no longer make the convenient assumption that the comparison functions vanish at the endpoints (2.6). Note that our functional is extended linearly where appropriate to ensure the validity of the integral.

We start with a similar formulation to (2.7). However, we induce a small variation at the endpoints where for \( i \in \{0, 1\} \), \([X_i(\epsilon) = x_i]_{\epsilon=0} \). The resultant functional is

\[ J(\epsilon) = \int_{X_0(\epsilon)}^{X_1(\epsilon)} F(x, Y(x), Y'(x), Y''(x)) \, dX. \]

Provided \( \frac{\partial F}{\partial \epsilon} \) is continuous in \( \epsilon \) and \( x \) over the domain, we can use the Leibniz Rule finding

\[ J'(\epsilon) = \frac{dF}{d\epsilon} \frac{dX_1}{d\epsilon} - F \frac{dX_0}{d\epsilon} + \int_{X_0(\epsilon)}^{X_1(\epsilon)} \frac{\partial}{\partial \epsilon} F(x, Y(x), Y'(x), Y''(x)) \, dX. \]
Following a similar procedure to (2.8), we find

\[
J'(0) = F \left. \frac{dX_0}{d\varepsilon} \right|_{\varepsilon_0} - \left. F \frac{dX_1}{d\varepsilon} \right|_{\varepsilon_0} + \left[ \left( \frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) \right) \eta(x) + \frac{\partial F}{\partial \eta'} \eta'(x) \right]_{x_0}^{x_1} \\
+ \int_{x_0}^{x_1} \left[ \frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial y''} \right) \right] \eta(x) \ dx.
\]

(2.9)

At the endpoints, we have

\[
Y(X) = y(X) + \varepsilon \eta(X),
\]

(2.10)

\[
Y'(X) = y'(X) + \varepsilon \eta'(X).
\]

(2.11)

Differentiating (2.10) with respect to \(\varepsilon\) gives the expression

\[
\frac{dY}{d\varepsilon} = y'(X) \frac{dX}{d\varepsilon} + \eta(X) + \varepsilon \eta'(X) \frac{dX}{d\varepsilon}.
\]

Evaluating at \(\varepsilon = 0\) gives

\[
\eta(x) = \left. \frac{dY}{d\varepsilon} \right|_{\varepsilon_0} - \left. y'(X) \frac{dX}{d\varepsilon} \right|_{\varepsilon_0}.
\]

Following the same procedure with (2.11), we find

\[
\eta'(x) = \left. \frac{dY'}{d\varepsilon} \right|_{\varepsilon_0} - \left. y''(X) \frac{dX}{d\varepsilon} \right|_{\varepsilon_0}.
\]

Finally, we substitute these expressions for \(\eta(x)\) and \(\eta'(x)\) into (2.9) to find

\[
J'(0) = \left[ \left( F - y' \left( \frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) \right) - y'' \frac{\partial F}{\partial y''} \right) \left. \frac{dX}{d\varepsilon} \right|_{\varepsilon_0} \right]_{x_0}^{x_1} \\
+ \left[ \left( \frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) \right) \left. \frac{dY}{d\varepsilon} \right|_{\varepsilon_0} + \frac{\partial F}{\partial \eta'} \left. \frac{dY'}{d\varepsilon} \right|_{\varepsilon_0} \right]_{x_0}^{x_1} \\
+ \int_{x_0}^{x_1} \left[ \frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial y''} \right) \right] \eta(x) \ dx.
\]

These boundary conditions are most concisely expressed using the canonical coordinates
from the Hamiltonian formulation of mechanics. For a second order variational problem, these canonical coordinates are defined as

\[ p = \frac{\partial F}{\partial y'} - \frac{d}{dx} \left( \frac{\partial F}{\partial y''} \right), \]

\[ q = \frac{\partial F}{\partial y''}, \]

\[ H = F - py' - qy''. \]

Here, \( H(p, q) \) represents the Hamiltonian or the total energy of the system with \( p \) and \( q \) representing coordinates in phase space. Degenerate forms of the Euler-Lagrange equation show \( p \) is constant provided \( F \) is independent of \( y \). Similarly, \( H \) is constant when \( F \) is independent of \( x \). We additionally note from Gelfand and Fomin [22] that our variations can be defined using delta notation as

\[ \delta x = \frac{dX}{d\epsilon} \bigg|_{\epsilon_0}, \quad \delta y = \frac{dY}{d\epsilon} \bigg|_{\epsilon_0}, \quad \delta y' = \frac{dY'}{d\epsilon} \bigg|_{\epsilon_0}. \]

We note that these terms are only non-zero when permitted to vary. With this simplification, the second order Euler-Lagrange equation with variable boundary is expressed as

\[ \frac{\partial F}{\partial y} - \frac{d}{dx} \left( \frac{\partial F}{\partial y'} \right) + \frac{d^2}{dx^2} \left( \frac{\partial F}{\partial y''} \right) = 0, \]

with the natural boundary conditions,

\[ [p \delta y + q \delta y' - H \delta x]_{x_0}^{x_1} = 0. \]

This notation will be heavily used in the variational problems encountered in Chapters 4 and 5. We note that in the case of piecewise functionals, the natural boundary conditions must be equivalent at the shared boundaries.
Chapter 3

Interaction of graphene oxide structures

In this chapter, we study the interaction of graphene oxide under varying degrees of oxidation and hydration. Firstly, we provide an extended overview of graphene oxide and discuss its disordered, nonstoichiometric structure. We construct a continuum model for graphene oxide interaction through decomposing the molecular structure into three continuous surfaces. This model is compared with equivalent molecular dynamics simulation results. An extended version of this model is presented where a single walled carbon nanotube is encapsulated between the graphene oxide sheets. The resultant equilibrium states are investigated.

3.1 Graphene oxide background

Synthesising suspensions of graphene oxide (GO) is a low cost method of mass producing graphitic materials. These suspensions can be dried to form thin, conductive films with higher mechanical strength, flexibility and chemical stability compared to standard metal-based options. Such films find application as components in touch screens, liquid crystal displays and organic light-emitting diodes. The performance of these films can be further enhanced through the incorporation of other nanomaterials such as single-walled carbon nanotubes (SWNT). It is then, important to understand how graphene oxide sheets interact with one another especially given the varied composition of these materials.

Graphene oxide consists of a monolayer graphene sheet with oxidated functional groups
Figure 3.1: The standard procedure for producing graphene oxide from bulk graphite. A graphite sample is oxidated and layers are exfoliated from the bulk. These layers are subsequently converted to reduced graphene oxide through a reduction process [26].

Mass-production of graphene oxide is achieved through the chemical oxidation of graphite followed by an exfoliation process. The fastest and most conventional method of oxidising graphite is a revised version of Hummer’s Method involving reacting graphite powder with a mixture of potassium permanganate (KMnO$_4$) and concentrated sulfuric acid (H$_2$SO$_4$) [23]. This reactive process introduces molecules of oxygen to the pure graphite causing the layered sheets to become hydrophilic. Individual sheets of graphite oxide can be exfoliated off the bulk graphite oxide in an organic solvent or water aided by ultrasonication or a mechanical stirring process [24, 25]. The exact properties of graphene oxide vary depending on its synthesis, processing and experimental conditions [25]. This production process is shown in Fig. 3.1.

The exact chemical structure of graphene oxide has proven difficult to determine and a wide variety of models have been proposed since its discovery. Lerf et. al. [27] constructed a model, shown in Fig. 3.2, where the main functional groups attached to the basal
Figure 3.2: The Lerf-Klinowski model for graphene oxide. Epoxy (C–O–C) and hydroxyl (C–OH) groups bond to the basal plane with carboxyl (CO$_2$H) groups decorating the edges [23].

plane consist of epoxy (C–O–C) and hydroxyl (C–OH) groups with carboxyl and carbonyl groups attached to the edges of the carbon structure [27, 28]. The Lerf-Klinowski model has become the most widely accepted model for graphene oxide in recent times and nuclear magnetic resonance (NMR) experimental results support the model [23, 29, 30]. This model of graphene oxide is nonstoichiometric, or unable to easily represent as a chemical formula, and mostly amorphous due to distortions from the high fraction of sp$^3$ C–O bonds [31]. Partial oxidation of the substrate has been shown to be more thermodynamically favourable than complete oxidation. The degree of oxidation, commonly measured by the C:O ratio of the carbon atoms to the attached oxygen atoms, has a strong effect on the exact properties of graphene oxide.

Unlike pristine graphene, known for its exceptional electrical conductivity, graphene oxide functions as an electrical insulator due to disturbance of the sp$^2$ bonding between carbon atoms by functional groups [23]. Additionally the broken symmetry of the hexagonal structure reduces the effective Young’s modulus of graphene oxide to 207.6 $\pm$ 23.4 GPa.

These weaknesses can be addressed through a chemical or thermal reduction process which strips the functional groups from the basal plane of carbon. This attempts to recover the hexagonal lattice of graphene and restore electrical conductivity. The chemi-
cal reduction of graphene oxide is considered to be one of the most viable methods of mass-producing graphene. However, due to remaining defects, the resulting sheets are significantly lower in quality compared to sheets produced by mechanical exfoliation.

Graphene oxide composites are typically fabricated from colloidal suspensions of graphene oxide sheets in water [32]. A liquid crystal (LC) is a state where anisotropic particles form a crystalline structure that also has the fluidity of a liquid. Liquid crystals of graphitic hydrocarbons have promising potential use in advanced electronics and optoelectronics [33]. Graphene is a hydrophobic material and when dispersed in solution, it easily agglomerates or restacks to form graphite [34]. As a result, it is only suitable for a LC structure under very specific conditions. The formation of a LC structure requires a high aspect ratio and sufficient dispersibility/solubility [35]. Graphene sheets are not soluble and disperse poorly due to aromatic $\pi-\pi$ stacking. The hydrophilic properties of graphene oxide make it easily dispersible and thus a more suitable candidate. Well-dispersed graphene oxide best forms a LC structure in water and organic solvents [35].

Thin films incorporating graphene oxide can be produced through a dip-coating and drying process. The moderate conductivity of reduced graphene oxide lends to potential use in electronic devices. These films can also be combined with polymer or ceramic matrixes to enhance their mechanical and electrical properties. Other uses include nanocomposite materials, energy storage, biomedical applications, catalysis and as a surfactant.

Whether graphene oxide does form a LC structure also depends on the pH levels of the solution. In more acidic conditions, graphene oxide aggregates to form GO/water/GO sandwich-like structures [36]. However, under more basic conditions, the hydrophilic nature of graphene oxide and electrostatic interactions lead to the formation of a colloidal solution [34, 37]. This is caused by the deprotonation of the (-COOH) groups on the edges of the graphene oxide sheet which increase its charge and causes these edges to become comparatively more hydrophilic than the central region [29]. This difference causes amphiphilic behaviour in graphene oxide [36]. This property is more pronounced in larger sheets of graphene oxide and makes it suitable for use in LC structures [29].
3.2 Interaction energy between two sheets of graphene oxide

We adapt the Lerf-Klinowski structural model to construct a surface representation of graphene oxide using a series of continuous, flat, disk surfaces. The interaction energy, $E$, is defined as the total energy induced between molecules by van der Waals and electrostatic forces with all other forces considered trivial. The van der Waals force is calculated using the Lennard-Jones potential function and electrostatic force using the Coulomb potential. These equations are then applied to sheets of graphene oxide under different oxidation and hydration levels. The composition of the graphene oxide sheets is varied so the change in the energy is investigated given different levels of oxidation. Hydration is simulated by inserting monolayers of water between the sheets of graphene oxide. The analytical solution calculates results that match well against molecular dynamic simulation data and values given in literature.

The approach of modelling discrete atomic structure as continuous surfaces has been used previously for calculating van der Waals interaction between carbon nanostructures [19]. This model is employed to reduce computation costs involved with modelling interactions involving graphene oxide structures.

Using the continuum approach for modelling nanostructures as demonstrated in [19], a model of graphene oxide is constructed from a series of continuous sheets. This section first details the structure of the functional groups used to construct the model and then determines the van der Waals and electrostatic interaction energy between two sheets of the graphene oxide model.

3.2.1 Modelling approach

The oxidation of graphite to form graphene oxide introduces various deformations to the graphene basal plane. Some of the bonds between carbon atoms are stretched and distorted by the presence of the functional groups which displace the attached carbon atoms slightly out of the plane forming a sp$^3$ hybrid carbon structure [31]. Despite these
defects, the hexagonal lattice composing the base of graphene oxide is largely intact [24]. Additionally, in the construction of graphene films, the self-assembly of graphene oxide through a 2D Langmuir-Blodgett process can generate large sheets at a micrometre scale that remain largely flat and wrinkle-free. Consequently, distortions are ignored and it is assumed that the carbon atoms are structured like a sp² graphene sheet.

The functional groups decorating the surface of the basal plane are assumed, as in the Lerf-Klinowski model, to solely consist of epoxy and hydroxyl groups. The energies of a graphene oxide sheet are greatly reduced when epoxy and hydroxyl groups are gathered together in one area [38]. Despite this, the arrangement of the functional groups on the graphene oxide sheet still largely depends on the method and conditions involved during synthesis [29]. This model follows studies by Mkhoyan et. al. [31] which suggest the functional groups form a uniformly random distribution on both sides of the sheet.

![Figure 3.3: Geometric structure of an epoxy group on graphene oxide where carbon atoms are shown in black and oxygen atoms are shown in red.](image)

The structure of the epoxy and hydroxyl groups from the DFT study performed by Yan et. al. [38] are employed in deriving the positions of the oxygen and hydrogen atoms relative to the carbon basal plane. An epoxy functional group is constructed of a single oxygen atom bonded to two neighbouring carbon atoms. The C–O bond length at relaxation is given to be 1.44 Å, and the two attached carbons C–C bond length is stretched to 1.51 Å. Further distortions include the carbon atoms moving out of the plane by 0.34 Å. From this information, it is deduced that the oxygen atoms lie at a perpendicular distance
Figure 3.4: Geometric structure of a hydroxyl group on graphene oxide where carbon atoms are shown in black, oxygen atoms in red and hydrogen atoms in white.

of $1.23 + 0.34 = 1.57 \text{ Å}$, from the carbon basal plane. The structure of an epoxy group is shown in Fig. 3.3.

A hydroxyl functional group is constructed of an OH group bonded to a carbon atom. The C–O bond length at relaxation is given to be 1.44 Å, the O–H bond length is given as 0.98 Å and the C–O–H bond angle is 107.9°. The attached carbon atom is distorted out of the plane by 0.37 Å. For simplicity, it is assumed that hydrogen and oxygen atoms lie in the same plane perpendicular to the basal plane. Consequently, the hydrogen and oxygen atoms lie at perpendicular distance of $1.37 + 0.37 = 1.74 \text{ Å}$ from the basal plane. Taking the average of the C–O distance in hydroxyl and the height of the epoxy group, the average height of an oxygen/hydrogen atom from the basal plane is $(1.57 + 1.74)/2 = 1.66 \text{ Å}$. This structure of a hydroxyl group is shown in Fig. 3.4.

A single sheet of graphene oxide is represented by a construction of three distinct, continuous, flat surfaces, each lying perpendicular to the same axis. The central surface is equivalent to a sheet of graphene, while the upper and lower surfaces represent the attached functional groups as illustrated in Fig. 3.5. The basal plane of carbon is assumed to be fundamentally identical to sp$^2$ graphene while surfaces representing the functional groups are modelled as two surfaces of combined oxygen/hydrogen, representing the attached epoxy (C–O–C) and hydroxyl (C–OH) elements, positioned both above and below the carbon sheet. The distance between the carbon plane and the oxygen/hydrogen planes
is defined as \( \delta = 1.66 \text{ Å} \). In this continuous approximation, the atoms are distributed uniformly on each surface.

![Figure 3.5](image1.png)

**Figure 3.5:** A continuum model for a single graphene oxide sheet represented by a surface of graphene and two surfaces of mixed hydrogen and oxygen atoms.

![Figure 3.6](image2.png)

**Figure 3.6:** Interaction between two graphene oxide sheets. Here, \( z \) denotes the distance between sheets and \( \delta \) denotes the distance separating C and OH layers.

