Radiation Damage in Graphite

Line Defects and Processes

Submitted by

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Abstract

Graphite is used as a moderator in advanced gas cooled nuclear reactors (AGRs) across the country. The graphite is damaged over time due to a bombardment of neutrons and this has a wide range of effects on the physical properties of the graphite. This thesis focuses on the dimensional change of the nuclear graphite.

The first part of this thesis is based on two dimensional dislocation dynamics (2D-DD) and describes a program which has been written to model the movement of line defects in an anisotropic elastic continuum. Classical elasticity theory is applied to a single crystal containing dislocations to calculate the dimensional change of the crystal and the energy stored in the continuum by the dislocations. Several modes are described, beginning with the standard model of dimensional change which concerns point defect aggregation into prismatic loop dislocations. Extending these theories the program has been developed further to model the dimensional change as a result of gliding basal dislocations. This program was created as a proof of concept model to help show that significant energy can be stored in the lattice by dislocations as well as by the well established point defect energies.

The second part of this thesis uses ab initio calculations to measure geometries and energies of line defects in bilayer graphene and graphite which can be used to quantify the models used in the two dimensional dislocation dynamics. Density functional theory (DFT) with a local density approximation (LDA) has been utilised as implemented by the AIMPRO package. These calculations use state of the art filtration methods to allow optimisations on many atom structures which were previously unattainable. The first DFT calculation of a basal dislocation dipole in bilayer graphene has been carried out, a structure which has previously only been optimised using classical molecular dynamics. The results of these ab initio calculations can be used to quantify the 2D-DD results.
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## Abbreviations

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<th>Abbreviation</th>
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<tr>
<td>2D-DD</td>
<td>2 Dimensional Dislocation Dynamics</td>
</tr>
<tr>
<td>AGR</td>
<td>Advanced Gas-cooled Reactor</td>
</tr>
<tr>
<td>AIMPROM</td>
<td>\textit{ab initio} Modelling Program</td>
</tr>
<tr>
<td>AIREBO</td>
<td>Adaptive Intermolecular Reactive Empirical Bond Order</td>
</tr>
<tr>
<td>DF-TEM</td>
<td>Dark Field Transmission Electron Microscopy</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalised Gradient Approximation</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>HTR</td>
<td>High Temperature Reactor</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LJ</td>
<td>Lennard-Jones</td>
</tr>
<tr>
<td>PKA</td>
<td>Primary Knock-on Atom</td>
</tr>
<tr>
<td>REBO</td>
<td>Reactive Empirical Bond Order</td>
</tr>
<tr>
<td>SDG</td>
<td>Secondary Displacement Group</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>VHTR</td>
<td>Very High Temperature Reactor</td>
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1. Introduction

Carbon atoms can be found in many different allotropes; perhaps the most obvious being diamond and graphite but more recently fullerenes,\textsuperscript{1-3} nanotubes\textsuperscript{4-7} and graphene\textsuperscript{8-10} have come to the spotlight.

The focus of this thesis is graphite. Graphite is a layered material with its crystal structure made up of many sheets of graphene. Graphene sheets are single atomic layers of carbon atoms arranged in hexagonal rings with strong interplane bonding, see Figure 1.1. The layers have weak intralayer bonds such that the material has an ability to shear easily with applied stress.

The layers of the graphite are most commonly arranged in an AB stacking sequence. This is where every other layer is exactly lined up with the bottom layer (A layers) and the odd layers (B) are shifted by a bond length so that they have atoms exactly in the centre of a hexagon ring in the A layers. The crystal of graphite therefore has layers stacked in an alternating order ABABAB\ldots.

This alternating stacking brings about two configurations of atoms in the crystal; alpha atoms and beta atoms. In AB stacked graphite the alpha atoms are atoms which have atoms in adjacent layers which are directly above and below it. Beta atoms are located above the centre of a hexagon ring and have no atom above or below in the adjacent layers.

Graphite has been an important material for the nuclear industry for many years. It was used as both a structural building material and a neutron moderator in both the Magnox and the Advanced Gas-cooled Reactors (AGRs) in the UK. The earliest Magnox reactors at Calder Hall began operation in the 1956\textsuperscript{11} with the newest of the reactors, Wylfa in Anglesea, which closed in December 2015.\textsuperscript{12} The Magnox reactors were superseded by the higher temperature AGRs built in the 1970's and 1980's which began operation with Hunterston in 1976 and are still in operation today.
Figure 1.1.: The atomic structure of graphite showing the unit cell of AB stacked graphite (in gold) where $a = 2.46\,\text{Å}$ and $c = 6.7\,\text{Å}$ twice the inter layer separation, $3.35\,\text{Å}$.

The AGR design was developed in the UK and was based on the previous generation of Magnox reactors. The main developments being that they operate at a higher temperature and therefore have a better thermal efficiency. The main alternative reactor design is the pressurised water reactor (PWR) which was used across the world, however there is not much between them in terms of running efficiency but the major advantage of the AGR is that the design allows fuel stringers to be changed without shutting down the reactor.

Nuclear power provides almost 20% of the UK electricity supply, with the 7 dual core AGR sites supplying over 7.5 GW of power to the National Grid, a huge output considering an offshore wind turbine outputs a meagre 3 MW when operating at 100%. Based on an average efficiency of 30%, the UK would need over 8000 new wind turbines just to replace its nuclear reactors.

Unfortunately these reactors cannot run forever. The currently operational AGRs were originally intended to operate for 30 years however there have been extensions to this lifespan across the fleet. The most recent extensions for Dungeness B putting its decommission date in 2028 and Torness and Heysham 2 to 2030. However with the next generation of nuclear reactors at Hinkley Point C (pressurised water reactors) not due to become operational until at least 2023, and no other form of sustainable electricity production available to fill the increasing demand for electricity in the UK,
it has become vital to prolong the operational life of the current AGRs.

The ageing of the graphite in the AGRs plays a vital role in determining the lifespan of these reactors. Over time the graphite within the reactors is bombarded with fast neutrons, causing defects in the crystallographic structure of the material. These defects lead to changes in many properties of the material, ranging from the coefficient of thermal expansion and changes in elastic constants of the material to the dimensions of the single crystal and hence bulk material.\textsuperscript{20} The processes utilised to explain this dimensional change are described in the following section.