The total interaction energy between two sheets of graphene oxide is the sum of all surface interactions. These interactions consist of the interaction between the two graphene surfaces (\( E_{G-G} \)), the total interaction between a graphene surface and the oxygen/hydrogen surface on different graphene oxide sheets (\( E_{G-OH} \)) and the total interactions between each pair of oxygen/hydrogen surface on different graphene oxide sheets (\( E_{OH-OH} \)). We
now define the total interaction energy $E = E(z)$ where $z$ represents the perpendicular distance between the two carbon planes as shown in Fig 3.6. Summing all interactions gives

$$E(z) = E_{G-G}(z) + 2E_{G-OH}(z + \delta) + 2E_{G-OH}(z - \delta) + 2E_{OH-OH}(z) + E_{OH-OH}(z + 2\delta) + E_{OH-OH}(z - 2\delta).$$

**Table 3.1: Lennard-Jones constants**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (eV)</td>
<td>0.0045</td>
<td>0.0026</td>
<td>0.0019</td>
</tr>
<tr>
<td>$\sigma$ (Å)</td>
<td>3.851</td>
<td>3.500</td>
<td>2.886</td>
</tr>
<tr>
<td>$A$ (eV Å$^{-6}$)</td>
<td>29.45</td>
<td>9.49</td>
<td>2.19</td>
</tr>
<tr>
<td>$B$ (eV Å$^{-12}$)</td>
<td>48033.03</td>
<td>8718.39</td>
<td>631.65</td>
</tr>
</tbody>
</table>

The various constants used in the model are defined in Table 3.1. Firstly, the Lennard-Jones constants are taken from the Universal Force Field (UFF) atomic potentials [39]. In the cases where the Lennard-Jones constants are required for a pair of different atoms, the Lorentz-Berthelot mixing rules are employed. The point charges required to measure the Coulombic potential, as shown in Table 3.2, are taken from the atomic point charge model calculated by Stauffer et. al. [40] for the electrostatic potential (ESP) of graphene oxide from *ab initio* calculations. We also require the permittivity constant for water, $\varepsilon = 0.18461$ F m$^{-1}$.

**Table 3.2: The electrostatic potential of charged groups on graphene oxide.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>ESP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water O</td>
<td>$-0.56e$</td>
</tr>
<tr>
<td>H</td>
<td>$+0.28e$</td>
</tr>
<tr>
<td>Epoxy O</td>
<td>$-0.24e$</td>
</tr>
<tr>
<td>C</td>
<td>$+0.12e$</td>
</tr>
<tr>
<td>Hydroxyl O</td>
<td>$-0.38e$</td>
</tr>
<tr>
<td>C</td>
<td>$+0.12e$</td>
</tr>
<tr>
<td>H</td>
<td>$+0.26e$</td>
</tr>
</tbody>
</table>
The density of the carbon graphene surface is taken to be \( \eta = 0.3812 \text{ Å}^{-2} \). The density of the oxygen/hydrogen surfaces is taken from the C:O ratio of the graphene oxide sheet which varies given the oxidation of the sheet. Note that the comparative density of the oxygen and hydrogen atoms is halved as they are distributed over two surfaces.

Recall from (2.2) that the interaction energy between two surfaces \( S_1 \) and \( S_2 \) is expressed as

\[
E = \eta_1 \eta_2 \iint \phi(\rho) dS_1 dS_2
= \eta_1 \eta_2 \iint \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} + \frac{Q_S Q_S}{4\pi \varepsilon_0 \rho} \right) dS_1 dS_2,
\]

where the potential function \( \phi(\rho) \) is composed of the Lennard-Jones (2.3) and Coulomb (2.4) potentials. This surface integral is now applied to the circular sheets of the graphene oxide model using standard polar coordinates. The interaction energy (3.1) can then be expressed as

\[
E = \eta_1 \eta_2 \int_0^R \int_0^{2\pi} \int_0^R \int_0^{2\pi} \phi(\rho) r_1 r_2 d\theta_2 d\theta_1 dr_1 dr_2 d\phi_2,
\]

where an arbitrary point on each circular surface is represented in polar coordinates as \((r_2 \cos \theta_2, r_2 \sin \theta_2, z)\) and \((r_1 \cos \theta_1, r_1 \sin \theta_1, 0)\). The square distance between two arbitrary points is simply \( \rho^2 = (r_2 \cos \theta_2 - r_1 \cos \theta_1)^2 + (r_2 \sin \theta_2 - r_1 \sin \theta_1)^2 + z^2 \). Due to the angular symmetry of the circular sheets, we fix \( \theta_2 = 0 \). Finally, taking \( \theta = \theta_1 \) to simplify notation, the square of the distance is expressed as

\[
\rho^2 = (r_2 - r_1 \cos \theta)^2 + r_1^2 \sin^2 \theta + z^2
= r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta + z^2.
\]

As \( \theta_2 \) is fixed to be constant, (3.2) becomes

\[
E = 2\pi \eta_1 \eta_2 \int_0^R \int_0^{2\pi} \int_0^R \int_0^{2\pi} \phi(\rho) r_1 r_2 d\theta d\phi \; dr_1 dr_2.
\]
\[= 2\pi \eta_1 \eta_2 \int_0^{R_2} \int_0^{R_1} \int_{-\pi}^{\pi} r_1 r_2 \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} + \frac{Q S_1 S_2}{4\pi \varepsilon \rho} \right) d\theta dr_1 dr_2\]

\[= 2\pi \eta_1 \eta_2 \left( -AJ(3) + BJ(6) + \frac{Q S_1 S_2}{4\pi \varepsilon} J(1/2) \right),\]

where

\[J(n) = \int_0^{R_2} \int_0^{R_1} \int_{-\pi}^{\pi} \frac{r_1 r_2}{\rho^{2n}} d\theta dr_1 dr_2. \quad (3.3)\]

We solve this integral layer-by-layer, initially taking

\[J_1(n) = \int_{-\pi}^{\pi} \frac{1}{\rho^{2n}} d\theta.\]

As cosine is an even function, \(J_1\) can be expressed as

\[J_1(n) = 2 \int_0^{\pi} \frac{1}{(r_1^2 + r_2^2 + z^2 - 2r_1 r_2 \cos \theta)^n} d\theta.\]

Let \(K_1 = r_1^2 + r_2^2 + z^2\) and \(K_2 = 2r_1 r_2\). Then

\[J_1(n) = 2 \int_0^{\pi} \frac{1}{(K_1 - K_2 \cos \theta)^n} d\theta.\]

Using the identity \(\cos \theta = 1 - 2 \sin^2(\theta/2)\),

\[J_1(n) = 2 \int_0^{\pi} \left( K_1 + K_2 - 2K_1 \sin^2 \left( \frac{\theta}{2} \right) \right)^{-n} d\theta = \frac{2}{(K_1 + K_2)^n} \int_0^{\pi} \left( 1 - \frac{2K_1}{K_1 + K_2} \sin^2 \left( \frac{\theta}{2} \right) \right)^{-n} d\theta.\]

Taking \(\omega = \theta/2\) for simplification,

\[J_1(n) = \frac{4}{(K_1 + K_2)^n} \int_0^{\pi/2} \left( 1 - \frac{2K_1}{K_1 + K_2} \sin^2 \omega \right)^{-n} d\omega. \quad (3.4)\]

This integral is converted into the form of a hypergeometric function by taking \(t = \sin^2 \theta\)
and $d\theta = (1/2)t^{1/2}(1-t)^{-1/2} \, dt$. Equation (3.4) then becomes

$$J_1(n) = \frac{2}{(K_1 + K_2)^n} \int_0^{\pi/2} t^{1/2}(1-t)^{-1/2} \left( 1 - \frac{2K_1}{K_1 + K_2} \right)^{-n} \, dt$$

$$= \frac{2\pi}{(K_1 + K_2)^n} F \left( n, \frac{1}{2}; 1; \frac{2K_1}{K_1 + K_2} \right). \quad (3.5)$$

Using the quadratic transformation,

$$F(a, b; 2b; z) = (1 - \frac{z}{2})^{-a} F \left( \frac{a + 1}{2}, \frac{a + 1}{2} + 1, \frac{z}{2}; z^2 \right),$$

we convert (3.5) into a more convenient form,

$$J_1(n) = \frac{2\pi}{K_1^n} F \left( n, n + \frac{1}{2}; 1; \frac{K_2}{K_1} \right).$$

Next, we take

$$J_2(n) = \int_0^{R_1} r_1 \cdot J_1(n) \, dr_1$$

$$= \int_0^{R_1} \frac{r_1}{(r_1^2 + r_2^2 + z^2)^n} F \left( \frac{n}{2}, \frac{n + 1}{2}, 1, \left( \frac{2r_1 r_2}{r_1^2 + r_2^2 + z^2} \right)^2 \right) \, dr_1$$

$$= \int_0^{R_1} \frac{r_1}{(r_1^2 + r_2^2 + z^2)^n} \sum_{m=0}^\infty \frac{(\frac{n}{2})_m(n+1)_m}{(m!)^2} \left( \frac{2r_1 r_2}{r_1^2 + r_2^2 + z^2} \right)^{2m} \, dr_1$$

$$= \sum_{m=0}^\infty \frac{(\frac{n}{2})_m(n+1)_m}{(m!)^2} \left( 2r_2 \right)^{2m} \int_0^{R_1} \frac{r_1^{2m+1}}{(r_1^2 + r_2^2 + z^2)^{2m+n}} \, dr_1.$$ 

Letting $\alpha = r_2^2 + z^2$ to simplify, we find

$$J_2(n) = \sum_{m=0}^\infty \frac{(\frac{n}{2})_m(n+1)_m}{(m!)^2} \left( 2r_2 \right)^{2m} \int_0^{R_1} \frac{r_1^{2m+1}}{(r_1^2 + \alpha)^{2m+n}} \, dr_1.$$ 

This integral is solved using the method described in Appendix A.1 in which we obtain

$$J_2(n) = \sum_{m=0}^\infty \frac{(\frac{n}{2})_m(n+1)_m}{(m!)^2} \left( 2r_2 \right)^{2m} \frac{R_1^{2m+2}}{(2m+2)(R_1^2 + \alpha)^{2m+n}} F \left( 2m + n, 1; m + 2; \frac{R_1^2}{R_1^2 + \alpha} \right).$$
We find an expression for (3.3) as

\[
J(n) = \int_{0}^{R_2} r_2 \cdot J_2(n) \, dr_2
\]

\[
= \sum_{m=0}^{\infty} \frac{\left( \frac{n}{2} \right)_m \left( \frac{n+1}{2} \right)_m 4^m R_1^{2m+2}}{(m!)^2 \,(2m+2)} \times \int_{0}^{R_2} \frac{r_2^{2m+1}}{(R_1^2 + \alpha)^{2m+n}} \cdot F \left( 2m + n, 1; m + 2; \frac{R_2^2}{R_1^2 + \alpha} \right) \, dr_2
\]

\[
= \sum_{m=0}^{\infty} \frac{\left( \frac{n}{2} \right)_m \left( \frac{n+1}{2} \right)_m 4^m R_1^{2m+2}}{(m!)^2 \,(2m+2)} \times \sum_{q=0}^{\infty} \frac{(2m+n)_q (1)_m}{(m+2)_q \, q!} \int_{0}^{R_2} \frac{r_2^{2m+1}}{(R_1^2 + \alpha)^{2m+n}} \cdot \left( \frac{R_1^2}{R_1^2 + \alpha} \right)^q \, dr_2
\]

\[
= \sum_{m=0}^{\infty} \frac{\left( \frac{n}{2} \right)_m \left( \frac{n+1}{2} \right)_m 4^m R_1^{2m+2}}{(m!)^2 \,(2m+2)} \times \sum_{q=0}^{\infty} \frac{(2m+n)_q R_1^{2q}}{(m+2)_q} \int_{0}^{R_2} \frac{r_2^{2m+1}}{(r_2^2 + R_1^2 + z^2)^{q+2m+n}} \, dr_2.
\]

Once again using the method described in Appendix A.1, we find our final result

\[
J(n) = \sum_{m=0}^{\infty} \frac{\left( \frac{n}{2} \right)_m \left( \frac{n+1}{2} \right)_m 4^m (R_1 R_2)^{2m+2}}{(m!)^2 \,(2m+2)^2} \times \sum_{q=0}^{\infty} \frac{(2m+n)_q R_1^{2q}}{(m+2)_q} \frac{R_1^2}{(R_1^2 + R_2^2 + z^2)^{q+2m+n}} F \left( q + 2m + n, 1; m + 2; \frac{R_2^2}{R_1^2 + R_2^2 + z^2} \right).
\]

### 3.2.2 Effects of oxidation levels on graphene oxide interlayer distance

The degree of oxidation of graphene oxide varies depending on synthesis conditions. The typical measure of the oxidation level is the ratio of carbon and oxygen atoms [41]. Generally, the range of oxidation varies from a C:O ratio of 4:1 to 2:1, although chemical reduction gives a ratio of 12:1 and higher [24, 41]. Fully oxidised graphene oxide has around 50 percent coverage of functional groups and an ideal composition of C₈O₂(OH)₂ or C₆O₁(OH)₂ [41].

Different degrees of oxidation are simulated with the above graphene oxide model by
varying the density of the oxygen/hydrogen layers. The interaction energy for three differently oxidised graphene oxide sheets is shown in Fig. 3.7. It is clear that the functional groups play an important role in determining the interlayer distance and energy between graphene oxide sheets. We note that the interlayer distance is the distance at which the interaction energy between the two graphene oxide sheets is minimised. It is also observed that the more oxidised a sheet of graphene oxide, the further apart the interlayer distance and the stronger the van der Waals binding energy between two sheets. The interlayer distance of 5.5 to 6.0 Å matches well with that of dehydrated graphene oxide sheets which have been experimentally measured at values from 5.9 to 6.7 Å [42, 43].

To further provide comparison to our analytical result, a molecular dynamics simulation was performed. The setup conditions are explained in Appendix B.1. A pair of periodic graphene oxide sheets was constructed and the system was then run until equilibrium was reached. Results of the simulation are shown in Fig 3.8. After the simulation is com-
Figure 3.8: a) A pair of 2nm × 2nm periodic sheets of graphene oxide shown after minimisation. b) The same sheets displayed after a 1000ps simulation. Both images are created using the Visual Molecular Dynamics (VMD) molecular visualization program [44].

completed, the averaged interlayer distance between the sheets was found to be 4.7 Å. This is reasonably comparable to 5.7 Å given by the equivalent analytical result. It is likely the difference between the results is largely caused by the distribution of the functional groups on the surface.

3.2.3 Effects of hydration levels on graphene oxide interlayer distance

Graphene oxide is highly absorbent and tends to have some water molecules collected between the layers. The effect of this intercalated water on the intermolecular distance is examined by inserting a monolayer of water between the two graphene oxide sheets.

The oxygenated functional groups on the surface of graphene oxide cause it to have strongly hydrophilic properties [24]. Subsequently, it is very hard to remove all the water from graphene oxide and intermellar water molecules are always present in the structure, even after prolonged drying [32, 45]. Intercalated water has only marginal effects on the layer structure of graphene oxide sheets, however it causes the interlayer distance to increase up to 12 Å [23, 41].

The hydrogen atoms in the water couple to the oxygens in the functional groups via hydrogen bonds or electrostatic interactions [37]. The electrostatic interactions between the oxygenated groups and water form an interfacial H-bond network, that is, the inter-
action between the layers is mediated by a network of hydrogen bonded water molecules [46]. As graphene oxide becomes more hydrated, there is a gradual, linear increase in the interlayer distance. However, once the hydration of the graphene oxide sheets passes around 75 percent humidity, the interlayer distance between the sheets sharply increases in steplike transitions. This suggests the introduction of monolayers of water between the sheets [37, 43, 47].

The intercalated water is represented as a surface fixed directly in the centre between the two graphene oxide layers. The graphene oxide sheets are then allowed to interact as before with a total interaction energy \( E_{GO} \). Additional interactions between each graphene oxide surface and the water surface are defined as \( E_{G-W} \) for the carbon and water surface interaction and \( E_{OH-W} \) for the oxygen/hydrogen and water surface interaction. The total interaction energy for a system with a single intercalated monolayer of water is

\[
E = E_{GO} + 2 \cdot (E_{G-W} + E_{OH-W}).
\]

The values of the Lennard Jones constants for water are taken from Table 3.1. The water molecules are assumed to be tightly packed and the density to be constant over the surface. We approximate the area occupied by a molecule of water as the area of a circle with radius equal to the molecular distance of water at room temperature which is given by 2.965 Å [48]. The density of water molecules on this surface is then equal to \( 1/(\pi \cdot 2.965^2) = 0.0362 \, \text{Å}^{-2} \). Consequently, the total density of the hydrogen is 0.0241 Å\(^{-2}\) and the total density of the oxygen is 0.0121 Å\(^{-2}\). The results are plotted in Fig 3.9.

Upon adding each additional monolayer of water, the interlayer distance increases by around 3 Å. This correlates with literature which suggests a similar result [43, 47]. The distance between fully hydrated graphene oxide layers can be measured up to 12 Å which is similar to the result given here by adding two monolayers of water to the model.

The molecular dynamics simulation of graphene oxide with a single layer of water molecules gives the interlayer distance between the sheets as 7.7 Å after the simulation is completed. Results of the simulation are shown in Fig 3.10.
Interaction energy between GO sheets and water

Figure 3.9: The interaction energy between two graphene oxide sheets of varied oxidation (C:O) given one (blue) and two (black) monolayers of water intercalated between the sheets.

Figure 3.10: a) A pair of 2nm × 2nm periodic sheets of graphene oxide separated with water molecules shown after minimisation. b) The same sheets displayed after a 1000ps simulation.
3.3 Intercalation of a carbon nanotube between sheets of graphene oxide

A significant issue in constructing graphene or graphene oxide films is the negative relationship between the number of layers in the structure and its conductivity [49]. An alternative is a hybrid graphene structure constructed from alternate layers of graphene oxide sheets and carbon nanotubes [50]. An example of such a film is shown in Fig. 3.11. The interaction between the nanotubes and graphene oxide sheets increases the robustness of the film, with a stronger adhesion relative to pure graphene [51]. This modification has been shown to greatly improve electrical conductivity and is an ideal structure for energy storage purposes [52]. In this section, we again use the continuum approach to model a single-walled carbon nanotube intercalated between graphene oxide sheets and investigate the total interaction energy of the new system.

Figure 3.11: Construction process of a hybrid film consisting of layered sheets of graphene oxide and carbon nanotubes [53].

3.3.1 Modelling approach

A single-walled carbon nanotube is positioned between two graphene oxide sheets separated by a distance $Z\text{Å}$. The nanotube is permitted to rotate around its axis and has freedom of movement perpendicularly to the sheets as shown in Fig. 3.12. We note that the graphene oxide sheets have a similar construction as shown in Fig 3.6. However, for image clarity we here display graphene oxide as a singular sheet. The centre of the nan-
Figure 3.12: A single-walled carbon nanotube lying between two sheets of graphene oxide. The distance from the centre of the tube to a lower sheet is given as \( z \) Å. The angle of the nanotube from the horizontal plane is given by \( \psi \in [0, \pi/2] \).

The nanotube is located at a height \( z \) from the surface where \( z \in [0, Z] \). The angle the nanotube makes with the vertical axis is defined as \( \psi \in [0, \pi/2] \). For ease of calculation, we expand our model of graphene oxide sheets to surfaces of infinite radius. The nanotube is modelled as a continuous hollow cylinder with surface density taken as equivalent to a graphene sheet. Recall from (2.2) that the interaction energy between two surfaces \( S_1 \) and \( S_2 \) can be expressed as

\[
E_s = \eta_1 \eta_2 \int_{S_1} \int_{S_2} \phi(\rho) \, dS_1 \, dS_2
\]

\[
= \eta_1 \eta_2 \int_{S_1} \int_{S_2} \left[ -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right] \, dS_1 \, dS_2
\]

\[
= \eta_1 \eta_2 \left[ -AK(3) + BK(6) \right],
\]  

(3.6)
where $A$ and $B$ are respectively the attractive and repulsive constants, $\eta_1$ and $\eta_2$ are respectively the density of the nanotube and the sheet and

$$K(n) = \int_{s_1} \int_{s_2} \frac{1}{\rho^{2n}} dS_1 dS_2, \quad n = 3, 6. \quad (3.7)$$

Note we do not use the Coloumbic potential in this case as the carbon nanotube is taken to be uncharged.

![Figure 3.13: Interaction between a point and an infinite plane.](image)

Finding an analytic solution for $K(n)$ proves more difficult than the previous case of sheet-sheet interaction. Thus we build a step-by-step solution starting from simpler cases. First, consider the interaction between an infinite sheet and a single point located at a fixed distance $\delta$ above the plane, as shown in Fig. 3.13.

The component of the Lennard-Jones interaction as given in (3.7) is expressed as

$$K_1(\delta) = \int_{r=0}^{\infty} \int_{\theta=-\pi}^{\pi} \frac{r dr d\theta}{\rho^{2n}}$$

$$= \int_{r=0}^{\infty} \int_{\theta=-\pi}^{\pi} \frac{r dr d\theta}{(r^2 + \delta^2)^n}$$

$$= 2\pi \int_{r=0}^{\infty} \frac{r dr}{(r^2 + \delta^2)^n}.$$
We make the substitution \( u = r^2 + \delta^2 \). Then,

\[
K_1(\delta) = 2\pi \int_{r=0}^{\infty} \frac{du}{u^n} = \frac{\pi}{(n-1)\delta^{2n-2}}.
\]

![Figure 3.14: Interaction between a tilted circle and an infinite plane.](image)

We now expand the previous result to find the interaction between an infinite plane and a circle with vertical offset of \( z \) tilted around the \( y \)-axis by \( \psi \) degrees as shown in Fig. 3.14. This circle has the coordinates \((a \cos \theta \sin \psi, a \sin \theta, a \cos \theta \cos \psi + z)\). We find the interaction between this tilted circle and the infinite plane to be

\[
K_2(z) = \int_{-\pi}^{\pi} K_1(a \cos \theta \cos \psi + z) \cdot a d\theta
= \frac{\pi a}{(n-1)} \int_{-\pi}^{\pi} \frac{d\theta}{(a \cos \theta \cos \psi + z)^{2n-2}}.
\]
As $K_2$ is an even function,

$$K_2(z) = \frac{2\pi a}{(n-1)} \int_0^{\pi} \frac{d\theta}{(a \cos \theta \cos \psi + z)^{2n-2}}.$$ 

Applying the identity $\cos \theta = 1 - 2\sin^2(\theta/2)$,

$$K_2(z) = \frac{2\pi a}{(n-1)} \int_0^{\pi} \frac{d\theta}{(a \cos \psi + z - 2a \cos \psi \sin^2(\theta/2))^{2n-2}}.$$ 

Let $\alpha = a \cos \psi + z$, $\beta = 2a \cos \psi$ and $\omega = \theta/2$. Then

$$K_2(z) = \frac{4\pi a}{(n-1)} \int_0^{\pi/2} \frac{d\omega}{(\alpha - \beta \sin^2 \omega)^{2n-2}}.$$ 

Let $t = \sin^2 \omega$, $d\omega = 1/2 \cdot t^{-1/2}(1-t)^{-1/2} dt$. Then

$$K_2(z) = \frac{2\pi a}{(n-1) \alpha^{2n-2}} \int_0^{\pi/2} t^{-1/2}(1-t)^{-1/2} \left(1 - \frac{\beta}{\alpha} t \right)^{2-2n} dt.$$ 

This is the form of a hypergeometric function and subsequently, we find

$$K_2(z) = \frac{2\pi^2 a}{(n-1) \alpha^{2n-2}} F \left(2n-2, \frac{1}{2}; 1; \frac{2\beta}{\alpha} \right)$$

$$= \frac{2\pi^2 a}{(n-1)(a \cos \psi + z)^{2n-2}} F \left(2n-2, \frac{1}{2}; 1; -\frac{4a \cos \psi}{a \cos \psi + x \tan \psi + z} \right).$$

Finally, we expand the previous result to determine the interaction between a tilted cylinder of length $2L$ and an infinite plane as shown in Fig. 3.15. A tilted cylinder is constructed out of the tilted circles. Since a line passing through the centre of the cylinder has the form $x \tan \psi + z$, we find

$$K(n, z, \psi) = \int_{-L}^{L} K_2(x \tan \psi + z) dx$$

$$= \int_{-L}^{L} \frac{2\pi^2 a}{(n-1)((a \cos \psi + x \tan \psi + z)^{2n-2}} F \left(2n-2, \frac{1}{2}; 1; -\frac{4a \sin \psi}{a \cos \psi + x \tan \psi + z} \right) dx.$$
Expanding the hypergeometric function, we have

\[
K(n, z, \psi) = \frac{2\pi^2 a}{(n-1)} \sum_{q=0}^{\infty} \frac{(2n-2)_q (1/2)_q}{(1)_q q!} \times \int_{-L}^{L} \frac{1}{(a \cos \psi + x \tan \psi + z)^{2n-2}} \left(\frac{4a \cos \psi}{a \cos \psi + x \tan \psi + z}\right)^q dx
\]

\[
= \frac{2\pi^2 a}{(n-1)} \sum_{q=0}^{\infty} \frac{(2n-2)_q (1/2)_q (4a \cos \psi)^q}{(1)_q q!} \int_{-L}^{L} \frac{1}{(a \cos \psi + x \tan \psi + z)^{2n-2+q}} dx.
\]

(3.8)

For simplification, we let \( \alpha = a \cos \psi + z \) and \( m = 2n - 2 \). Substituting \( u = \alpha + x \tan \psi \), \( du = \tan \psi dx \), (3.8) becomes

\[
K(n, z, \psi) = \frac{2\pi^2 a}{(n-1)} \sum_{q=0}^{\infty} \frac{(m)_q (1/2)_q (4a \cos \psi)^q}{(1)_q q! \tan \psi} \int_{\alpha-L \tan \psi}^{\alpha+L \tan \psi} \frac{1}{u^{m+q}} du
\]
We write $K(n, z, \psi) = K_1(n, z, \psi) + K_2(n, z, \psi)$ where

$$K_1(n, z, \psi) = \frac{2\pi^2 a}{(n-1)} \sum_{q=0}^{\infty} (m)_q (1/2)_q (4a\cos \psi)^q \frac{1}{(1)_q q! \tan \psi(1-m-q) (\alpha + L\tan \psi)^{m+q-1}}$$

$$= \frac{2\pi^2 a (\alpha + L\tan \psi)^{1-m}}{(n-1) \tan(\psi)} \sum_{q=0}^{\infty} \frac{(m)_q (1/2)_q (4a\cos \psi)^q}{(1)_q q! \tan \psi(1-m-q) (\alpha + L\tan \psi)^{m+q-1}}$$

$$K_2(n, z, \psi) = \frac{2\pi^2 a}{(n-1)} \sum_{q=0}^{\infty} (m)_q (1/2)_q (4a\cos \psi)^q \frac{1}{(1)_q q! \tan \psi(1-m-q) (\alpha - L\tan \psi)^{m+q-1}}$$

$$= \frac{2\pi^2 a (\alpha + L\tan \psi)^{1-m}}{(n-1) \tan(\psi)} \sum_{q=0}^{\infty} \frac{(m)_q (1/2)_q (4a\cos \psi)^q}{(1)_q q! \tan \psi(1-m-q) (\alpha - L\tan \psi)^{m+q-1}}$$

Using the relationship

$$K(n, z, \psi) = \frac{2\pi^2 a (\alpha + L\tan \psi)^{1-m}}{(1-m)(n-1) \tan(\psi)} \sum_{q=0}^{\infty} \frac{(m)_q (1/2)_q (4a\cos \psi)^q}{(1)_q q! \tan \psi (\alpha + L\tan \psi)^{m+q-1}}$$

$$= \frac{2\pi^2 a (\alpha + L\tan \psi)^{1-m}}{(1-m)(n-1) \tan(\psi)} F \left( m-1, \frac{1}{2}; 1; \frac{4a\cos \psi}{\alpha + L\tan \psi} \right)$$

The same methodology can be used to simplify $K_2$. Hence, the final expression for $K$ is

$$K(n, z, \psi) = \frac{2\pi^2 a}{(3-2n)(n-1) \tan(\psi)}$$

$$\times \left[ F \left( 2n-3, \frac{1}{2}; 1; \frac{4a\cos \psi}{\alpha + L\tan \psi} \right) - F \left( 2n-3, \frac{1}{2}; 1; \frac{4a\cos \psi}{\alpha + z - L\tan \psi} \right) \right]$$

We may now express the energy between a nanotube and a single layer (3.6) in terms of
the position and rotational angle of the nanotube as

\[ E_s(z, \psi) = \eta_1 \eta_2 [-A K(3, z, \psi) + B K(6, z, \psi)] . \]

Note that the nanotube rotation, \( \psi \), is preserved under a complete rotation of the system by \( \pi \) radians. Therefore, we write the interaction energy between the nanotube and a pair of sheets separated by distance \( Z \) as

\[ E_p(z, \psi, Z) = E_s(z, \psi) + E_s(Z - z, \psi) . \]

Finally, we include the interaction for the basal plane and both oxidated layers of the GO structure. The solution for the total interaction energy is

\[ E = E_p(z, \psi, Z) + E_p(z + \delta, \psi, Z + 2\delta) + E_p(z - \delta, \psi, Z - 2\delta) \]

\[ + E_p(z + \delta, \psi, Z + 2\delta) + E_p(z - \delta, \psi, Z - 2\delta) , \]

where the appropriate Lennard-Jones constants are taken from Table 3.1.

### 3.3.2 Results

Here, we examine the interaction energy of a carbon nanotube and a pair of encompassing graphene oxide sheets. We select armchair nanotubes of chirality (16,16) with a radius of 10.84 Å, a size generally considered average for experimental use. The nanotube length is fixed at 100 Å and the oxidation ratio is taken as C/O = 4. Plotting the interaction energy under these chosen parameters, as shown in Fig. 3.16, demonstrates two interesting features, which are exhibited for all sensibly chosen parameters. The global minima occurs when the nanotube lies perfectly horizontal and is situated a distance 20.75 ± 1 Å from the basal plane of the GO sheets, with this slight variation depending on the oxidation of the sheets. Further examination of the global minima, as displayed in Fig. 3.17, shows a decrease in the total energy for less-oxidated, reduced graphene oxide sheets. This is cor-
Figure 3.16: Interaction energy of a nanotube between sheets of graphene oxide separated by 100 Å. The distance from the lower sheet to the tube is given by $z$ and the angle of the tube to the horizontal is given by $\psi$.

Roborated by the results in literature and suggests oxidated sheets may form a more stable structure [51]. We additionally note a local minima when the centre of the nanotube is situated equidistantly from both sheets. A nanotube situated at the local minima slowly rotates vertically as the encompassing sheets are separated. This behaviour is shown in Fig. 3.18.
Figure 3.17: The total van der Waals energy of a nanotube lying in the horizontal equilibrium position. The oxidation ratio, denoted as C/O, is the ratio of carbon (C) to oxygen (O) atoms in the graphene oxide sheets.

Figure 3.18: The angle, $\psi$, of a carbon nanotube at the equilibrium position situated halfway between a pair of graphene oxide sheets. Results are shown for varying separation distances, $Z$. 
Chapter 4

Conformation of graphene folds around carbon nanotubes

In this chapter, we examine the morphology of graphene folded around a carbon nanotube. Firstly, we provide an overview of graphene folding and its relationship to surface functionalisation. We construct a model defining the structure of a graphene sheet as it folds around a nanotube. Variation techniques are employed to find the minimal conformation structure and a comparison is made with simulation results. A more refined model is also examined incorporating compression effects on nanotubes as observed in simulation.

4.1 Functionalisation and graphene folding

Graphene is known to have extraordinarily high carrier mobility. This seemingly makes it ideal for use in nanoelectronics, particularly transistors. However, graphene has zero bandgap and consequently, devices utilising large sheets of graphene are unable to be switched off rendering them useless in logical circuits [54, 55]. Opening a tuneable, well-defined bandgap without impacting the high carrier mobility of graphene remains an important challenge in graphene research [54]. Edges and defects are more reactive than in the bulk sheet and so chemically functionalising the edges of graphene sheets has proven to solve this problem. Unfortunately, chemical doping tends to randomly induce defects in the sheet and can only be directed to the edges of the plane or the surface as
a whole [55–57]. Subsequently, controlled surface functionalisation remains an ongoing challenge. Recent research suggests controlled out-of-plane deformations of graphene as a possible alternative. Carbon atoms of highly curved surfaces exhibit increased chemical potential. The folding of graphene induces strain energy, causing an increase in reactivity. The fold is still energetically stable due to plane-plane interaction.

Deng et. al. [58] suggests that controlled geometric deformations such as wrinkles allow modulation of electronic properties. Wrinkle structures are also formed during the chemical vapor deposition (CVD) process of growing graphene on metal substrates. The wrinkle formation in CVD is a topic of study in Chapter 5. Other potential applications of wrinkles on graphene include energy storage and bio-interfacing. Graphene folds have also been shown to be stronger than graphene under compressive forces [59].

One of the more novel applications of grafolds is as a localized intercalation platform. Intercalation of small molecules into the folded structures of graphene or grafolds creates a one-dimensional functionalisation of the graphene sheets allowing researchers to experiment with the mechanical, electrical and optical properties affected by the interlayer interaction. Experiments involving intercalation into folds have been performed with $C_{60}$ fullerenes [33]. Intercalation, or functionalisation, of the chemically reactive folds can further extend grafolds’ mechanical, chemical, electronic and optical diversity [33, 60, 61].