The graphite also experiences radiation damage in the form of radiolytic oxidation which reduces the strength of the material by increasing its porosity. An increased porosity is known as ‘weight loss’ and occurs as the CO\textsubscript{2} cooling gas in the open porosity is broken down into active species, believed to be CO\textsubscript{3},\textsuperscript{21} which can then react with the graphite.\textsuperscript{22} In AGRs the shortening of the lifespan of the graphite due to radiolytic oxidation is delayed by using graphite with low porosity and by adding a methane inhibitor to the gas. In large pores the active species reacts with the methane causing a protective layer between the graphite and the cooling gas. This process does not occur in smaller diameter pores (below 5\textmu m) and the oxidising species remove carbon atoms from the graphite causing weight loss and increased porosity.\textsuperscript{23}
Looking ahead, graphite will continue to be of importance to the nuclear industry, in particular the next generation nuclear plant (NGNP) efforts in the USA which currently include very high temperature reactors (VHTR) with graphite neutron moderators.24 There has also been extensive research into graphite moderated reactors in China25 in particular the high temperature pebble bed reactor design which has been chosen for construction.26 As such research into the behaviour and properties of graphite exposed to neutron irradiation will continue to be of importance for many years to come.

Despite graphite being such an important material historically and with the potential to be of high importance for many more years, the material is still not fully characterised, with its response to neutron irradiation not fully understood. The work undertaken for this thesis has been primarily working towards a quantitative link between neutron irradiation, or fluence, and dimensional change including the dependence of temperature and stresses on the dimensional change.

1.1. Standard Model of Irradiation Damage in Graphite

The long established theory of irradiation damage in graphite is based on a point defect model. This section will describe the currently accepted model of both dimensional change (Section 1.1.2) and stored energy (Section 1.1.4) in graphite exposed to neutron irradiation.

1.1.1. Neutron Irradiation

Over the lifetime of the nuclear reactors the graphite components of the core will be subject to a high neutron fluence. Fast neutrons (with a mean energy of about 2 MeV) move through the moderator and gradually lose electron energy until eventually they collide with a carbon atom within the lattice and knock it out of position. This atom is known as the primary knock on atom (PKA) and this PKA then moves through the lattice knocking other atoms out of their lattice sites creating cascades of defects, known as secondary displacement groups (SDG). A schematic of this process is shown in Figure 1.3.27

The displaced atoms can come to rest between the layers of graphite in positions
which were not original lattice sites; these are known as interstitial atoms. Each time an interstitial atom is formed there will be a corresponding vacant lattice site known as a vacancy. Together these make a Frenkel pair. Figure 1.4 shows a monovacancy\textsuperscript{28} in graphite and a spiro interstitial,\textsuperscript{29,30} named for its similar appearance to the spiro-pentane molecule. It is these point defects, interstitials and vacancies, which have been used to describe the damage observed in irradiated graphite.

Figure 1.3.: Schematic of the cascade of defects in graphite as a result of neutron irradiation. The primary knock on atom is labelled as PKA and there are clusters of secondary displacement groups labelled as SDG. Reproduced from Telling & Heggie\textsuperscript{27}

Figure 1.4.: \textbf{Left}: Atomic representation of a monovacancy in graphite. Reproduced from Latham \textit{et al.}\textsuperscript{31} \textbf{Right}: Atomic representation of a spiro interstitial in graphite. Reproduced from Telling \textit{et al.}\textsuperscript{30}
1.1.2. Dimensional Change

It is well known that graphite under neutron irradiation will experience dimensional change. These dimensional changes have been observed in the graphite used in nuclear reactors since the ’40s. Kelly et al.\textsuperscript{32} explain that the dimensional change of a crystallite of graphite gives rise to a contraction in the basal plane and expansion, perpendicular to the planes, along the direction of the \textit{c}-axis. The standard model currently explains this by the creation and migration of interstitial atoms which form prismatic loops between the layers of the graphite, pushing the planes apart and causing expansion in \textit{c}. The \textit{a} contraction is explained by vacancies forming lines through the basal plane and pulling the planes in to fill these lines. Figure 1.5 shows an interstitial loop and a vacancy line as described in his 1969 paper.\textsuperscript{33} In this paper Thrower outlines a range of dark field transmission electron microscopy (DF-TEM) work in which one can observe the existence of these interstitial loops.

In order to understand and quantify the physical property changes of irradiated polycrystalline nuclear graphite it is important to characterise the single crystal behaviour. However it is almost impossible to find or manufacture single crystals of graphite to study.

It is possible to manufacture graphite such that the crystals are well oriented
allowing experiments to be carried out on a macroscopic sample with results which should be similar to the single crystal. This graphite is known as highly oriented pyrolytic graphite (HOPG).\textsuperscript{34} The structure of this graphite is a mosaic of crystallites which all lie in approximately the same alignment with their \( c \) axes less than a degree apart in the highest quality HOPGs.\textsuperscript{35}

The physical property changes of HOPG under neutron irradiation have been extensively measured in experiments using energetic neutrons. The irradiation is observed to alter properties such as the thermal expansion coefficient, thermal conductivity, strength and elastic constants and therefore Young’s modulus, Poisson ratio and shear modulus, and most importantly for this work; the dimensions of the graphite change with neutron fluence.\textsuperscript{36}

The mechanical anisotropy and instability of its dimensions mean that single crystal graphite is a poor choice of engineering material. Nuclear graphites are polycrystalline and have an almost isotropic distribution of crystallite directions. The manufacturing process is known to leave a distribution of slit like pores and gas access pores in the bulk material.\textsuperscript{37} These pores amount to around a 20\% porosity, the very best graphite has about 16\% porosity.\textsuperscript{38} In bulk nuclear graphite the dimensions of the material are observed to initially decrease with neutron fluence such that the graphite shrinks in volume until a turnaround point where the dimensions begin to increase again. The standard interpretation of this behaviour is that the \( c \)-axis expansion is not seen initially as crystallites expand to fill inner porosity; known as accommodation cracks. As the fluence increases further the graphite volume continues to expand beyond its original non irradiated volume.