### 4.2 Modelling approach

Previously, we have constructed models using a continuum approach, relating carbon nanostructures to well understood geometric shapes. However when the optimal structure is unknown, new techniques are required. The use of calculus of variations for carbon nanostructures can be seen from [62–68]. In these papers, using the calculus of variations, a mathematical model is proposed to determine the joining curve between various carbon nanostructures, including two carbon nanotubes, a carbon nanotube and a sheet of graphene, a carbon nanotube and a $C_{60}$ fullerene, a carbon nanotube and a carbon nanocone and two fullerenes. We note that joining between two nanostructures can en-
hance the physiochemical and electrochemical performances of the combined materials. Further, in [69], the calculus of variations is used to predict the structure of graphene folding. In this chapter, we investigate a similar structure to that in [69], but here there is additional interaction resulting from the intercalation of a single-walled carbon nanotube situated in a fold of graphene sheet. Due to the translational symmetry of the fold along the nanotube axes, we only need to consider a two dimensional cross-section of the system.

We comment that this model only includes the mathematics of the energy inherent in the curved surface, which can be thought of as a result from the chemical bonding. The model does not directly take into account the discrete chemical issues, such as the positions of carbon atoms and bonds. However, as shown in [69], curved profiles of the graphene fold obtained through minimising the elastic energy using the calculus of variations are in excellent agreement with experimental results, density functional theory calculations and also molecular dynamics simulations as shown in this chapter.

In the following sections, we consider mathematical models for two grafold profiles. The first is when we assume that the cross-section of the encapsulated nanotube in the fold is circular and the second case we assume ellipse cross-section of the nanotube. We then show results from our mathematical models. Molecular dynamics simulations have previously been performed for the evolution of folding graphene structures [70, 71]. Here, we also conduct simulations and a comparison is made between the equilibrium state of a molecular dynamics simulation of the system and the resultant structure formulated by variational calculus.

### 4.2.1 Circular cross-section nanotube

We construct a model to determine the optimal geometric structure of a graphene sheet wrapped around a single-walled nanotube. We assume that the dominant energies are the van der Waals (vdW) interaction energy and the elastic bending energy involved in the bending of the sheet. Furthermore, we assume the vdW interaction between graphene-graphene and nanotube-graphene are equal and denote the resulting equilibrium distance
2δ. The nanotube is assumed to have a circular cross-section with a fixed radius \( r \).

We assume that the vdW energy dominates as the sheet wraps around the nanotube and so represent this curve as a perfectly circular arc. Additionally, when the edges of the folded sheets are at a sufficient distance from the tube, the elastic bending energy rapidly decreases and the sheets stack in a horizontal fashion as in graphene.

Invariance of the structure along the length of the nanotube allows us to reduce the problem to two dimensions as shown in Fig. 4.1. We also assume reflective symmetry in the \( x \)-axis and so we can solely consider the upper half plane of the structure. The curve, \( C \), is split into four distinct sections denoted by \( C_0 \), \( C_1 \), \( C_2 \) and \( C_3 \). We define \( C_0 \) as a circular arc bounded by the points \( P_0 = (−R, 0) \) and \( P_1 = (x_0, y_0) \) where \( R = r + 2\delta \) is the arc radius. Additionally, \( C_3 \) is defined as a horizontal line bounded on the left by \( P_3 = (x_2, \delta) \). Our interest is in the formation of the central curves \( C_1 \) and \( C_2 \) which are bounded by the points \( P_1 = (x_0, y_0) \) and \( P_3 = (x_2, \delta) \) and meet at a critical point of zero curvature \( P_2 = (x_1, y_1) \). It should be noted that we do not initially know the exact location of \( P_1 \) and \( P_3 \) which are determined as variable boundaries.

**Figure 4.1:** Representation of a graphene sheet wrapped around a carbon nanotube with a circular cross-section.
Euler first proposed that the potential energy function of an ideal elastic line of fixed length could be minimised by integrating the square of the curvature over the entire length of the curve. We therefore model the elastic bending energy, $E_e$, as

$$E_e = \gamma \int_C \kappa^2 ds,$$

where $\kappa$ is the line curvature, $s$ is the arc-length and $\gamma$ is a constant denoting the bending rigidity of graphene sheet. We assume the curve sections $C_1$ and $C_2$ are dominated by the elastic bending energy and that $\kappa$ is strictly negative on $C_2$ and strictly positive on $C_1$.

We model the vdW energy, $E_v$, as a Heaviside step function under the assumption that the structure is in equilibrium due to the vdW force. Additionally, we assume that $C_0$ and $C_3$ are the sections of the curve primarily affected by the vdW force.

$$E_v = -\int_C (\varepsilon u(x_0 - x) + \varepsilon u(x - x_2)) ds,$$

Here we have $\varepsilon$ as the scaling constant denoting the vdW energy per area length for the curve sections $C_1$ and $C_3$ and $u(x)$ represents the Heaviside step function. Our total energy $E$ is then

$$E = E_e + E_v = \int_C (\gamma \kappa^2 - \varepsilon u(x_0 - x) - \varepsilon u(x - x_2)) ds.$$

We rescale our energy to the more mathematically convenient form,

$$\hat{E} = \frac{E}{\gamma} = \int_C \left( \kappa^2 - \alpha u(x_0 - x) - \alpha u(x - x_2) \right) ds,$$

where we have defined $\alpha = \varepsilon / \gamma$. We apply an isoperimetric constraint on the total arc-length of $C$ defined by

$$\int_C ds = L.$$

We also define the length of the curves as $L_0, L_1, L_2$ and $L_3$ respectively. Our constraint
can then also be interpreted as

\[ L_0 + L_1 + L_2 + L_3 = L. \]

We can define an explicit expression for the length of the curve \( C_0. \) As \( C_0 \) is a circular arc, we parametrise the curve using the coordinates

\[ (x(\xi), y(\xi)) = (-R \cos \xi, R \sin \xi), \]

where \( \xi \) is the angle measured clockwise from the horizontal axis. It follows that \( L_0 = R \xi_0, \) where \( \xi_0 \) is the angle of the right endpoint of \( C_0. \)

We construct a functional by combining the total potential energy acting on the curve together with the product of the constraint and a Lagrange multiplier \( \lambda, \) finding

\[
J(y) = \int_C \left( \kappa^2 - \alpha u(x_0 - x) - \alpha u(x - x_1) + \lambda \right) ds \\
= \int_{C_0} \left( \kappa^2 + \lambda - \alpha \right) ds + \int_{C_1 + C_2} \left( \kappa^2 + \lambda \right) ds + \int_{C_3} (\lambda - \alpha) ds \\
= \frac{1}{R^2} \int_{C_0} ds + \int_{C_1 + C_2} \left( \kappa^2 + \alpha \right) ds + (\lambda - \alpha)L \\
= \frac{\xi}{R} \left[ \int_{x_0}^{x_2} \left( \frac{y'^2}{(1 + y'^2)^3} + \alpha \right) \sqrt{1 + y'^2} \right] dx + (\lambda - \alpha)L. \quad (4.1)
\]

In order to minimise the energy and determine the optimal structure, it is required that we minimise the functional \( J(y). \) We denote the integrand of \( J \) as a new function \( F. \) That is,

\[ F(y', y'') = \left( \frac{y'^2}{(1 + y'^2)^3} + \alpha \right) \sqrt{1 + y'^2}. \]

This problem is now in the form of a second order variational calculus problem with the
Euler-Lagrange equation given as

\[ F_y - \frac{d}{dx} F_{y'} + \frac{d^2}{dx^2} F_{y''} = 0, \tag{4.2} \]

with the fixed boundary conditions \( y(x_2) = \delta \) and \( y'(x_2) = 0 \) and the natural boundary condition \( H \big|_{x_2} = 0 \) at the right endpoint. We also require the natural boundary conditions \([p \delta y + q \delta y' - H \delta x]_{x_0} \) on \( C_0 \) and \( C_1 \) to be equivalent. Here we use the canonical coordinates \( p, q \) and \( H \) as defined in Chapter 2. As the function \( F \) is also independent of \( x \), \( H \) is a conserved quantity and from the natural boundary at \( P_3 \), \( H = 0 \) at all points in the domain. Given that \( F \) is not dependent on \( y \), we can integrate (4.2) to deduce

\[ F_{y'} - \frac{d}{dx} F_{y''} = \beta \]

\[ p = \beta, \]

where \( \beta \) is constant. Recall that the point \( P_1 = (x_0, y_0) \) lies on the curve \((-R \cos \xi, R \sin \xi)\).

We then express the natural boundary condition in terms of the variation in \( \xi \) namely,

\[ \delta y \big|_{x_0} = \frac{dy}{d\xi} \delta \xi \big|_{x_0} = R \cos \xi \delta \xi \big|_{x_0} = -x_0, \]

\[ \delta y' \big|_{x_0} = \frac{d}{d\xi} \left( \frac{dy}{dx} \right) \delta \xi \big|_{x_0} = \frac{d}{d\xi} (\cot \xi) \delta \xi \big|_{x_0} = \frac{-1}{\sin^2 \xi} \delta \xi \big|_{x_0}. \]

The natural boundary condition for \( C_2 \), incorporating the condition from (4.1), becomes,

\[ \left[ \frac{1}{R} \right] \delta \xi \big|_{x_0} = \left[ -\beta x_0 - 2\frac{y''}{(1 + y'^2)^{5/2}} \frac{1}{\sin^2 \xi} \delta \xi \big|_{x_0} \right] \]

\[ = \left[ -\beta x_0 + 2\frac{(\sin^2 \xi)^{5/2}}{R \sin^3 \xi} \frac{1}{\sin^2 \xi} \delta \xi \big|_{x_0} \right] \]

\[ = \left[ -\beta x_0 + \frac{2}{R} \right] \delta \xi \big|_{x_0}, \]

which upon simplification, gives \( x_0 = 1/(R \beta) \).

A solution to this style of problem has been previously derived in [69] where the general
parametric solution for the curves $C_i$, $i \in \{0, 1\}$, is given as

\[
x_i(\phi) = c_i \mp \frac{2(\alpha + \beta)^{1/2}}{\beta} \left(1 - k^2 \sin^2 \phi\right)^{1/2}, \tag{4.3}
\]

\[
y_i(\phi) = d_i \pm \frac{2(\alpha + \beta)^{1/2}}{\beta} \left(E(\phi, k) - \frac{\alpha}{\alpha + \beta} F(\phi, k)\right), \tag{4.4}
\]

where $c_i$ and $d_i$ are constants, $k = (2\beta/(\alpha + \beta))^{1/2}$ and $F(\phi, k)$ and $E(\phi, k)$ represent the incomplete elliptic integrals of the first and second kind, respectively. Further details are also given in Section 5.2.2. This solution uses the coordinate transformation

\[
y'(x) = \tan(2\phi - \pi/2). \tag{4.5}
\]

We can derive our new endpoints as follows. At $P_1$, we have

\[
y(x_0) = (R^2 - x_0^2)^{1/2},
\]

\[
y'(x_0) = -x_0(R^2 - x_0^2)^{-1/2}.
\]

Using the transformation (4.5), we have $\phi_0 = \pi/4 + 1/2 \cdot \tan^{-1} \left(x_0(R^2 - x_0^2)^{-1/2}\right)$ where $\phi_0$ is the left endpoint. Similarly, we know $y'(x_1) = 0$ and therefore the right endpoint $\phi_1 = \pi/4$. We find the value of the constants $c_0$ and $d_0$ by substituting the left endpoint into the solution (4.3) and (4.4). Substituting $\phi_0$ into the solution (4.3) for $x$, we have

\[
x(\phi_0) = c_0 - \frac{2(\alpha + \beta)^{1/2}}{\beta} \left(1 - k^2 \sin^2 \phi_0\right)^{1/2}.
\]

We can simplify part of this equation by noting that

\[
\sin^2 \phi_0 = \frac{1}{2} \left(1 - \cos(2\phi_0)\right) = \frac{1}{2} \left(1 + \frac{1}{\beta R^2}\right).
\]
Thus, upon substitution, we find
\[
x(\phi_0) = c_0 - \frac{2(\alpha + \beta)^{1/2}}{\beta} \left( 1 - \frac{2\beta}{\alpha + \beta} \frac{\beta R^2 + 1}{2\beta R^2} \right)
\]
\[
\frac{1}{R\beta} = c_0 - \frac{2(\alpha + \beta)^{1/2}}{\beta} \left( \frac{R^2\alpha - 1}{R^2(\alpha + \beta)} \right)
\]
\[
c_0 = \frac{1 + 2(R^2\alpha - 1)^{1/2}}{R\beta}.
\] (4.6)

Matching the curves at \( P_2 \), we easily find \( c_1 = c_0 \). To find \( d_0 \) we substitute \( \phi_0 \) into the solution (4.4) for \( y \) to get
\[
y(\phi_0) = d_0 + \frac{2(\alpha + \beta)^{1/2}}{\beta} \left( E(\phi_0,k) - \frac{\alpha}{\alpha + \beta} F(\phi_0,k) \right)
\]
\[
d_0 = \left[ \frac{r^4\beta^2 - 1}{r\beta} \right]^{1/2} - \frac{2(\alpha + \beta)^{1/2}}{\beta} \left( E(\phi_0,k) - \frac{\alpha}{\alpha + \beta} F(\phi_0,k) \right).
\] (4.7)

Matching the curves at \( P_2 \), we find,
\[
d_1 = d_0 + \frac{4(\alpha + \beta)^{1/2}}{\beta} \left( E(\phi_1,k) - \frac{\alpha}{\alpha + \beta} F(\phi_1,k) \right),
\] (4.8)

where \( \phi_1 = \sin^{-1}(1/k) \). Finally, we need to determine the values of the constants \( \alpha \) and \( \beta \). We know \( \alpha \) is directly defined as the ratio of vdW interaction, \( \varepsilon \), to the bending rigidity of graphene, \( \gamma \). The vdW energy is given as \( \varepsilon = 0.0214 \text{eV} \AA^{-2} \) [72] and the possible values of \( \gamma \) range from 0.800 to 1.60 eV [73]. As such, we obtain \( \alpha = 0.0268 \AA^{-2} \) when \( \gamma = 0.800 \text{ eV} \) and \( \alpha = 0.0134 \AA^{-2} \) when \( \gamma = 1.60 \text{ eV} \). To find \( \beta \) we use the endpoint boundary condition
\[
y(\pi/4) = \delta,
\] (4.9)

which upon substitution into the solution (4.4), the value for \( \beta \) can be determined numerically.
4.2.2 Elliptical cross-section nanotube

We can extend the model from the case of circular cross-section to account for the compression of nanotubes by modelling the cross-section of our tube as an ellipse where \( a \) and \( b \) are the major and minor semi-axis length on the \( x \)- and \( y \)-axes, respectively. A schematic of a graphene sheet wrapped around a carbon nanotube with an elliptical cross-section is illustrated in Fig. 4.2.