The rate of dimensional change of single crystal graphite will vary with irradiation conditions. For example the rate of dimensional change at lower irradiation temperatures is much greater than the rate of dimensional change at higher temperatures.\textsuperscript{32} Low temperature irradiations (around 150 °C) give a much higher \( c \)-axis expansion at a lower fluence than graphite crystals irradiated at over 250 °C. See Figure 1.6 which shows the dimensional change of HOPG which has been heat treated to 3600 °C and then exposed to a range of irradiation temperatures from 150 to 650 °C. Owing to the difficulty in isolating a single crystal of graphite it can be assumed that the results of experiments on HOPG or flakes or graphite will have similar results
to if those experiments could be carried out on single graphite crystallites.\textsuperscript{32,39,40}

In a crystal of graphite the dimensional change is dependent on the axes in question. The crystal expands in the \( c \) direction, perpendicular to the basal planes while shrinking in the \( a \) and \( b \) dimensions parallel to the basal planes. At temperatures above 250°C the ratio of the \( c \) expansion to \( a \) contraction is approximately 2:1, roughly conserving volume. The dimensional changes in both the \( c \)-axis and basal plane directions at various irradiation temperatures have been measured experimentally; a graph of the resulting dimensional changes can be seen in Figure 1.6.\textsuperscript{41} The dimensional change is unsaturating and continues to increase at all observed fluences for graphite irradiated above 250°C.

The rate of dimensional change of HOPG has also been reported by Kelly et al.,\textsuperscript{32} a graph of the rate of dimensional change with increasing neutron dose has been reproduced in Figure 1.7. The rate of crystal dimensional change in the \( c \)-axis direction with increasing neutron dose is seen to be constant for low doses (below \( \approx 4 \times 10^{20} \) n/cm\(^2\)). The rate of dimensional change then increases by almost four times by approximately \( 6 \times 10^{20} \) n/cm\(^2\) before falling back to the original rate for high neutron doses (above \( \approx 10 \times 10^{20} \) n/cm\(^2\)). This could be explained by considering that there may be more than one mechanism for dimensional change in graphite.

Initial damage to the graphite is heterogenous and the cascades of defects are evenly spread and unlikely to overlap. These cascades introduce basal dislocations into the graphite which are prevented from annihilation by interstitial pinning points. As the dislocations are held in and more cascades occur over time the density of basal dislocations increases with irradiation. When the density of dislocations gets very high the regions of damage start to overlap and the dislocations interact with one another. There are a number of interactions which could occur, such as annihilation, formation of kink bands and buckling of the basal planes. Buckling could occur in a number of situations, for example when dislocations of opposing signs come together on neighbouring (or next neighbour) planes. Basal dislocation interactions are able to cause a significant expansion in the \( c \) axis which is potentially the cause of the rapid increase in the rate of expansion reported by Kelly, Nettley and Martin in their 1966 paper.\textsuperscript{32} This can be seen in the graph reproduced in Figure 1.7.
Figure 1.6.: This graph from Kelly\textsuperscript{41} shows the expansion of the $c$-axis of graphite with neutron irradiation dose and contraction in the $a$ axis at various temperatures.
1.1.3. Creep

In materials science creep is a well known process which occurs in a range of materials. Creep is the deformation over time of a material when it is subjected to a constant load.\textsuperscript{42} Irradiation creep occurs in many materials but it is relevant to this thesis to consider how creep acts on the graphite moderator of a nuclear reactor. In this case creep is actually a beneficial process, acting to lower the stresses in the graphite.\textsuperscript{43} However in addition to lowering the material stresses creep does affect the dimensions of the graphite.\textsuperscript{44} It is generally thought that the initial shrinkage of graphite occurs as cracks and voids in the graphite are closed. Once all the voids have been filled creep continues however the material now expands with the continuous deformation. A popular explanation of the mechanism for creep in graphite is the pinning-unpinning model by Kelly and Foreman.\textsuperscript{45} Kelly and Foreman theorise that creep could occur in graphite by basal slip where glissile basal dislocations move through the material along their glide planes when pinning points such as small interstitial clusters are disrupted by the neutron irradiation.

1.1.4. Stored Energy

AB stacked graphite is the lowest energy state for a crystal of graphite.\textsuperscript{30} This is where the sheets are displaced by a bond length so that half of the atoms are above
atoms in a neighbouring plane (alpha atoms) and the other half are above voids in the lattice (beta atoms). This can be seen in Figure 1.8. When atoms are displaced from these perfect lattice positions the energy of the structure is increased. This energy stored in the crystal can be released in the form of heat when the atoms are moved back to their original low energy positions by thermal annealing. This stored energy is known as Wigner energy.

Wigner energy can be very dangerous if allowed to build up as defects can store a very large amount of energy. Kelly reports values of up to 2700 Jg⁻¹ which equates to a temperature rise of well over a thousand degrees. In order to prevent a build-up of energy in the graphite there have been two approaches: the energy can be released in annealing cycles or the reactor can be run at a high enough temperature to release Wigner energy during operation. The first method was used in historic low temperature graphite moderated reactors such as the Windscale reactors. The reactors at Windscale were operated at low temperatures and then subjected to annealing cycles at about 250 °C to prevent stored energy building up.

The annealing cycles involved heating the graphite up to a temperature higher than the irradiation temperature, this allowed atoms to move back to vacant lattice sites and so defects anneal, releasing the stored energy in a controlled manner. Over time, with many annealing cycles, the graphite at Windscale became more damaged and pockets of Wigner energy were building up, unknown to the operators. In 1957 during an annealing cycle one of the Windscale reactor piles became too hot, likely
Figure 1.9.: This graph, reproduced from Kelly\(^\text{20}\) shows the rate of release of stored energy in graphite exposed to various doses of neutron irradiation.

because of a sudden release of Wigner energy and the uranium fuel caught fire. It is still the worst nuclear accident in UK history.\(^\text{46}\)

The current fleet of AGRs are operated at a much higher temperature (with graphite reaching about 400 °C). This higher temperature allows for annealing of defects during operation which prevents a build up of Wigner energy. This is a process known as auto-annealing and means that annealing cycles are not necessary.

The rate of release of stored energy at a range of annealing temperatures has been investigated using graphite irradiated at 30 °C in the Hanford reactor (Washington, USA) for a range of neutron doses. A graph of this rate of release of stored energy can be seen in Figure 1.9. There is clearly a peak in the rate of release of energy at approximately 200 °C. This is thought to be the peak in energy release which led to the disaster at Windscale. Note that higher neutron doses reduce the 200 °C peak and results in energy stored at higher temperatures.

The stored energy has also been investigated as a function of irradiation temperature. Figure 1.10 shows the stored energy at a range of temperatures and it can be seen that for higher temperatures the energy stored in the graphite is far lower.

The migration energy of a single interstitial atom in AB stacked graphite is widely
Figure 1.10.: This graph, reproduced from Kelly\textsuperscript{20} shows the rate of stored energy release for graphite samples irradiated at a range of irradiation temperatures.

contested however Latham et al.\textsuperscript{31} have concluded that the results of their \textit{ab initio} calculations show that the interstitial is very strongly bonded to the host atoms and therefore not mobile at 200 °C. It has been suggested that the migration of vacancies give rise to the peak in Wigner energy release\textsuperscript{31} with a vacancy migration energy of 1.2eV.