![Figure 4.2: Representation of a graphene sheet wrapped around a carbon nanotube with an elliptical cross-section due to compressive force.](image)

The formulation of the model is almost identical. However, the boundary condition at \( x_0 \) is more complicated changing the final constants. The point \( P_1 = (x_0, y_0) \) lies on the curve \( (x(\xi), y(\xi)) = (-A \cos \xi, B \sin \xi) \), where \( A = a + 2\delta \) and \( B = b + 2\delta \). The variations at the left endpoint are expressed as

\[
\delta y_0|x_0 = \frac{dy}{d\xi} \delta \xi | x_0 = B \cos \xi \delta \xi | x_0 = \frac{-B}{A} x_0 \delta \xi | x_0, \\
\delta y'_0|x_0 = \frac{d}{d\xi} \left( \frac{dy}{dx} \right) \delta \xi | x_0 = \frac{d}{d\xi} \left( \frac{-B}{A \cot \xi} \right) \delta \xi | x_0 = \frac{-B}{A \sin^3 \xi} \delta \xi | x_0.
\]

We can then write the total potential energy acting on the curve together with the product
of the constraint and a Lagrange multiplier $\lambda$ as

$$E = \int_C \kappa^2 ds + \int_{c_1 + c_2} (\kappa^2 + \alpha) ds + (\lambda - \alpha)L$$

$$= \int_{c_0} \frac{A^2 B^2}{(A^2 \sin^2 \xi + B^2 \cos^2 \xi)^3} ds + \int_{c_1 + c_2} (\kappa^2 + \alpha) ds + (\lambda - \alpha)L, \quad (4.10)$$

using the definition of curvature on an ellipse. This time, finding the natural boundary condition is more involved as we cannot trivially integrate the functional on $C_0$. In order to minimise the energy and find the optimal structure, it is required that we minimise the functional

$$J(y) = J_0(y) + J_1(y),$$

where

$$J_0(y) = \int_{c_0} \kappa^2 ds = \int_{-A}^{x_0} \frac{y''^2}{(1 + y'^2)^{5/2}} dx,$$

$$J_1(y) = \int_{c_1 + c_2} (\kappa^2 + \alpha) ds = \int_{x_0}^{x_2} \left( \frac{y''^2}{(1 + y'^2)^{5/2}} + \alpha \sqrt{1 + y'^2} \right) dx.$$

We denote the integrand of each $J_i$ as a new function $F_i$. That is,

$$F_0(y', y'') = \frac{y''^2}{(1 + y'^2)^{5/2}},$$

$$F_1(y', y'') = \frac{y''^2}{(1 + y'^2)^{5/2}} + \alpha \sqrt{1 + y'^2}.$$

Using the definition of curvature from (4.10), we find

$$F_0 = \frac{A^2 B^2}{(A^2 \sin^2 \xi + B^2 \cos^2 \xi)^3} \cdot \frac{(A^2 \sin^2 \xi + B^2 \cos^2 \xi)^{1/2}}{A \sin \xi}$$

$$= \frac{A B^8}{y ((A^2 - B^2)y^2 + B^4)^{5/2}}. \quad (4.11)$$
We note that
\[ y' = -\frac{B}{A} (B^2 - y^2)^{1/2}. \]

Our integrand (4.11) becomes
\[ F_0(y, y') = \frac{-A^2 B^7 y'}{(B^2 - y^2)^{1/2} ((A^2 - B^2) y^2 + B^4)^{5/2}}. \]

We can now derive the natural boundary condition at the point \( P_1 \) on \( C_0 \) as
\[ p \delta y|_{x_0} = \left[ -\frac{-A^2 B^7}{(B^2 - y^2)^{1/2} ((A^2 - B^2) y^2 + B^4)^{5/2}} \cdot -(B^2 - y^2)^{1/2} \right] \delta \xi|_{x_0} \]
\[ = \left[ \frac{A^2 B^7}{((A^2 - B^2) y^2 + B^4)^{5/2}} \right] \delta \xi|_{x_0}. \] (4.12)

On \( C_1 \), the boundary condition at the point \( P_1 \) can be derived by routine calculation as
\[ p \delta y + q \delta y'|_{x_0} = \left[ -\beta (B^2 - y^2)^{1/2} - \frac{2 A^2 B^7}{((A^2 - B^2) y^2 + B^4)^{5/2}} \right] \delta \xi|_{x_0}. \] (4.13)

We match the natural boundary conditions (4.12) and (4.13) as in the circular case, giving us the equation
\[ \beta x_0 - \frac{A^8 B}{(A^4 + (B^2 - A^2) x_0^2)^{5/2}} = 0. \] (4.14)

We derive our new endpoints as follows. At \( P_1 \), we have
\[ y(x_0) = \frac{B}{A} (A^2 - x_0^2)^{1/2}, \]
\[ y'(x_0) = -\frac{B}{A} x(A^2 - x_0^2)^{-1/2}. \]

Using the transformation (4.5), we have \( \phi_0 = \pi/4 - \tan^{-1} \left( B x_0 (A^2 - x_0^2)^{-1/2} / A \right) \) where \( \phi_0 \) is the left endpoint. Similarly, we know \( y'(x_1) = 0 \) and so the right endpoint is \( \phi_1 = \pi/4 \).

We find the value of the constants \( c_0 \) and \( c_1 \) by substituting the left endpoint into the
equations (4.3) and (4.4). Substituting $\phi_0$ into the solution (4.3) for $x$, we have

$$x(\phi_0) = c_0 - \frac{2(\alpha + \beta)^{1/2}}{\beta} \left(1 - k^2 \sin^2 \phi_0\right).$$

We simplify part of the equation using

$$\sin^2 \phi_0 = \frac{1}{2} (1 - \cos(2\phi_0))$$

$$= \frac{1}{2} \left(1 + \frac{Bx_0}{A^4 + (B^2 - A^2)x_0}\right).$$

Then, upon substitution, we have

$$c_0 = x_0 + \frac{2(\alpha + \beta)^{1/2}}{\beta} \left[1 - \frac{\beta}{\alpha + \beta} \left(1 + \frac{Bx_0}{A^4 + (B^2 - A^2)x_0}\right)\right]. \quad (4.15)$$

As in the circular case, $c_1 = c_0$. Similarly, to find $d_0$, we substitute $\phi_0$ into the solution (4.4) for $y$ and thus, we obtain

$$d_0 = \frac{B}{A} (A^2 - x_0^2)^{1/2} + \frac{2(\alpha + \beta)^{1/2}}{\beta} \left(E(\phi_0, k) - \frac{\alpha}{\alpha + \beta} F(\phi_0, k)\right). \quad (4.16)$$

Matching the curves at $P_2$, we find

$$d_1 = d_0 + \frac{4(\alpha + \beta)^{1/2}}{\beta} \left(E(\phi_1, k) - \frac{\alpha}{\alpha + \beta} F(\phi_1, k)\right), \quad (4.17)$$

where $\phi_1 = \sin^{-1}(1/k)$.

### 4.3 Results

Here, we consider grafolds of three different sized nanotubes, namely $(6, 6)$, $(8, 8)$ and $(10, 10)$ armchair nanotubes. We plot the curved shapes of these grafolds in Figs 4.3-4.5 and 4.6-4.8, by using (4.3) and (4.4) together with constants $c_i$ and $d_i$ given by (4.6), (4.7) and (4.8) for the circular cross-section nanotubes and (4.15), (4.16), and (4.17) for the elliptical cross-section nanotubes.
As a comparison to our analytical results, several molecular dynamics simulations are performed for the folds with (6,6), (8,8) and (10,10) armchair nanotubes. Details of these molecular dynamics simulations are provided in Appendix B.2. The resulting structures from the molecular dynamics simulations are overlayed with the curves generated by our mathematical model given in Section 4.2.1 for nanotubes of an equivalent radius, as shown in Figs 4.3, 4.4 and 4.5. Note that in these figures we have chosen values for $\gamma$ in the range of $0.8 - 1.6$ eV and the corresponding values of $\beta$ are determined numerically by solving (4.9). We show the left endpoint $x_0$ and root mean square comparison with the simulation result in Table 4.1.

The results from our mathematical model give a reasonable approximation to the curved structures obtained from the molecular dynamics simulations, especially for smaller radii, such as (6,6) and (8,8) nanotubes. However, as the nanotube becomes larger as shown for a (10,10) nanotube, the discrepancy between our model and the simulation becomes more pronounced, especially for the curve $C_2$. We also note that smaller values of the bending rigidity give better agreement to the molecular dynamics simulation. Since the larger

![Figure 4.3: Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for a circular cross-section of a (6,6) armchair nanotube.](image)

- $\gamma = 0.8$
- $\gamma = 1.0$

size nanotubes have been slightly compressed forming an elliptical cross-section rather
than a perfectly circular structure, we extended the model with an assumption of oval cross-section of a nanotube as shown in Section 4.2.2. To obtain analytical results for this case, we need to simultaneously solve two equations (4.9) and (4.14) to find $\beta$ and the point $x_0$ where the curve touches the ellipse. We select the eccentricity of our ellipse to be 0.9 to well fit the compressed tube. Again, analytical results are displayed together with the results from molecular dynamics simulations as also shown in Fig. 4.6, 4.7 and 4.8. For given values of $\gamma$, the resultant values of $\beta$ and $x_0$ can be found by solving (4.14).

We show the left endpoint $x_0$ and root mean square comparison with the simulation result in Table 4.2. We see that the result from assuming elliptical cross-section nanotube gives better fit for the morphology of the larger tube sizes. Again, the curves with smaller values of the bending rigidity give better approximation to the molecular dynamics simulation. However, we observe that varying $\gamma$ results in a wider range of our solution curves.

Understanding graphene folds and the effect from intercalated molecules are important for application of grafolds as functionalised surfaces. This chapter uses a classical approach of variational calculus to determine the resulting curved structures based on the interaction of a single-walled carbon nanotube with the fold of a graphene sheet. The

Figure 4.4: Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for a circular cross-section of a (8,8) armchair nanotube.
analytical results obtained are shown to agree well with molecular dynamics studies. This chapter shows that the structure of folds depends not only on graphene’s physical properties, but also on the size of the internal structures. For larger nanotubes, the interaction between the tube and graphene sheet leads to a more compressed structure, with less curvature. This result has implications for the design of functionalised surfaces where high curvature may be preferred as it may lead to more interactive sites with greater chemical potential.

Table 4.1: Numerical solutions for the endpoint $x_0$ and root mean square comparison for (6,6), (8,8) and (10,10) circular cross-section nanotubes with different values of the bending rigidity, $\gamma$.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>(6,6) $x_0$</th>
<th>RMS (Å)</th>
<th>(8,8) $x_0$</th>
<th>RMS (Å)</th>
<th>(10,10) $x_0$</th>
<th>RMS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>2.84</td>
<td>0.152</td>
<td>0.8</td>
<td>2.6</td>
<td>0.227</td>
<td>0.8</td>
</tr>
<tr>
<td>1</td>
<td>3.48</td>
<td>0.408</td>
<td>1</td>
<td>3.12</td>
<td>0.345</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>1.2</td>
<td>3.63</td>
<td>0.413</td>
<td>1.2</td>
<td>3.34</td>
<td>0.614</td>
</tr>
<tr>
<td>1.4</td>
<td>1.4</td>
<td>4.19</td>
<td>0.417</td>
<td>1.4</td>
<td>3.79</td>
<td>0.728</td>
</tr>
<tr>
<td>1.6</td>
<td>1.6</td>
<td>4.98</td>
<td>0.322</td>
<td>1.6</td>
<td>4.25</td>
<td>0.819</td>
</tr>
</tbody>
</table>
CHAPTER 4. GRAPHENE FOLDS AROUND NANOTUBES

Figure 4.6: Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for an elliptical cross-section of a (6,6) armchair nanotube.

Table 4.2: Numerical solutions for the endpoint $x_0$ and root mean square comparison for (6,6), (8,8) and (10,10) elliptical cross-section nanotubes with different values of the bending rigidity, $\gamma$.

<table>
<thead>
<tr>
<th></th>
<th>(6,6)</th>
<th></th>
<th>(8,8)</th>
<th></th>
<th>(10,10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>$x_0$</td>
<td>RMS (Å)</td>
<td>$\gamma$</td>
<td>$x_0$</td>
<td>RMS (Å)</td>
</tr>
<tr>
<td>0.8</td>
<td>2.63</td>
<td>0.209</td>
<td>0.8</td>
<td>2.37</td>
<td>0.252</td>
</tr>
<tr>
<td>1</td>
<td>3.24</td>
<td>0.256</td>
<td>1</td>
<td>2.85</td>
<td>0.414</td>
</tr>
<tr>
<td>1.2</td>
<td>4.09</td>
<td>0.201</td>
<td>1.2</td>
<td>3.35</td>
<td>0.525</td>
</tr>
<tr>
<td>1.4</td>
<td></td>
<td></td>
<td>1.4</td>
<td>3.84</td>
<td>0.583</td>
</tr>
<tr>
<td>1.6</td>
<td>1.6</td>
<td>4.52</td>
<td>0.557</td>
<td>1.6</td>
<td>3.89</td>
</tr>
</tbody>
</table>
Figure 4.7: Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for an elliptical cross-section of a (8,8) armchair nanotube.

Figure 4.8: Comparison between the curves given by MD simulation (grey) and the analytical solutions with different values of the bending rigidity for an elliptical cross-section of a (10,10) armchair nanotube.
Chapter 5

Conformation of graphene wrinkles on substrate

In this chapter, we examine wrinkle formation in graphene during the chemical vapor deposition process. Firstly, we discuss the causes and effects of some common deformations of graphene structures. We construct a pair of models for the strain-induced, out-of-plane buckling of graphene grown on a substrate. We initially model an arch-shaped wrinkle and subsequently expand this model to incorporate self-adhesion between the wrinkle edges. Variation techniques are utilised to determine the optimal conformation structure for both models. We find these models exhibit a similar structure to experimental analysis.

5.1 Wrinkles and chemical vapor deposition

Graphene is often visualised as a perfectly flat material. Contrary to this assumption, graphene sheets typically exhibit varying surface corrugations. Structural defects result in bonding asymmetry which is relaxed by an out-of-plane deformation. Even relatively pristine free-standing graphene is still affected by thermal vibrations resulting in ripple formation and self-folding at the edges. Graphene grown on a substrate is subject to wrinkle formation from in-plane stresses. Wrinkled structures can be formed by the overlapping of graphene islands during production. Additionally, high-densities of wrinkles are formed by compressive strain induced by thermal effects during the cooling process.
Deformations of graphene greatly impact the properties of the sheet. Amongst other effects, graphene wrinkles cause anisotropic electron mobility, potential band-gap opening, locally-modified chemical reactivity and a reduction in both mechanical strength and thermal conductivity. The impact of these effects largely depends on the desired applications. Tuneable wrinkles enable functionalisation of the sheet and have potential in energy storage and selective bandgap engineering [76]. However, wrinkles are generally regarded as structural defects.

We examine wrinkled structures induced during chemical vapor deposition (CVD). Wrinkle formation is inherent to this process. Subsequently, understanding the nature of these wrinkles remains an important research objective [77]. Chemical vapor deposition is a popularly used technique for producing high-quality, large-area graphene sheets. This method involves the bottom-up process of growing of graphene on a crystallographic substrate. Methane gas is introduced into a reaction chamber containing a substrate. Graphene produced on transition metal substrates can be categorised as weak binding from physisorption as occurs on Cu, Al, Pt, Ag and Au as well as strong binding from chemisorption occurring with Ni, Co, Ru, Pd and Ti interaction. We are primarily interested in the most commonly employed substrates, Cu(111) and Ni(111). High temperatures within the chamber cause the methane to decompose and the resultant carbon atoms attach to the substrate. The solubility of carbon into copper is insignificant, resulting in a self-terminating process producing uniform mono-layer graphene over most of the surface [78, 79]. As the graphene layer and the substrate cool, the lattice of both materials contract. The substrate shrinks notably, while the sheet expands slightly with the end result of compressing the graphene monolayer laterally. In addition, the van der Waals (vdW) adhesion between the graphene sheet and substrate is weak and highly prone to interlayer slipping and delamination. Sufficient compression strain therefore is relieved through out-of-plane buckling and localised wrinkle formation occurs in the graphene layer as seen in Fig. 5.1 [80, 81]. Wrinkles tend to form around defects and defect lines in the substrate [81–83]. These wrinkles and other folded structures have been identified
CHAPTER 5. CONFORMATION OF GRAPHENE WRINKLES ON SUBSTRATE

through scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Figure 5.1: A top-down SEM image displaying graphene wrinkles formed by the CVD process [84].

5.2 Modelling approach

We have previously discussed the use of calculus of variation for carbon nanostructures in Section 4.2. Similar techniques may be used to predict the structure of wrinkles formed on substrate. Specifically, we examine the buckling resulting from lateral strain applied to the sheet. Wrinkle configurations are taken to be induced from the energy balance between the bending rigidity of graphene and the vdW adhesion between the sheet and substrate.

In the following sections, we consider mathematical models for two graphene wrinkle profiles. We first examine a small delamination characterised by an “arch” shape. Under increasing strain, the sides of the wrinkle are found to approach one other. Subsequently, we examine a second model where these sides are adhered. Such a structure has been previously speculated in the literature [85].

5.2.1 Arch wrinkle structure

We construct a model to determine the optimal structure of a graphene wrinkle induced on a substrate through compressive force. The general construction of this model follows
from study in Chapter 4. We assume a pristine sheet of graphene is initially attached to a perfectly flat substrate through vdW adhesion forces. This substrate contracts under negative thermal expansion inducing work upon the sheet. Under sufficient work, the graphene sheet experiences an out-of-plane buckling forming a wrinkle structure. Transmission electron microscope (TEM) imaging suggests a one-dimensional nature to these wrinkles [82]. Subsequently we take the graphene wrinkle to be invariant along its length, reducing the problem to a two-dimensional curve as shown in Fig. 5.2. We assume reflective symmetry in the y-axis and solely consider the first quadrant.

The dominant energies are taken to be comprised of the elastic bending energy of the graphene sheet and the vdW interaction energy between the sheet and the substrate. The sheet is initially situated at the vdW equilibrium distance, $\delta$, from the substrate. We additionally introduce a fixed lateral compression, $2l$, to the sheet.