An alternative interpretation of these experimental results could be that the energy in damaged graphite could also be stored in dislocation strain fields not just in point defect energies. Basal dislocations held into the crystal by interstitial pinning points could be released when the temperature allows these interstitials to become mobile, removing the pinning points. A combination of energies released by interstitial and vacancy annihilation and energies released by annihilation of basal dislocations could account for the Wigner energy release which is observed.

The following chapter outlines what is meant by a dislocation, dislocation types and theory and how the energy stored in a dislocation is calculated. These concepts are all based on classical elasticity theory. The experimental observations of dislocations in graphene and graphite are also outlined. This information is then used to create a dislocation dynamics program to model the dimensional change and stored energy
in a two-dimensional graphite system using elastic continuum methods. Before this it is useful to consider the evidence for the occurrence of dislocations in damaged graphite.
2. Dislocation Theory

2.1. Dislocations

Dislocations are topological imperfections in the regular structure of a crystal. They can be edge dislocations, extra or missing material in the lattice; screw dislocations, where there is a shear of part of the crystal with respect to another part; or a mixture of both types where there is extra or missing material and a shear of material. Dislocations cause variations in the stress in the crystal which can result in expansion or contraction of the material. Dislocations can store energy in the crystal due to both the dislocation itself and interactions with other dislocations in the material. Most interactions of dislocations will act to reduce the stored energy in the material.

2.1.1. The Burgers Vector

Dislocations are characterised by a quantity known as the Burgers vector. Dislocations are carriers of slip and the amount of slip they carry is given by this vector, \( \mathbf{b} \). They can also be seen as the boundary between slipped and unslipped regions of the crystal.

Consider a lattice containing a dislocation and draw a closed circuit, clockwise, around the dislocation. Then draw an identical circuit in a perfect lattice. The vector which completes the circuit, from finish to start, in the perfect crystal is known as the Burgers vector. This is known as the finish to start, right hand (FS-RH) convention. An example of the circuits which dictate the Burgers vector can be seen in Figure 2.1.

2.1.2. The Glide Plane

Dislocations have planes through the crystal on which they can move most easily. The number of glide planes can vary depending on the type of dislocation (i.e. the
alignment of its Burgers vector and the crystallography of the material. For example for dislocation in a graphene sheet there are three glide planes due to the symmetry of the atomic bonding within the sheet. In the case of pure basal edge dislocations in graphite the glide plane is parallel to the basal plane and perpendicular to the dislocation line. The glide plane is the boundary between slipped and unslipped regions of the crystal this is represented by the dashed line in Figure 2.2.

### 2.1.3. Dislocation Core

The width of the core of the dislocation is given by the distance over which the slip across the glide plane varies from $-b/4$ to $+b/4$. This can be understood more clearly
Figure 2.3.: Schematic diagram showing a basal dislocation in a simple lattice. The width, shown in blue, is measured to either side of the dislocation to a point where the displacement is equal to \( \frac{b}{4} \) giving a total displacement of \( \frac{b}{2} \) where \( b \) is the Burgers vector of the dislocation.

by considering the schematic diagram in Figure 2.3 where the width is measured to a point either side of the dislocation where the disregistry of atoms is \( \frac{b}{4} \) giving a total slip of \( \frac{b}{2} \) between these points.

2.1.4. Types of Dislocation

Dislocations can be classified as either edge or screw type, or a mix of both. In this thesis edge type dislocations are considered in a single crystal of graphite. Edge dislocations can be in either a basal or prismatic direction. The prismatic edge dislocation has a Burgers vector in the \( c \) direction (perpendicular to the graphite planes), whereas the basal edge dislocation has a Burgers vector parallel to the basal planes. Figure 2.4 shows schematics of both basal and prismatic edge dislocations.

In the case of basal edge dislocations the Burgers vector of the simplest dislocation, as depicted in the left hand image of Figure 2.4, is equal to the unit vector in the basal plane.

In graphite a perfect basal dislocation is described as a 60° basal edge dislocation, this nomenclature stems from the angle between the Burgers vector and the line direction of the dislocation. The line direction describes the alignment of the dislocation with
Figure 2.4.: Schematic diagrams of edge dislocations in a graphite lattice (view along the armchair direction), dislocations are represented by the T. **Left:** a basal edge dislocation. **Right:** a partial prismatic edge dislocation.

respect to the lattice. An example of this is shown in Figure 2.6 (on Page 22) where the dislocation line runs along the z-axis.

The 60° perfect basal dislocation in graphite is seen to dissociate into two lower energy partial dislocations; a 90° partial and a 30° partial. A top down view of this can be seen in Figure 2.5 reproduced from Telling and Heggie.\(^\text{30}\) The 90° partial is a pure edge dislocation with the Burgers vector and line direction running perpendicular to each other and parallel to the basal plane. The 60° partial is a mixed dislocation with the Burgers vector at a 30° angle to the line direction. There is a region of graphite between the two partial dislocations which has been slipped one bond length from its low energy AB stacking state to a faulted stacking lamellae. The 90° partial dislocation has the effect of shifting an A layer in the stacking sequence to a C layer such that the stacking is then ABABCACAC. The central stacking fault layers (with the ABC and BCA stacking sequences) are in a stacking arrangement known as rhombohedral graphite. The 30° partial dislocation rotates the C plane so that the stacking returns to the low energy AB stacking pattern. During this dissociation the Burgers vector is conserved such that the Burgers vector of the perfect 60° dislocation is equal to the vector sum of the Burgers vectors of the 90° partial and the 30° partial dislocations.

Later in this thesis for simplicity perfect edge dislocations will be used in the 2D-DD program.
The prismatic edge dislocation shown in the right hand image of Figure 2.4 is a partial prismatic dislocation and has a Burgers vector equal to \( \frac{c}{2} \), in graphite 0.335 nm. This is the equivalent of an additional single layer of graphite such as an interstitial loop. A perfect prismatic dislocation has a Burgers vector equal to \( c \), in our case 0.667 nm. The perfect prismatic dislocation is an additional pair of layers which conserves the ABAB stacking order.

### 2.1.5. Elastic strain Due to Dislocations

Introducing dislocations into a material introduces stresses which will result in atoms in the crystal being displaced from their original crystallographic positions. The elastic strain fields of dislocations have been studied in great detail and theory is based on the generalised Hooke’s law, \( \sigma_{ij} = C_{ijkl} \varepsilon_{kl} \) where stress, \( \sigma \), is related to strain, \( \varepsilon \), by a stiffness tensor \( C_{ijkl} \). This follows the Einstein summation convention so that when an index appears twice we sum the term over all values of the index. We follow the usual convention of replacing the stiffness tensor with a \( 6 \times 6 \) matrix of stiffness constants \( c_{mn} \) where \( ij \) maps to \( m \), and \( kl \) to \( n \) in the following way (11 \( \rightarrow \) 1, 22 \( \rightarrow \) 2, 33 \( \rightarrow \) 3, 12 \( \rightarrow \) 6, 23 \( \rightarrow \) 4, 31 \( \rightarrow \) 5). The strain can be related to displacement, \( u \), by:

\[
\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)
\]

(2.1)

This relation can be used to derive equations for the displacement of a point due
to a dislocation, and thus the displacement of the boundary due to a system of dislocations can be calculated. These equations have been derived for hexagonal anisotropic materials, such as graphite, by Hirth and Lothe. The displacement equations in the $x$ and $y$ directions for a point, due to a dislocation in an anisotropic material are:

**displacement in $x$,**

$$u_x = -\frac{b_x}{4\pi} \left( \tan^{-1} \frac{2xy\lambda \sin \phi}{x^2 - \lambda^2 y^2} + \frac{\bar{c}_{11}'^2 - \bar{c}_{12}'^2}{2\bar{c}_{11}' \bar{c}_{66}' \sin 2\phi \ln \frac{q}{t}} \right)$$

$$- \frac{b_y}{4\pi \lambda \bar{c}_{11}' \sin 2\phi} \left[ (\bar{c}_{11}' - \bar{c}_{12}') \cos \phi \ln q t - (\bar{c}_{11} + \bar{c}_{12}) \sin \phi \tan^{-1} \frac{x^2 \sin 2\phi}{\lambda^2 y^2 - x^2 \cos 2\phi} \right]$$

(2.2)

**displacement in $y$,**

$$u_y = \frac{\lambda b_x}{4\pi \bar{c}_{11}' \sin 2\phi} \left[ (\bar{c}_{11}' - \bar{c}_{12}') \cos \phi \ln q t - (\bar{c}_{11} + \bar{c}_{12}) \sin \phi \tan^{-1} \frac{y^2 \lambda^2 \sin 2\phi}{x^2 - \lambda^2 y^2 \cos 2\phi} \right]$$

$$- \frac{b_y}{4\pi} \left( \tan^{-1} \frac{2xy\lambda \sin \phi}{x^2 - \lambda^2 y^2} - \frac{\bar{c}_{11}'^2 - \bar{c}_{12}'^2}{2\bar{c}_{11}' \bar{c}_{66}' \sin 2\phi \ln \frac{q}{t}} \right)$$

(2.3)

where in both equations $b_x$ and $b_y$ are the $x$ and $y$ components of the Burgers vector of the dislocation, $x$ and $y$ are distances from the dislocation axis and $c'_{ij}$ values are elastic constants where $i$ and $j$ denote the crystal direction along which the constant is measured. The prime indicates that the constants used are oriented such that the 3 direction coincides with the dislocation axis. $\bar{c}_{11}'$ is the average elastic constant along the basal plane, given by the equation $\bar{c}_{11}' = \left( c_{11}' c_{22}' \right)^{1/2}$. The remaining quantities are given as follows: $\lambda = \left( \frac{c_{11}'}{c_{22}'} \right)^{1/4} = 2.3$, $\cosh 2\delta = \frac{\bar{c}_{11}'^2 - \bar{c}_{12}'^2 - 2\bar{c}_{11}' \bar{c}_{66}'}{2\bar{c}_{11}' \bar{c}_{66}'} = 19.4$ and $\phi = \frac{1}{2} \cos^{-1} \frac{c_{12}'^2 + 2c_{12}' c_{66}' - c_{11}'}{2\bar{c}_{11}' \bar{c}_{66}'}$.

The unrotated constants from Cousins and Heggie will be used in this thesis. The values can be seen in Table 2.1.

Simply substituting these values for the elastic constants into the equations we see that $2c_{66}' + c_{12}' - c_{11}' < 0$ which causes the angle $\phi$ to evaluate to a complex angle.

The following substitutions from Hirth and Lothe are made to reduce the complex components to real expressions:
Table 2.1.: The elastic constants for graphite, as published in Cousins and Heggie

| $c'_11 = c_{11} =$ | 1060 GPa |
| $c'_22 = c_{33} =$ | 36.5 GPa |
| $c'_12 = c_{13} =$ | 7.9 GPa |
| $c'_66 = c'_44 = c_{44} =$ | 5.05 GPa |

\[
\begin{align*}
\cos 2 \phi &= - \cosh 2 \delta \\
\sin 2 \phi &= i \sinh 2 \delta \\
\cos \phi &= i \sin \delta \\
\sin \phi &= \cosh \delta \\
q^2 &= x^2 + y^2 \lambda^2 + 2i2 \sinh \delta \\
\tilde{t}^2 &= x^2 + y^2 \lambda^2 - 2i2 \sinh \delta \\
\ln \frac{q}{\tilde{t}} &= i \tan^{-1} \frac{2xy\lambda \sinh \delta}{x^2 + y^2 \lambda^2 \sinh^2 \delta} \\
\tan^{-1} ia &= \frac{1}{2i} \ln \frac{1-a}{1+a}
\end{align*}
\]

where $a$ is real, $x, y, \phi, \lambda$ and $\delta$ are as defined previously.

These equations have been published in more depth in Young et al. which is reproduced in Appendix B.

Lehto and Oberg have developed a simple formula to measure the expansion of a material when a dislocation dipole is inserted. They state that the expansion of a material due to the introduction of a prismatic dipole should be equal to $bW/L$, where $b$ is the Burgers vector of the dislocations, $W$ is the width of the dipole and $L$ is the width of the material. This equation will be used as a point of comparison between the expansion given in the modelling in this thesis and the predicted expansion based on this relationship.