The curve is modelled as three distinct curves denoted as $C_0$, $C_1$ and $C_2$. Here $C_0$ and
$C_1$ represent the free sections of the wrinkle, while $C_2$ represents the horizontal section of the curve remaining adhered to the substrate. The curves defining the wrinkle, $C_0$ and $C_1$, are bounded by the points $P_0 = (0, y_0)$ and $P_2 = (x_2, \delta)$ and meet at the critical point of zero curvature $P_1 = (x_1, y_1)$. The height, $y_0$, and width, $x_2$, of the wrinkle remain unfixed.

Employing a similar modelling strategy to Chapter 4, the elastic bending energy, $E_e$, is defined as

$$E_e = \gamma \int_C \kappa^2 ds,$$

where $\kappa$ is the line curvature and $\gamma$ is a constant denoting the bending rigidity of graphene. We also model the vdW energy, $E_v$, as

$$E_v = -\int_C \epsilon u(x - x_2) ds,$$

where the scaling constant $\epsilon$ denotes the vdW energy per area length for the curve section $C_3$ and $u(x)$ represents the Heaviside step function assuming that the structure is at equilibrium with respect to the vdW force. The total potential energy, $E$, rescaled by the bending rigidity $\gamma$, is

$$\hat{E} = \frac{E}{\gamma} = \frac{E_e + E_v}{\gamma} = \int_C (\kappa^2 - \alpha u(x - x_2)) ds,$$

where $\alpha = \epsilon / \gamma$. We must incorporate constraints to force a non-trivial curve structure. First, the graphene sheet is taken to be inextensible forcing the total arc length of the curve to be fixed at a length $L$. That is,

$$\int_C ds = L. \quad (5.1)$$

The lateral compression is taken as $l$ since we consider half of the wrinkle. This compression fixes $x_3 = L - l$, which can be expressed as a constraint in the form

$$\int_0^{x_3} dx = L - l.$$
Combining these constraints, we find

\[
\int_C ds - \int_0^{x_3} dx = l \\
\int_C ds - \int_{C_0 + C_1}^{x_2} dx = l.
\] (5.2)

Formulating a functional from the scaled energy and the constraint (5.2) multiplied by a Lagrange multiplier \(\beta\), gives

\[
J(y) = \int_C (\kappa^2 - \alpha u(x - x_2)) ds - \beta \left( \int_{C_0 + C_1}^{x_2} ds - \int_0^{x_2} dx \right)
\]

\[
= \int_{C_0 + C_1}^{x_2} (\kappa^2 - \beta) ds - \alpha \int_{C_2}^{x_2} ds + \beta \int_0^{x_2} dx
\]

\[
= \int_{C_0 + C_1}^{x_2} (\kappa^2 + \alpha - \beta) ds + \beta \int_0^{x_2} dx - \alpha L
\]

\[
= \int_0^{x_2} \left( (\kappa^2 + \alpha - \beta)(1 + y'^2)^{1/2} + \beta \right) dx - \alpha L.
\] (5.3)

Determining the minimal energy conformation is equivalent to minimising the functional \(J(y)\). We denote the integrand in (5.3) as a new function \(F\). That is,

\[
F(y', y'') = \frac{y''^2}{(1 + y'^2)^{3/2}} + (\alpha - \beta)(1 + y'^2)^{1/2} + \beta.
\]

This problem is of the form of a second order variational calculus problem with the corresponding Euler-Lagrange equation,

\[
F_y - \frac{d}{dx} F_{y'} + \frac{d^2}{dx^2} F_{y''} = 0,
\] (5.4)

with fixed boundary conditions \(y(x_2) = \delta\) and \(y'(x_2) = 0\). As \(P_0\) and \(P_2\) are permitted to vary along the \(y\)-axis and \(x\)-axis respectively, the natural boundary conditions \(p \delta y = 0\)\right|_{x_0} \quad \text{and} \quad H \delta x = 0\right|_{x_2} \quad \text{are prescribed. As \(F\) is independent of both \(x\) and \(y\), both \(H\) and \(p\) are
conserved quantities. We deduce from the natural boundary conditions that $H$ and $p$ are identically zero over the domain. The Euler-Lagrange equations therefore simplify to

$$\begin{align*}
H &= F - py' - qy'' = 0 \\
F - y''F_y &= 0. \quad (5.5)
\end{align*}$$

Upon substitution and some routine calculation, (5.5) may be rearranged into

$$\begin{align*}
\frac{y''^2}{(1 + y'^2)^{3/2}} + (\alpha - \beta)(1 + y'^2)^{1/2} + \beta - \frac{2y''^2}{(1 + y'^2)^{5/2}} &= 0 \\
\kappa^2 &= (\alpha - \beta) + \beta(1 + y'^2)^{-1/2} \\
\kappa &= \pm \left((\alpha - \beta) + \beta(1 + y'^2)^{-1/2}\right)^{1/2}. \quad (5.6)
\end{align*}$$

The conformation of the curve is now expressed by its curvature. We therefore make the substitution, $y' = \tan \theta$, converting this problem into the standard intrinsic equations for a plane curve. Here, $\theta = \theta(s)$ represents the tangential angle to the curve where $s$ is the position along the arc-length of the curve. We note that

$$\begin{align*}
\kappa &= \frac{d\theta}{ds}, \quad dx = \cos \theta, \quad dy = \sin \theta.
\end{align*}$$

Applying the chain rule, the curvature (5.6) can be expressed as

$$\kappa = \cos \theta \frac{d\theta}{dx} = \sin \theta \frac{d\theta}{dy} = \pm \left((\alpha - \beta) + \beta \cos \theta\right)^{1/2}.$$

With some rearrangement, we construct the parametric equations

$$\begin{align*}
\frac{dx}{d\theta} &= \pm \frac{\cos \theta}{\left((\alpha - \beta) + \beta \cos \theta\right)^{1/2}}, \\
\frac{dy}{d\theta} &= \pm \frac{\sin \theta}{\left((\alpha - \beta) + \beta \cos \theta\right)^{1/2}}.
\end{align*}$$
For ease of solving, we make the substitution \( \theta = 2\phi \) finding

\[
\frac{dx}{d\phi} = \pm \frac{2\cos(2\phi)}{(\alpha - 2\beta \sin^2 \phi)^{1/2}},
\]

\[
\frac{dy}{d\phi} = \pm \frac{2\sin(2\phi)}{(\alpha - 2\beta \sin^2 \phi)^{1/2}},
\]

(5.7)
(5.8)

where we have simplified using the identity \( \cos(2\phi) = 1 - 2\sin^2 \phi \). A solution for \( y(\phi) \) can be found with simple substitution. Integrating (5.8), we have

\[
y(\phi) = d \pm \int \frac{4\sin \phi \cos \phi}{(\alpha - 2\beta \sin^2 \phi)^{1/2}} d\phi.
\]

Let \( u = \alpha - 2\beta \sin^2 \phi \) and \( du = -4\beta \sin \phi \cos \phi d\phi \). We find,

\[
y(\phi) = d \mp \frac{1}{\beta} \int u^{-1/2} du
\]

\[= d \mp \frac{2}{\beta} (\alpha - 2\beta \sin^2 \phi)^{1/2}.
\]

We now find a solution for \( x(\phi) \). Integrating (5.7), we have

\[
x(\phi) = c \pm \int \frac{2 - 4\sin^2 \phi}{(\alpha - 2\beta \sin^2 \phi)^{1/2}} d\phi
\]

\[= c \pm \frac{2}{\beta} \int \frac{\alpha - 2\beta \sin^2 \phi - \alpha + \beta}{(\alpha - 2\beta \sin^2 \phi)^{1/2}} d\phi
\]

\[= c \pm \frac{2}{\beta} \int \left( (\alpha - 2\beta \sin^2 \phi)^{1/2} - (\alpha - \beta) (\alpha - 2\beta \sin^2 \phi)^{-1/2} \right) d\phi
\]

\[= c \pm \frac{2\alpha^{1/2}}{\beta} \int \left( \left( 1 - \frac{2\beta}{\alpha} \sin^2 \phi \right)^{1/2} - \frac{\alpha - \beta}{\alpha} \left( 1 - \frac{2\beta}{\alpha} \sin^2 \phi \right)^{-1/2} \right) d\phi. \quad (5.9)
\]

This expression can be solved in terms of elliptic integrals. The incomplete elliptic integral of the first kind is defined as

\[
F(\phi, k) = \int_{0}^{\phi} \frac{d\theta}{(1 - k^2 \sin^2 \theta)^{1/2}},
\]
and the incomplete elliptic integral of the second kind is defined as

\[ E(\phi, k) = \int_0^\phi (1 - k^2 \sin^2 \theta)^{1/2} d\theta, \]

where the elliptic modulus \( k \in [0, 1] \). It follows that (5.9) can be expressed as

\[ x(\phi) = c \pm \frac{2\alpha^{1/2}}{\beta} \left( E(\phi, k) - \frac{\alpha - \beta}{\alpha} F(\phi, k) \right), \]

where \( k = \left( \frac{2\beta}{\alpha} \right)^{1/2} \). The constants are determined from the boundary conditions. We first separate the parametric equations based on the sign of the curvature. The critical point, \( \phi_0 \), at zero curvature is evaluated as

\[ \alpha - 2\beta \sin^2(\phi_0) = 0 \]
\[ \phi_0 = \sin^{-1}(1/k). \]

On the curve \( C_i \) where \( i \in \{0, 1\} \),

\[ x_{C_i}(\phi) = c_i \pm \frac{2\alpha^{1/2}}{\beta} \left( E(\phi, k) - \frac{\alpha - \beta}{\alpha} F(\phi, k) \right), \]
\[ y_{C_i}(\phi) = d_i \pm \frac{2}{\beta} (\alpha - 2\beta \sin^2 \phi)^{1/2}, \]  

(5.10)

where \( \phi \in [0, \phi_0] \) on both curves. At the left endpoint \( P_0 \) of the curve \( C_0 \), where \( \phi = 0 \), we find

\[ x_{C_0}(0) = c_0 = 0. \]

We match the two curves \( C_0 \) and \( C_1 \) at the critical point \( P_1 \) where \( \phi_0 = \sin^{-1}(1/k) \). Here,

\[ x_{C_1}(\phi_0) = x_{C_0}(\phi_0) \]
\[ c_1 - \frac{2\alpha^{1/2}}{\beta} \left( E(\phi_0, k) - \frac{\alpha - \beta}{\alpha} F(\phi_0, k) \right) = c_0 + \frac{2\alpha^{1/2}}{\beta} \left( E(\phi_0, k) - \frac{\alpha - \beta}{\alpha} F(\phi_0, k) \right), \]
giving rise to
\[ c_1 = \frac{4\alpha^{1/2}}{\beta} \left( E(\phi_0, k) - \frac{\alpha - \beta}{\alpha} F(\phi_0, k) \right). \]

At the right endpoint \( P_2 \) of the curve \( C_2 \), where \( \phi = 0 \), we have
\[ y_{C_1}(0) = d_1 + \frac{2\alpha^{1/2}}{\beta}, \]
\[ d_1 = \delta - \frac{2\alpha^{1/2}}{\beta}. \]

Matching again at \( P_1 \), we find our final constant from
\[ y_{C_0}(\phi_0) = y_{C_1}(\phi_0) \]
\[ d_0 + \frac{2}{\beta} (\alpha - 2\beta \sin^2(\phi_0))^{1/2} = d_1 - \frac{2}{\beta} (\alpha - 2\beta \sin^2(\phi_0))^{1/2}, \]
giving rise to \( d_0 = d_1 \). Finally, we determine the value of the Lagrange multiplier \( \beta \).

Recall the constraint (5.2) as
\[ \int_{c_0 + c_1} ds - \int_{0}^{x_2} dx = l. \]

Thus we have
\[ \int_{c_0 + c_1} ds - x_{C_1}(0) = l. \quad (5.11) \]

We can find the length of the curves \( C_0 \) and \( C_1 \) using (5.10) and the inherent symmetry of the elastica to be
\[ \int_{c_0 + c_1} ds = 2 \int_{c_0} ds \]
\[ = 2 \int_{0}^{\phi_0} \left( \left( \frac{dx}{d\phi} \right)^2 + \left( \frac{dy}{d\phi} \right)^2 \right)^{1/2} d\phi \]
\[ = 2 \int_{0}^{\phi_0} \left( \frac{4\sin^2(2\phi) + 4\cos^2(2\phi)}{(\alpha - 2\beta \sin^2 \phi)^{1/2}} \right) d\phi \]
\[
\frac{4}{\alpha^{1/2}} \int_{0}^{\phi_0} \left( \frac{1}{(1 - k^2 \sin^2 \phi)^{1/2}} \right) d\phi \\
= \frac{4}{\alpha^{1/2}} F(\phi_0, k).
\]

Substituting this result into (5.11), we find

\[
\frac{4}{\alpha^{1/2}} F(\phi_0, k) - \frac{4\alpha^{1/2}}{\beta} \left( E(\phi_0, k) - \frac{\alpha - \beta}{\alpha} F(\phi_0, k) \right) = l \\
\frac{4\alpha^{1/2}}{\beta} (F(\phi_0, k) - E(\phi_0, k)) = l.
\]

This equation is then numerically solved to find \( \beta \) for a given value of compression \( l \). We use the minimal conformation to calculate the corresponding minimal energy. Recall

\[
E = \gamma \int_{C_0 + C_1} \kappa^2 ds - \varepsilon \int_{C_2} ds.
\]

From the inherent symmetry of elastica curves, this may be expressed as

\[
E = 2\gamma \int_{C_0} \kappa^2 ds - \varepsilon \int_{C_2} ds.
\]

Using the relationship \( \kappa(s) = d\theta/ds \), we write \( \kappa(s) ds = d\theta \) and thus we find

\[
E = 2\gamma \int_{0}^{\theta_0} |\kappa| d\theta - \varepsilon \int_{C_2} ds, \quad (5.12)
\]

for the critical value \( \theta_0 = 2\phi_0 \). We force the integrand to be strictly positive, swapping the limits if required. We make the substitution \( \phi = \theta / 2 \) to find

\[
E = 4\gamma \int_{0}^{\phi_0} \left( \alpha - 2\beta \sin^2 \phi \right)^{1/2} d\phi - \varepsilon \int_{C_2} ds \\
= 4\gamma \alpha^{1/2} E(\phi_0, k) - \varepsilon \left( L - \int_{C_0 + C_1} ds \right)
\]
\[ 4 \gamma \alpha^{1/2} E(\phi_0, k) - \varepsilon \left( L - \frac{4}{\alpha^{1/2}} F(\phi_0, k) \right) \]

\[ = 4 \gamma \alpha^{1/2} (E(\phi_0, k) + F(\phi_0, k)) - \varepsilon L, \quad (5.13) \]

using \( \alpha = \varepsilon / \gamma \). Finally, we note that for larger choice of compression value, the wrinkle conformation forms a s-shaped structure as shown in Fig. 5.3. While the initial formulation is slightly different, the problem quickly reduces to an identical solution. That is, the regions of positive and negative curvature in both formulations are represented by the same set of equations. We therefore take the model is taken as valid provided the point \( P_3 \) remains greater than half the graphene-graphene vdW equilibrium distance measured from the \( y \)-axis. For even larger compression values, a new model is required.

**Figure 5.3:** Representation of an arch-shaped graphene wrinkle with an s-shaped structure.
5.2.2 Self-adhered wrinkle structure

The previous section captures the conformation of a small wrinkle induced upon an adhered graphene sheet. We note that a sufficiently narrow wrinkle could self-adhere to produce a more stable energy-optimal structure [85]. We expand the previous formulation to account for this potential structural evolution. The curve representing the cross-section of this self-adhered wrinkle is shown in Fig. 5.4. We consider the curve as five distinct sections denoted by $C_0$, $C_1$, $C_2$, $C_3$ and $C_4$. Here $C_0$, $C_1$ and $C_3$ represent the free sections of the wrinkle, $C_4$ represents the horizontally aligned section remaining adhered to the substrate and $C_2$ represents the vertically aligned, self-adhered section of the wrinkle. The complexity of this structure renders it unwieldy to be modelled in its entirety. We decompose the structure into two segments denoted as $A$ and $B$ respectively. These

**Figure 5.4:** Representation of an self-adhered graphene wrinkle partially attached to a substrate, separated by an equilibrium distance, $\delta_1$, measured from the $x$-axis. The wrinkle adheres to itself at an equilibrium distance $2\delta_0$. This graph is symmetrical under reflection over the $y$-axis.
segments are shown in Fig. 5.5 where segment $A$ has been rotated for the convenience of modelling as a function of $x$.

We follow our previous assumptions where the elastic bending energy dominates the free sections and vdW energy dominates the fixed, adhered sections. We denote the vdW energy as $\varepsilon_0$ for graphene-graphene interaction and $\varepsilon_1$ for graphene-substrate interaction. The resultant vdW equilibrium distances are given by $2\delta_0$ and $\delta_1$ respectively. The length of each segment is given as $L_0$ and $L_1$ respectively with total fixed length $L = L_0 + L_1$. We take the point $P_5$ to be compressed by the half-compression $l$.

We note that segment $A$ follows an identical formulation to the graphene fold modelled in Cox et al. [69] while segment $B$ is structurally similar to the formulation in Section 5.2.1. The total energy of the curve is given as the sum of the energy in each component part, $E = E_0 + E_1$ where

$$E_0 = \gamma \int_{C_0 + C_1}^{C_2} \kappa^2 \, ds - \varepsilon_0 \int_{C_2} \, ds,$$  \hspace{1cm} (5.14)  

$$E_1 = \gamma \int_{C_3}^{C_4} \kappa^2 \, ds - \varepsilon_1 \int_{C_4} \, ds.$$  \hspace{1cm} (5.15)

We minimise the energy of each segment independently.
Segment A

This section summarises the work presented in [69]. We note that the total potential energy for this segment consists of the elastic bending and vdW energies. The total potential energy (5.14) scaled by the bending rigidity $\gamma$, is given as

$$\hat{E}_0 = \int_{c_0+c_1}^{c_2} \kappa^2 \, ds - \alpha_0 \int_{c_2} ds,$$

with $\alpha_0 = \varepsilon_0 / \gamma$. We apply a length constraint equivalent to (5.1) multiplied by a Lagrange multiplier $\lambda$. The resultant functional is expressed as

$$J_0(y) = \hat{E}_0 + \lambda \int_{C_A} ds$$

$$= \int_{c_0+c_1}^{c_2} \kappa^2 \, ds - \alpha_0 \int_{c_2} ds + \lambda \int_{C_A} ds,$$

where $C_A = C_0 + C_1 + C_2$. We rearrange the equation into the form

$$J_0(y) = \int_{c_0+c_1}^{x_2} \left( \kappa^2 + \alpha_0 \right) ds - (\lambda - \alpha_0)L_0$$

$$= \int_{0}^{x_2} \left( \frac{y''}{(1+y'^2)^{3/2}} + \alpha_0 \right) (1+y'^2)^{1/2} \, dx - (\lambda - \alpha_0)L_0.$$ 

We are required to minimise the functional $J_0$ to determine the optimal energy structure. This involves solving the associated Euler-Lagrange equation (5.4) where $F$ is the integrand of the functional $J_0$ given as,

$$F(y',y'') = \frac{y''}{(1+y'^2)^{3/2}} + \alpha_0(1+y'^2)^{1/2}.$$ 

The fixed boundary conditions of the equation are $y(0) = 0$ and $y'(0) \to \infty$. As $x_2$ is permitted to vary, we additionally have the natural boundary condition $H \delta x = 0 \big|_{x_2}$.

As the functional is independent of $y$, the Euler-Lagrange equation may be reduced to
the degenerate form,
\[ F_y' - \frac{d}{dx} F_{y''} = \beta_0, \]  
(5.16)
for some arbitrary constant \( \beta_0 \).

Additionally, as the functional is independent of \( x \), the Hamiltonian \( H \) is a conserved quantity. The natural boundary condition at \( x_2 \) requires \( H \) to be zero and so \( H \) is identically zero over the entire domain. That is,

\[ H = F - y' \left( F_y' - \frac{d}{dx} F_{y''} \right) - y'' F_{y''} = 0. \]

We note that the expression in the bracket is equivalent to equation (5.16). Upon substitution, we find

\[ F - \beta_0 y' - y'' F_{y''} = 0. \]

Evaluating and simplifying this expression allows us to define the curve in terms of its curvature as

\[ \kappa = \pm \left( \alpha_0 - \frac{\beta_0 y'}{1 + y'^2} \right)^{1/2}. \]

We perform the substitution \( y'(x) = \tan \theta \) giving the result

\[ \kappa = \cos \theta \frac{d\theta}{dx} = \sin \theta \frac{d\theta}{dy} = \pm \left( \alpha_0 - \beta_0 \sin \theta \right)^{1/2}, \]

which may be rearranged to form the system

\[ \frac{dx}{d\phi} = \pm \frac{4 \sin \phi \cos \phi}{(\alpha_0 + \beta_0 - 2 \beta_0 \sin^2 \phi)^{1/2}}, \]
\[ \frac{dy}{d\phi} = \pm \frac{2 - 4 \sin^2 \phi}{(\alpha_0 + \beta_0 - 2 \beta_0 \sin^2 \phi)^{1/2}}, \]

where we have performed the substitution \( \theta = 2\phi - \pi/2 \). We can find \( x(\phi) \) through straight-forward integration techniques. Finding a solution for \( y(\phi) \) is more complex and requires the use of elliptical integrals. The details follow similar techniques as shown in
The resultant solutions for the curves $C_i, i \in \{0, 1\}$ are found to be

\[
x_{C_i}(\phi) = c_i \pm \frac{2\alpha_0^{1/2}}{\beta_0} \left( E(\phi, k_0) - \frac{\alpha_0 - \beta_0}{\alpha_0} F(\phi, k_0) \right),
\]

\[
y_{C_i}(\phi) = d_i \pm \frac{2}{\beta_0} (\alpha_0 - 2\beta_0 \sin^2 \phi)^{1/2},
\]

where $k_0 = \sqrt{\frac{2\beta_0}{\alpha_0 + \beta_0}}, \phi \in [0, \phi_0]$ on $C_0$ and $\phi \in [\pi/4, \phi_0]$ on $C_1$. The critical value at zero curvature is $\phi_0 = \sin^{-1}(1/k_0)$. Upon substituting the boundary conditions into our solution, we discover our constants as

\[
c_0 = c_1 = \frac{2(\alpha_0 + \beta_0)^{1/2}}{\beta_0},
\]

\[
d_0 = 0,
\]

\[
d_1 = \frac{2(\alpha_0 + \beta_0)^{1/2}}{\beta_0} (E(1/k_0, k_0) - F(1/k_0, k_0)).
\]

We now determine the minimal energy associated to this conformation. Recall,

\[
E_0 = \gamma \int_{C_0+C_1} \kappa^2 ds - \epsilon_0 \int_{C_2} ds,
\]

and using the relationships $\kappa(s) = d\theta/ds$ and $\theta = 2\phi$, we find through repeated substitutions as detailed in (5.12) the result

\[
E_1 = \gamma \left( \int_{\phi_0}^{\theta_1} |\kappa| d\theta + \int_{\theta_2}^{\theta_1} |\kappa| d\theta \right) - \epsilon_0 \int_{C_2} ds
\]

\[
= \gamma \left( \int_0^{\phi_0} (\alpha_0 - 2\beta_1 \sin^2 \phi)^{1/2} d\phi + \int_{\pi/4}^{\phi_0} (\alpha_1 - 2\beta_1 \sin^2 \phi)^{1/2} d\phi \right) - \epsilon_0 \int_{C_2} ds
\]

\[
= \gamma(\alpha + \beta)^{1/2} \left( 2E(\phi_0, k_0) - E(\pi/4, k_0) \right) - \epsilon_0 \left( L_0 - \int_{C_0+C_1} ds \right).
\]
We can derive the length of the curves $C_0$ and $C_1$ from (5.17) as

$$\int_{C_0 + C_1} ds = \int_0^{\phi_0} \left( \left( \frac{dx}{d\phi} \right)^2 + \left( \frac{dy}{d\phi} \right)^2 \right)^{1/2} d\phi + \int_{\phi_0}^{\pi/4} \left( \left( \frac{dx}{d\phi} \right)^2 + \left( \frac{dy}{d\phi} \right)^2 \right)^{1/2} d\phi$$

$$= \frac{2}{(\alpha + \beta)^{1/2}} (2F(\phi_0, k_0) - F(\pi/4, k_0)).$$

Upon substitution we find the energy to be

$$E_0 = 2\gamma(\alpha_0 + \beta_0)^{1/2} (2E(\phi_0, k) - E(\pi/4, k_0))$$

$$- \epsilon_0 \left( L_0 - \frac{2}{(\alpha + \beta)^{1/2}} (2F(\phi_0, k_0) - F(\pi/4, k_0)) \right). \tag{5.18}$$

**Segment B**

We note that the total potential energy of this segment consists of the elastic bending and vdW energies. The total potential energy (5.15) scaled by the bending rigidity $\gamma$, is given as

$$\hat{E}_1 = \int_{C_3} \kappa^2 ds - \alpha_0 \int_{C_4} ds,$$

where $\alpha_1 = \epsilon_1 / \gamma$. We note that the total length of the segment, $L_1$, and the $x$-distance traversed by the curve are both fixed. We can therefore, express the total length constraint as

$$\int_{C_3 + C_4} ds - \int_{x_3}^{x_5} dx = L_1 - (L - l - \delta_0)$$

$$\int_{C_3} ds - \int_{x_3}^{x_4} dx = \delta_0 + l - L_0, \tag{5.19}$$

noting the half-compression $l$ has been applied at the right endpoint $x_5 = L - l$. The scaled potential energy is combined with this constraint multiplied by a Lagrange multiplier $\beta_1$. 
so that the functional becomes

\[ J_1(y) = \int_{c_3}^{x_1} k^2 ds - \alpha_1 \int_{c_4}^{x_1} ds - \beta_1 \left( \int_{c_3}^{x_4} ds - \int_{x_3}^{x_4} dx \right). \]

This function is identical in structure to (5.3). We can simplify \( J_1 \) as

\[ J_1(y) = \int_{0}^{x_1} \left( (k^2 + \alpha_1 - \beta_1)(1 + y'^2)^{1/2} + \beta_1 \right) dx - \alpha_1 L, \]

and follow the same solution methodology to find the parametric solution for the conformation over the domain \( \phi \in [-\pi/4, 0] \) as

\[ x_{C_3}(\phi) = c_2 + \frac{2\alpha_1^{1/2}}{\beta_1} \left( E(\phi, k_1) - \frac{\alpha_1 - \beta_1}{\alpha_1} F(\phi, k_1) \right), \]

\[ y_{C_3}(\phi) = d_2 - \frac{2}{\beta_1} (\alpha_1 - 2\beta_1 \sin^2 \phi)^{1/2}, \]

where \( k_1 = \sqrt{\frac{3\beta_1}{\alpha_1}} \). We determine the constants from the boundary conditions. At the left endpoint \( P_3 \), where \( \phi = -\pi/4 \), we find

\[ x_{C_3}(-\pi/4) = c_2 + \frac{2\alpha_1^{1/2}}{\beta_1} \left( E(-\pi/4, k_1) - \frac{\alpha_1 - \beta_1}{\alpha_1} F(-\pi/4, k_1) \right), \]

\[ c_2 = \delta_0 + \frac{2\alpha_1^{1/2}}{\beta_1} \left( E(\pi/4, k_1) - \frac{\alpha_1 - \beta_1}{\alpha_1} F(\pi/4, k_1) \right). \]

Likewise, at the right endpoint \( P_4 \), where \( \phi = 0 \), we find

\[ y_{C_3}(0) = d_2 - \frac{2\alpha_1^{1/2}}{\beta_1}, \]

\[ d_2 = \delta_1 + \frac{2\alpha_1^{1/2}}{\beta_1}. \]

We now find the value of the Lagrange multiplier \( \beta_1 \). Recall our constraint (5.19) as

\[ \int_{c_3}^{x_4} ds - \int_{x_3}^{x_4} dx = \delta_0 + l - L_0, \]
Thus,
\[ \int_{C_3} ds - x_{C_3}(0) = l - L_0 \]  \hspace{1cm} (5.20)

The length of \( C_3 \) can be derived from our solution as
\[
\int_{C_3} ds = \int_{\pi/4}^{0} \frac{2}{(\alpha_1 - 2\beta_1 \sin^2 \phi)^{1/2}} d\phi \\
= \frac{2}{\alpha_1^{1/2}} \int_{0}^{\pi/4} \frac{2}{(1 - k_1 \sin^2 \phi)^{1/2}} d\phi \\
= \frac{2}{\alpha_1^{1/2}} F(\pi/4, k_1). \hspace{1cm} (5.21)
\]

Upon substitution into (5.20), the constraint becomes
\[
\frac{2}{\alpha_1^{1/2}} F(\pi/4, k_1) - \delta_0 - \frac{2\alpha_1^{1/2}}{\beta_1} \left( E(\pi/4, k_1) - \frac{\alpha_1 - \beta_1}{\alpha_1} F(\pi/4, k_1) \right) = l - L_0 \\
\delta_0 + l - \frac{2\alpha_1^{1/2}}{\beta_1} \left( F(\pi/4, k_1) - E(\pi/4, k_1) \right) = L_0. \hspace{1cm} (5.22)
\]

This expression is dependent on two unknowns, \( L_0 \) and \( \beta_1 \). We require an additional constraint to determine an explicit solution for both variables. Expressing the total energy in terms of one of these variables provides the necessary condition. We first determine the minimal energy associated to the conformation of segment \( B \). Recall
\[ E_1 = \gamma \int_{C_3} \kappa^2 ds - \varepsilon_1 \int_{C_4} ds. \]

and using the relationships \( \kappa(s) = d\theta/ds \) and \( \theta = 2\phi \), we find through repeated substitutions as detailed in (5.12) the result
\[
E_1 = \gamma \int_{\theta_0}^{\theta_1} \kappa d\theta - \varepsilon_1 \left( L_1 - \int_{C_3} ds \right) \\
\hspace{2cm} = \pi/4 \\
= 2\gamma \int_{0}^{\pi/4} (\alpha_1 - 2\beta_1 \sin^2 \phi)^{1/2} d\phi - \varepsilon_1 \left( L_1 - \int_{C_3} ds \right). 
\]
Substituting the length (5.21) into this expression, we find

\[ E_1 = 2\gamma\alpha_1^{1/2}E(\pi/4, k_1) - \varepsilon_1 \left( L - L_0 - \frac{2}{\alpha_1^{1/2}}F(\pi/4, k_1) \right). \]

We substitute the constraint (5.22) to express \( E_1 \) in terms of a single unknown variable, \( \beta_1 \), giving the result

\[ E_1 = 2\gamma\alpha_1^{1/2}E(\pi/4, k_1) - \varepsilon_1 \left( L - \delta_0 - l + \frac{2\alpha_1^{1/2}}{\beta_1} \left( E(\pi/4, k_1) - \frac{\alpha_1 - \beta_1}{\alpha_1}F(\pi/4, k_1) \right) \right). \]

We also substitute the constraint (5.22) into the energy of segment A (5.18) expressing \( E_0 \) in terms of \( \beta_1 \). The total energy may now be written as \( E(\beta_1) = E_0(\beta_1) + E_1(\beta_1) \). Numerically solving the expression \( E'(\beta_1) = 0 \) derives the value of \( \beta_1 \) which minimises the energy.