2.1.6. Dislocation Energies

A dislocation in an infinite continuum will have infinite energy and so it is convenient to measure the energy of the dislocation in a finite section of material. The core of a dislocation cannot be well represented by an elastic continuum. For these two reasons the convention is to measure the energy stored in the elastic continuum in a cylinder.
Figure 2.6.: This diagram shows the cylinder drawn around an edge dislocation over which the energy is summed. The line of the dislocation runs along \( z \) and it has a Burgers vector \( b \). The so-called self energy is calculated for the shaded outer cylinder (radius \( r_1 \)) as the energy of the core (radius \( r_0 \)) cannot be calculated by classical elasticity theory.

around the dislocation line. Figure 2.6 shows a cylinder of material containing an edge dislocation. The dislocation line runs perpendicular to the Burgers vector, \( b \), in this figure parallel to the \( z \)-axis. The cylinder of radius \( r_0 \) surrounding the dislocation line is the core of the dislocation. The self energy of the dislocation is the energy stored in the outer cylinder, radius \( r_1 \).

The total energy of the system is made up of the self energy and core energy of each dislocation along with the interaction energy of each dislocation with every other dislocation in the continuum,

\[
E_{\text{total}} = E_{\text{self}} + E_{\text{interaction}} + E_{\text{core}}
\]  

(2.4)

The self energy per unit length of the dislocation is given by:

\[
E_{\text{self}} = \frac{K_e b^2}{2\pi} \left( \ln \frac{R_d}{R_c} - 1 \right)
\]

(2.5)

where \( K_e \) is the energy coefficient for graphite which depends on the elastic constants of the material, \( b \) is the Burgers vector of the dislocation, \( r_0 \) is the core radius of the dislocation and \( r_1 \) is the radius within which the energy is calculated as indicated on Figure 2.6.
The interaction energy per unit length between two parallel dislocations is given by:

\[ E_{12} = \frac{K_e}{2\pi} b_1 b_2 \left( \ln \frac{R}{R_a} - \cos^2 \theta \right) \]  

(2.6)

where in this case \( b_1 \) and \( b_2 \) are the Burgers vectors of each dislocation, \( R \) is the separation between the dislocations \( \theta \) is the angle subtended between the line connecting the dislocations and one of their glide planes.

Both of these equations take the anisotropy of the graphite into consideration within the energy factor, \( K_e \). \( K_{ex} \) and \( K_{ey} \) are used for the \( x \) and \( y \) directions respectively. These coefficients are given by:

\[ K_{ex} = \left( c'_{11} + c'_{12} \right) \left[ c'_{44} \left( c'_{11} - c'_{12} \right) \right]^{1/2} \]  

(2.7)

\[ K_{ey} = \left( c'_{11} + c'_{12} \right) \left[ c'_{44} \left( c'_{11} + c'_{12} + 2c'_{44} \right) \right]^{1/2} \]  

(2.8)

where the \( c'_{ij} \) values are elastic constants described earlier. Again these constants are transformed so that the line direction (in a basal direction) is \( z \). In the case of graphite \( K_{ex} \approx 71 \text{ GPa} \) and \( K_{ey} \approx 13 \text{ GPa} \).

### 2.1.7. Forces on Dislocations

Dislocations can be mobile in the material and can move by both glide or climb. Dislocation glide is a conservative motion where the dislocation moves along a set of glide planes in the crystal. For example in the case of a basal edge dislocation in graphite the glide plane is parallel to the basal planes. It is well known that glide can occur along this localised plane due to the weak bonding between basal planes. The glide plane normal is given by the cross product of the axis and the Burgers vector. For screw dislocations this is undefined and so they can move on a number of different planes (cross-slip). Dislocation climb requires the dislocation to pick up or deposit material into the crystal. This is usually mediated by point defects in the form of emission or absorption of vacancies or interstitials. Basal dislocations are able to glide very easily and the direction they move within their glide plane will depend
on the net force on them.

The force on a dislocation due to the other dislocations in a system can be calculated and used to determine how the dislocation will move.

The force per unit length on a dislocation as a result of an existing straight, parallel dislocation is given by \( F = \sigma_{ij}b_j \), where \( b \) is the Burgers vector of the dislocation in question and \( \sigma_{ij} \) is the stress in the material due to the first dislocation, \( \sigma_{ij} = c_{ijkl}\varepsilon_{kl} \).

For the force on a dislocation due to an existing basal dislocation \( \sigma_{xy} \) is used and for the force on a dislocation due to a prismatic dislocation \( \sigma_{yy} \) is required. Equations for these stresses in an anisotropic material are given by Hirth and Lothe\(^{47} \) as:

\[
\sigma_{xy} = \frac{Mb_x c'_{66}}{2\pi\rho^4} \left(-x^3 + \frac{e'_{11} y}{c'_{22}}x^2 \right) + \frac{Mb_y c'_{66}}{2\pi\rho^4} \left(-x^2 y + \frac{e'_{11}}{c'_{22}}y^3 \right)
\]

\[
\sigma_{yy} = \frac{Mb_x c'_{66}}{2\pi\rho^4} \left(-x^2 y + \frac{e'_{11}}{c'_{22}}y^3 \right)
\]

\[
-\frac{Mb_y}{2\pi\rho^4 e'_{11}} \left[ \left(e'_{11} - e'_{12}\right) \left(e'_{11} + e'_{12} + 2e'_{66}\right) - e'_{11} c'_{66} \right] x y^2 + c'_{22} c'_{66} x^3
\]

In these equations \( M \) and \( \rho^4 \) are given by:

\[
M = \left(\frac{e'_{11} + e'_{12}}{c'_{22} c'_{66} \left( e'_{11} + e'_{12} + 2e'_{66}\right)} \right)^{1/2}
\]

\[
\rho^4 = x^2 + \frac{e'_{11} y^2}{c'_{22}} \left( e'_{11} + e'_{12} \right) \left( c'_{11} - c'_{12} - 2c'_{66}\right) x^2 y^2
\]

In our case we need to calculate the force due to dislocations with either \( b_x = 0 \) (prismatics) or \( b_y = 0 \) (basals), so we find that in each case terms cancel out, such that the force on a dislocation, 2, due to a dislocation, 1, in each case is as follows. Force on a basal dislocation due to another basal dislocation, \( b_{1y} = 0 \):

\[
F = \sigma_{xy} b_2 = -A1A7 b_1 b_2 \frac{y \left(x^2 - A2 y^2\right)}{\left(\left(x^2 + A2 y^2\right)^2 + A3 x^2 y^2\right)}
\]
Force on a basal dislocation due to a prismatic dislocation, \( b_1 x = 0 \):

\[
F = \sigma_{xy} b_2 = -A1A7b_1 b_2 \frac{\left( x \left( x^2 - A2y^2 \right) \right)}{\left( x^2 + A2y^2 \right)^2 + A3x^2 y^2}
\] (2.14)

Force on a prismatic dislocation due to a basal dislocation, \( b_1 y = 0 \):

\[
F = \sigma_{yy} b_2 = -A1A7b_1 b_2 \frac{\left( x \left( x^2 - A2y^2 \right) \right)}{\left( x^2 + A2y^2 \right)^2 + A3x^2 y^2}
\] (2.15)

Force on a prismatic dislocation due to another prismatic dislocation, \( b_1 x = 0 \):

\[
F = \sigma_{yy} b_2 = -A1b_1 b_2 \frac{\left( A4xy^2 + A5x^3 \right)}{\left( A6 \left( x^2 + A2y^2 \right)^2 + A3x^2 y^2 \right)}
\] (2.16)

In these equations the constants are:

\[
A1 = M = 14.79 \text{ Pa}^{3/2},
\]

\[
A2 = \frac{c_{11}}{c_{22}} = 5.47,
\]

\[
A3 = \frac{c_{11}' - c_{12}'}{c_{22}' a (c_{11}' + c_{12}' + 2c_{66}')} = 1.97 \times 10^{11} \text{ Pa}^{-2},
\]

\[
A4 = \left( c_{11}' - c_{12}' \right) \left( c_{11}' + c_{12}' + 2c_{66}' \right) - c_{11}' c_{66}' = 3.53 \times 10^{22} \text{ Pa}^2,
\]

\[
A5 = c_{22}' c_{66}' = 1.843 \times 10^{20} \text{ Pa}^2,
\]

\[
A6 = 2\pi c_{11}' = 1.238 \times 10^{12} \text{ Pa},
\]

and \( A7 = \frac{c_{66}'}{2\pi} = 8.037 \times 10^8 \text{ Pa} \).

As previously \( b_1 \) and \( b_2 \) are the magnitudes of the Burgers vectors of the two dislocations, and \( x \) and \( y \) are the separation distances in \( x \) and \( y \) respectively.

Note that the equations for the force on a prismatic due to a basal and a basal due to a prismatic are equal, which would be expected from equality of action and reaction.

These force equations give an attraction between oppositely signed Burgers vectors and repulsion of same signed Burgers vectors. This can be seen in Figure 2.7 where parallel dislocations with Burgers vectors in the same direction repel each other and parallel dislocations with oppositely signed Burgers vectors will attract each other. The maxima and minima on the graph (Figure 2.7) give stable configurations of dislocations at 0° and 45° to each other as shown in Figure 2.8.

The net force on each dislocation can be found by the sum of the forces on it from each of the other dislocations in the system.
Figure 2.7.: The force per unit length between two dislocations of like (gold line) and unlike (navy line) dislocations, showing repulsion of like dislocations and attraction of unlike dislocations with stable points at 45° i.e. where \( x = y \).

Figure 2.8.: Stable configurations of two dislocations. a: oppositely signed dislocations with a stable position at 45° to each other. b: same signed dislocations with a stable position at 45° to each other. c: dislocations with a stable position directly above the other.
Screw dislocations are not discussed in this thesis but are fully covered in the literature.52-56

2.1.8. Stresses on dislocations

Dislocations in a crystal will feel an additional force on them if there is an applied stress on the crystal. This applied stress will act on all dislocations within the crystal and introduces a force on the dislocation. The full tensor equations can be reduced to a very simple scalar equation by a considered choice of axis definition with respect to Burgers vector, $F = \sigma b$ where $\sigma$ is the stress in Pascals and $b$ is the Burgers vector of the dislocation in metres. The following section will derive the equations for the forces on a dislocation with different applied stresses. Here the axes definition has been chosen such that the edge dislocation line runs along the $z$ axis, with the basal plans parallel to $z$ and $x$.

In order to establish which stresses will effect the a dislocation it is useful to consider the stresses as a matrix of nine components, representing all possible crystallographic directions.

$$\sigma_{ij} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

The directions of these stresses can be seen in Figure 2.9. It can be seen that the tensional stresses are given by the components $\sigma_{ij}$ where $i = j$ and shearing stresses are given in the cases where $i \neq j$.

In the case of basal dislocations the Burgers vector has only an $x$ component and is given by the matrix

$$b = b \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$
The force on a dislocation as a result of an applied stress can be written in full vector form as:

\[ \mathbf{F} = -\sigma_{ij} \mathbf{n}_j \mathbf{b}_i \]

where \( \sigma_{ij} \) is the matrix of the applied stress as defined above, \( \mathbf{n} \) is a unit vector normal to the Burgers vector, this represents the line direction of the dislocation, and \( \mathbf{b}_i \) is as usual, the Burgers vector.

In this program the line direction of both prismatic and basal dislocations is parallel to the \( z \) axis and so \( \mathbf{n} \) is given by the matrix

\[
\mathbf{n} = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix}
\]

Multiplying the matrices we find that

\[
\mathbf{F} = -b \begin{bmatrix} \sigma_{xy} & \sigma_{xx} & 0 \end{bmatrix}
\]

This means that there are only two components of applied stress which will introduce an additional force on the dislocation. \( \sigma_{xy} \) will introduce a force on a basal dislocation in the \( x \) direction, parallel to the dislocation glide plane. \( \sigma_{xx} \) will introduce a force acting in the \( y \) direction, perpendicular to the glide plane, encouraging the dislocation to move in a climb direction. None of the nine directions of applied stress will lead to a force in the \( z \) direction.

In graphite the prismatic dislocations are essentially immobile and so the applied stress is unlikely to have an effect on the dislocation, however for completeness the same methodology can be applied to the prismatic dislocation to establish which applied stresses would give a component to the force.

The prismatic dislocations have a Burgers vector given by

\[
\mathbf{b} = b \begin{bmatrix} 0 & 1 & 0 \end{bmatrix}
\]
Figure 2.9.: A simple diagram showing the direction of the nine stress components, $\sigma_{ij}$ where $i$ and $j$ are $x$, $y$ or $z$.

Figure 2.10.: A simple diagram showing the orientation of a basal dislocation in the 2D-DD program. The Burgers vector runs parallel to $x$ and the line of the dislocation parallel to $z$. 
Multiplying the matrices we see that the components of force on the dislocation as a result of an applied stress is given by

\[ \mathbf{F} = -b \begin{bmatrix} \sigma_{yy} & \sigma_{xy} \\ \sigma_{xy} & 0 \end{bmatrix} \]

This shows that the two components of stress which result in a force component on the prismatic dislocation are \( \sigma_{yy} \) and \( \sigma_{xy} \) in the \( x \) and \( y \) directions respectively. Again there is no applied stress which leads to a force component in the \( z \) direction, parallel to the dislocation line.