**Curve reconstruction**

In order to reconstruct the original curve, we must trace back the transformations performed on segment A. We rotate the solution \( \pi/2 \) radians clockwise and shift it along the y-axis such that the two segments meet at the point \( P_3 \). This transformation for the curves \( C_i, i \in \{0, 1\} \) is

\[ x_{C_i}(\phi) \rightarrow y_{C_i}(\phi), \]

\[ y_{C_i}(\phi) \rightarrow \xi - x_{C_i}(\phi), \]

where \( \xi \) is given by

\[ \xi = y_{C_1}(-\pi/4) - \left( -x_{C_1}(\pi/4) - \int_{C_2} ds \right) \]
\[ y = y_C_3(-\pi/4) + x_C_1(\pi/4) + \int_{c_2} ds. \]

The complete parametric solution can then be expressed, for \( i \in \{0, 1\} \), as

\[
\begin{align*}
  x_{C_i}(\phi) &= c_i \pm \frac{2(\alpha_0 + \beta_0)}{\beta_0} \left( E(\phi, k_0) - \frac{\alpha_0}{\alpha_0 + \beta_0} F(\phi, k_0) \right), \\
  y_{C_i}(\phi) &= d_i \pm \frac{2(\alpha_0 + \beta_0)}{\beta_0} \left( 1 - k_0^2 \sin^2 \phi \right)^{1/2}, \\
  x_{C_3}(\phi) &= c_2 + \frac{\alpha_1^{1/2}}{\beta_1} \left( E(\phi, k_1) + \frac{\beta_1 - \alpha_1}{\alpha_1} F(\phi, k_1) \right), \\
  y_{C_3}(\phi) &= d_2 - \frac{\alpha_1^{1/2}}{\beta_1} \left( 1 - k_1^2 \sin^2 \phi \right)^{1/2},
\end{align*}
\]

with the corresponding constants

\[
\begin{align*}
  c_0 &= 0, \\
  c_1 &= \frac{4(\alpha_0 + \beta_0)^{1/2}}{\beta_0} \left( E(1/k_0, k_0) - \frac{\beta_1 - \alpha_1}{\alpha_1} F(1/k_0, k_0) \right), \\
  c_2 &= \delta_0 + \frac{2\alpha_1^{1/2}}{\beta_1} \left( 1 - k_1^2 \sin^2 \phi \right)^{1/2}, \\
  d_0 &= \delta_1 + L_0 + \frac{2\alpha_0^{1/2}}{\beta_0} + \frac{2(\alpha_1 - \beta_1)^{1/2}}{\beta_1} - \frac{2}{(\alpha_0 + \beta_0)^{1/2}} \left( 2F(1/k_0, k_0) - F(\pi/4, k_0) \right), \\
  d_1 &= d_0, \\
  d_2 &= \delta_1 + \frac{2\alpha_1}{\beta_1}.
\end{align*}
\]

### 5.3 Results

<table>
<thead>
<tr>
<th>Metal</th>
<th>Interlayer distance (Å)</th>
<th>Binding energy (eV Å⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Ni</td>
<td>2.018</td>
<td>0.0913</td>
</tr>
<tr>
<td>C-Cu</td>
<td>3.260</td>
<td>0.0132</td>
</tr>
<tr>
<td>C-C</td>
<td>3.34</td>
<td>0.0214</td>
</tr>
</tbody>
</table>

Table 5.1: Interfacial properties between graphene and selected substrates obtained from DFT calculations [86]. Interaction between graphene layers is taken from [72].
Table 5.2: The critical compression, $l$, associated to selected bending rigidities, $\gamma$, of a graphene sheet on copper and nickel substrates. This compression represents the transition point where the self-adhered wrinkle becomes more energetically favourable than the arch wrinkle.

<table>
<thead>
<tr>
<th>$\gamma$ (eV)</th>
<th>Copper compression (Å)</th>
<th>Nickel compression (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>15.91</td>
<td>0.8</td>
</tr>
<tr>
<td>1</td>
<td>18.76</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>21.27</td>
<td>1.2</td>
</tr>
<tr>
<td>1.4</td>
<td>23.56</td>
<td>1.4</td>
</tr>
<tr>
<td>1.6</td>
<td>25.66</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Here, we construct a pair of models for graphene wrinkle conformation as detailed in Sections 5.2.1 and 5.2.2. Based on [73], we use the value of the bending rigidity, $\gamma$ in the range 0.8 - 1.6 eV. We study the most commonly employed substrates, Cu(111) and Ni(111). The minimal mismatch in lattice structure, under 5%, make these substrates ideal CVD candidates [86]. Graphene-metal interactions are often studied using density functional theory (DFT) calculations. From [86], which uses the local density approximation (LDA) method, we obtain values for the binding energy and interlayer distance, as shown in Table 5.1. Graphene wrinkles observed with scanning tunnelling microscopy (STM) exhibit a wrinkle density of approximately 1 per $\mu$m$^2$ [79]. Subsequently, we select our half-length, $L$, as 500 nm.

The total energy of the arch wrinkle model is examined for copper and nickel substrates over the domain of valid compressions, $l$, as shown in Fig. 5.6 and Fig. 5.8 respectively. We contrast these results with the total energy of the self-adhered wrinkle model over the same domain as shown in Fig. 5.7 and Fig. 5.9 respectively. We observe that for a copper substrate, the self-adhered wrinkle is more energetically favourable. Conversely, the arch wrinkle is always more energetically favourable on a nickel substrate. Table 5.2 displays the critical points where the self-adhered wrinkle becomes the optimal geometrical configuration. We suggest this effect results from the relationship between the respective binding energies as shown in Table 5.1. As the forces binding the graphene sheet to a nickel substrate dominate over self-adhesion, the larger self-adhered wrinkle is not energetically favourable. However, as graphene-copper interaction is significantly weaker, the
self-adhesion dominates over the graphene-copper binding forces.

CVD grown wrinkles on copper substrate, examined using atomic force microscopy (AFM), show height ranging from 2-6 nm [79, 85, 87]. This correlates well with our theoretical data as shown in Table 5.3. However, experimentally measured wrinkles are an order of magnitude wider than theoretical calculations [87]. It has been speculated that
Self-adhered wrinkle energy on copper substrate

![Graph showing energy as a function of wavelength](image)

**Figure 5.7:** The total energy of a self-adhered graphene wrinkle on copper substrate for selected bending rigidities, $\gamma$.

A collapsed self-adhered wrinkle could account for this discrepancy [85]. Regardless, this remains an issue requiring further theoretical investigation.
Figure 5.8: The total energy of an arch-shaped graphene wrinkle on nickel substrate for selected bending rigidities, $\gamma$. 

Arch wrinkle energy on nickel substrate

$\gamma = 0.8$
$\gamma = 1.0$
$\gamma = 1.2$
$\gamma = 1.4$
$\gamma = 1.6$
Figure 5.9: The total energy of a self-adhered graphene wrinkle on nickel substrate for selected bending rigidities, $\gamma$. 
Chapter 6

Conclusion

Over this thesis, we have explored various analytical approaches for modelling graphitic structures. The initial work in chapter 3 studied the intermolecular interaction between sheets of graphene oxide. We modelled the structure of graphene oxide as a series of surfaces representing carbon and attached functional groups. This continuum model was shown to accurately model graphene oxide and could be tuned to account for varying states of hydration and oxidation. This was confirmed with comparisons to molecular dynamics simulations.

We further demonstrated an adaption of this model with the addition of a carbon nanotube encapsulated into the structure. Analysis showed the optimal configuration of this nanotube was to lie flat relatively close to the surface of a sheet.

Potential future work could incorporate multiple nanotubes and graphene oxide sheets. Such hybrid structures are of great research interest. Additionally, the modelling techniques used could be adapted for more exotic materials including two-dimensional boron.

Later work in Chapters 4 and 5 employed variation calculus to determine optimal conformation structures. We investigated the conformation of graphene folded around a carbon nanotube. Such forms of intercalation provide a one-dimensional functionalisation of graphene. This problem was simplified by considering a two-dimensional cross-section, modelling the graphene as an elastic line. We constructed two models, a perfectly-circular nanotube cross-section and a compressed elliptical cross-section.

We displayed that the structure depended both on the physical properties on the graphene
sheet but also the size of the intercalated molecules. A lower graphene bending rigidity was shown to correlate more strongly with results taken from molecular dynamic simulation. Additionally, the elliptical model proved slightly more accurate for larger nanotubes.

While this thesis solely focuses on the intercalation of single-walled carbon nanotubes, the techniques used within can be adapted to model the intercalation of more complex molecular structures. Furthermore, future work could adapt this model to handle three-dimensional intercalation structures.

Finally, we utilised variation calculus to investigate wrinkle formation in CVD-grown graphene. We constructed a pair of models representing both arch-shaped and self-adhered wrinkle structures. These models provide the optimal conformation of a graphene wrinkle dependant on the chosen substrate and compression length. We found that wrinkles formed on a copper substrate exhibited a larger height and width than that of nickel. Additionally, we noted a relationship between the dominant wrinkle conformation and the binding energy of the substrate and graphene.

However, we also noted a width discrepancy between the modelled wrinkle and experimental data. Extending the model to capture the equilibrium state of a collapsed graphene wrinkle may assist in understanding this issue. Further investigation of the surface chemistry between graphene and substrate may also provide additional insight.

In concluding, this thesis provides analytic solutions based on macroscale modelling techniques which provide a useful, and often cheaper, method of calculating conformations.
Bibliography


Appendix A

Additional mathematical details

A.1 Integration method required for deriving interaction energy

It is required to find the solution of an integral of the form

\[ S(n) = \int_{0}^{R} \frac{x^m}{(x^2 + \alpha)^n} \, dx \]

\[ = \alpha^{-n} \int_{0}^{R} \frac{x^m}{(1 + \frac{x^2}{\alpha})^n} \, dx. \]

Let \( t = x^2 / \alpha \), then \( x = (\alpha t)^{1/2} \) and \( dx = (1/2) \alpha (\alpha t)^{-1/2} \, dt \). Under this substitution, our equation becomes

\[ S(n) = \frac{1}{2} \alpha^{1-n} \int_{0}^{R^2/\alpha} (1 + t)^{-n} (\alpha t)^{m/2} (\alpha t)^{-1/2} \, dt \]

\[ = \frac{1}{2} \alpha^{(m-2n-1)/2} \int_{0}^{R^2/\alpha} (1 + t)^{-n} t^{(m-1)/2} \, dt. \]

Let \( t' = \alpha t / R^2 \), \( dt' = \alpha / R^2 \, dt \) to force the limits to the interval \([0, 1]\). Then,

\[ S(n) = \frac{1}{2} \alpha^{(m-2n-1)/2} \int_{0}^{1} \left( 1 + \frac{R^2}{\alpha} t' \right)^{-n} \left( \frac{R^2}{\alpha} t' \right)^{(m-1)/2} \frac{R^2}{\alpha} \, dt' \]

\[ = \frac{1}{2} \alpha^{-n} R^{m+1} \int_{0}^{1} \left( 1 + \frac{R^2}{\alpha} t' \right)^{-n} t'^{(m-1)/2} \, dt'. \]
Let $t' = 1 - s$, $dt' = -ds$. Then

$$S(n) = \frac{1}{2} \alpha^{-n} R^{m+1} \int_1^0 \left( 1 + \frac{R^2}{\alpha} (1 - s) \right)^{-n} (1 - s)^{(m-1)/2} ds$$

$$= \frac{1}{2} \alpha^{-n} R^{m+1} \left( \frac{R^2 + \alpha^2}{\alpha} \right)^{-n} \int_0^1 \left( 1 - \frac{R^2}{R^2 + \alpha^2} s \right)^{-n} (1 - s)^{(m-1)/2} ds$$

$$= \frac{1}{2} R^{m+1} (R^2 + \alpha)^{-n} \int_0^1 \left( 1 - \frac{R^2}{R^2 + \alpha^2} s \right)^{-n} (1 - s)^{(m-1)/2} ds.$$ 

The integral can finally be written in the form of the hypergeometric function

$$S(n) = \frac{R^{m+1}}{(m+1)(R^2 + \alpha)^n} F \left( n, 1; \frac{m + 3}{2}; \frac{R^2}{R^2 + \alpha} \right). \quad (A.1)$$
Appendix B

Selected LAMMPS molecular dynamics input code

B.1 Simulation of graphene oxide sheets

The molecular dynamics simulations performed in Chapter 3 utilised using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD simulator. A pair of graphene oxide sheets encompassing water molecules were modelled in a $2\text{nm} \times 2\text{nm} \times 2\text{nm}$ simulation box. This system was repeated periodically such that the sheets were infinite. The numbers of epoxy and hydroxyl groups were kept the same and were distributed randomly over both sides of each sheet to give a C:O ratio of 1:4. Simulations were performed under the NVT canonical ensemble at 300 K. Temperature control was managed using the Nose-Hoover thermostat. The system energy was first minimised using the conjugate gradient (CG) algorithm and was then run at a timestep of 0.5 femtoseconds.

A second simulation was run incorporating water molecules intercalated between the sheets. Water molecules were simulated using the extended simple point charge (SPC/E) water model. The SHAKE algorithm was applied to the water to reduce high frequency vibrations of the hydrogen bonding. Interactions between the graphene oxide sheets were modelled using the reactive forcefield ReaxFF which is known to be accurate in modelling hydrocarbon nanostructures [88]. The water and GO interactions were calculated
by Lennard-Jones 6-12 potential between the oxygen and carbon atom using \( \varepsilon = 0.0937 \) kcal/mol and \( \sigma = 3.19 \) Å [46]. Coulombic forces were calculated using a particle-particle particle-mesh (PPPM) solver. The following code segment shows the general input for the hybrid system modelling GO and water interaction.

```plaintext
# SIMULATION OF A PAIR OF GRAPHENE OXIDE SHEETS IN WATER
# INITIALISATION
units real
atom_style full
boundary p p p
dimension 3
newton on

# ATOM DEFINITION
pair_style hybrid lj/cut/coul/long 9.8 reax/c NULL checkqeq no
bond_style harmonic
angle_style harmonic
kspace_style ppm 0.0001
pair_modify mix arithmetic
read_data data.waterGO

# SETTINGS
pair_coeff * * reax/c ffield.reax.cho C O H O H
pair_coeff 4 4 lj/cut/coul/long 0.1553 3.166
pair_coeff 5 5 lj/cut/coul/long 0.0 0.0
angle_coeff 1 100.0 109.47
bond_coeff 1 1000.0 1.0

fix 1 all shake 0.0001 20 0 b 1 a 1
fix 2 all nvt temp 300.0 300.0 100.0

# RUN SIMULATION
timestep 0.5 # 0.5 fmsec
dump myDump all custom 1 dumpWaterGO.lammpstrj id type x y z
```
APPENDIX B. SELECTED LAMMPS CODE

run 500000

B.2 Simulation of graphene folds around nanotubes

The molecular dynamics simulations performed in Chapter 4 utilised the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to perform molecular dynamics (MD) simulations. A folded sheet of graphene around a single-walled carbon nanotube was modelled in a $10 \text{ nm} \times 10 \text{ nm} \times 10 \text{ nm}$ simulation box. This system was repeated periodically along the axis of the nanotube. All interactions were modelled using the AIREBO forcefield. The simulation was equilibrated under the NPT isothermal-isobaric ensemble at a temperature of 300 K and pressure of 1 bar. Temperature and pressure were controlled by the Nose-Hoover thermostat and barostat. The energy of the system was minimised by using the conjugate gradient (CG) algorithm and was run at a time-step of 0.5 femtoseconds.

The following code segment details the input for modelling the graphene folding around the $(16, 16)$ nanotube. The topology of a graphene sheets curved around a nanotube was defined using the equilibrium topology of the structures. Some initial velocity was applied to the upper and lower segments of the sheets causing the sheet to wrap around the tube. The velocity of all particles in the structure was then set to zero and the system was re-run under standard conditions. As we are concerned with the equilibrium structure and not the system dynamics, this was a viable method for minimising the computational time.

```python
# SIMULATION OF GRAPHENE FOLDED AROUND A SWNT (16,16)
# INITIALISATION
units metal
atom_style full
boundary p p p
dimension 3
newton on
```
APPENDIX B. SELECTED LAMMPS CODE

# ATOM DEFINITION
read_data data .NanoFold16
pair_style airebo 3.0
pair_modify mix arithmetic

# SETTINGS
region uR block 0 65 0 9.83804 -1 1
region lR block 0 65 0 9.83804 -28 -26

group uG region uR
group lG region lR

velocity uG set NULL NULL -20
velocity lG set NULL NULL 20

pair_coeff * * CH. airebo C
fix 1 all npt temp 300.0 300.0 100.0 iso 0.0 0.0 1000.0

# RUN SIMULATION
minimize 1.0e-4 1.0e-6 1000 10000

thermo_style multi
timestep 0.0005 # 0.5 fmsec
thermo 1000
dump myDump all custom 100 dumpNanoFold16.lammpstrj id type x y z
run 100000
velocity all set 0 0 0
run 100000

write_data data .NanoFold16_out
Publications and presentations of the author

Journal publications


Conference proceedings


Manuscript in preparation

Selected Presentations

- “Interaction between graphene oxide sheets”, Australia Nanotechnology Network (ANN) Early Career Workshop 2014, University of Technology Sydney
- “Intercalation of graphene oxide and carbon nanotubes”, Australia and New Zealand Industrial and Applied Mathematics (ANZIAM) Annual Conference 2015, Gold Coast
- “Functionalisation of graphene folds”, Australia and New Zealand Industrial and Applied Mathematics (ANZIAM) Annual Conference 2016, Canberra
- “Intercalating a carbon nanotube into graphene folds”, Nanomath 2016, Centre d’Élaboration de Matériaux et d’Etudes Structurales (CEMES-CNRS), Toulouse
- “Intercalation of carbon nanotubes into a graphene sheet”, 24th International Congress of Theoretical and Applied Mechanics (ICTAM), Montréal
- “Wrinkle structures formed during graphene growth”, Australian Mathematical Society (AustMS) Annual Conference 2016, Canberra
- “Conformation of wrinkle structures formed during chemical vapor deposition”, Australia and New Zealand Industrial and Applied Mathematics (ANZIAM) Annual Conference 2017, Hahndorf