It can be useful when working with dislocations to consider the stress introduced into a crystal as a result of the dislocation. Figure 2.11 shows the long range shape and direction of the stress in an isotropic crystal due to single dislocations. This diagram shows the theoretical regions of positive and negative stresses due to a single edge dislocation with the dislocation line running into the page at the origin of the axes.

This thesis has replicated the behaviour shown here for basal edge dislocations in graphite which can be seen in Section 3.3 on page 80.

The existence of dislocations in graphite is not a new idea and there are several
key concepts which have been explored over the years. Some of these are outlined in the following section.

### 2.2. Dislocations in Graphite

This section describes the historical observations of dislocations in irradiated nuclear graphite along with a number of models which have been used to conceptualise dislocations in graphite and other materials.

#### 2.2.1. Historic observations of dislocations in graphite

Study of the structure of graphite became popular in the late 1950’s with studies such as that of Dawson and Follett\(^5^8\) in 1959. In their paper Dawson and Follett described their investigation of defects in synthetic graphite, they included electron microscopy images of dislocations by means of looking at the Moiré patterns of their samples. A section of one of their microscopy images, containing a non-basal dislocation, can be seen in Figure 2.12.

Moiré patterns are hexagonal patterns which are produced when two layers of graphite are displaced by a small relative rotation angle. These patterns are still used today to observe the structure of graphitic systems. A recent example is work by
Figure 2.13: This Moiré pattern arises due to a basal dislocation creating a stacking fault in a bilayer graphene sample. $l_W$ shows the line direction of the dislocation and $D$ is the vector connecting the two sides of the wrinkle.

Cosma et al., who used Moiré patterns to observe the presence of dislocations in few layer graphite. Figure 2.13 shows a Moiré superlattice resulting from a basal dislocation in a bilayer graphene structure.

Bacon and Warren were also studying graphite in the late 1950’s and carried out x-ray diffraction measurements on graphite. Their studies found that there were prismatic loops in the irradiated graphite which appear to form at large distances from pre-existing loops. They also noted that there was a temperature dependence on the amount of damage in the irradiated graphite; graphite irradiated at room temperature was seen to contain about three times more damage than graphite irradiated at 150°C.

Over the following few years there were many more studies of defects in graphite using transmission electron microscopy (TEM). Amelinckx and Delavignette observed basal dislocations in graphite, reporting that the basal dislocations were seen to split into two partial dislocations, separated by a stacking fault. They described these dislocations as extremely mobile along the basal plane. This was later confirmed by theoretical calculations by Telling and Heggie who showed that the Peierls stress is effectively zero.

Likewise Izui and Fujita used TEM to view the moire patterns produced by their
graphite samples. In their papers they outlined four fundamental types of dislocations which can be present in graphite: basal edge and screw dislocations, non-basal edge dislocations, prismatic edge dislocations and non-basal screw dislocations. This thesis focuses on the basal edge dislocation (extra material in the basal plane of the material) and the prismatic edge dislocation (extra material parallel to the basal plane, e.g. prismatic loops and ribbons). Schematic representations of these four dislocation types can be seen in Figure 2.14 as presented by Izui and Fujita, where images c.) and d.) are the dislocation types contained within this thesis.

In 1969, Thrower published an extensive report of TEM studies of irradiated graphite. Figure 2.15 shows the evolution of graphite irradiated at 100°C at increasing doses ($4 \times 10^{16}$ neutrons cm$^{-2}$ to $8 \times 10^{17}$ neutrons cm$^{-2}$). These images show the basal dislocations becoming more curved with increasing dose until closed loops were formed at very high doses ($8 \times 10^{17}$ neutrons cm$^{-2}$).

The standard model of irradiation damage in graphite, described in the previous chapter, relies on the formation of interstitial loops in the crystal. These loops have been observed experimentally and their size is seen to depend on the temperature at which the irradiation occurs. Figure 2.16 is reproduced from Reynolds and Thrower and shows the radius of interstitial loops for a range of irradiation temperatures as the temperature of the sample increases. In each irradiation temperature the loops are seen to anneal when the temperature becomes high enough, with larger interstitial loops requiring a higher anneal temperature.

This graph gives an interstitial loop radius of the order 10 nm for graphite irradiated at 650°C, an upper limit for the temperature in the core of an AGR.
Figure 2.15.: This series of images is taken from Thrower\textsuperscript{33} and shows the evolution of defects in graphite irradiated at 100 °C at the following doses: \textbf{a.} $4 \times 10^{16}$ neutrons cm$^{-2}$, \textbf{b.} $8 \times 10^{16}$ neutrons cm$^{-2}$, \textbf{c.} $2.6 \times 10^{17}$ neutrons cm$^{-2}$ and \textbf{d.} $8 \times 10^{17}$ neutrons cm$^{-2}$.
Figure 2.16.: Graph of the radius of interstitial loops in graphite irradiated at a range of temperatures for increasing annealing temperature. Reproduced from Reynolds and Thrower.\textsuperscript{64}
2.2.2. Conceptual models of dislocations

A number of theoretical models can be used to conceptualise dislocations in a material. Over the years these models have been used to simplify calculations and aid in our understanding of the effect dislocations have on a crystal lattice.

The Frenkel-Kontorova model

The Frenkel-Kontorova model was introduced in 1938 and can be used to describe a range of physical concepts, in particular dislocations.

This model begins by approximating the atoms below the dislocation slip plane, shown in Figure 2.2, as an elastic continuum. The potential of the lower portion of the crystal can then be represented by a sinusoidally oscillating potential. The atoms in the layer above the slip plane can then be considered as a series of balls connected by springs. In a perfect graphite crystal with no dislocation this model gives a series of balls in the bottom of their corresponding potential wells. This is drawn schematically in diagram a.) of Figure 2.17.

As the C-C bond is a very strong bond these springs can be hypothesised to be very stiff and difficult to stretch or compress. However the potential wells are notably very shallow with respect to the spring length. This makes it possible to introduce dislocations to the material.

To consider a dislocation in the Frenkel-Kontorova model there must be either too many balls in a potential well or a well with no balls. A well containing no balls represents a basal edge dislocation with an extra half plane in the material below the slip plane, diagram b.) of Figure 2.17. In order to accommodate this the surrounding balls must be pulled slightly inwards away from their minimum energy position at the bottom of their well.

A well containing two balls represents a basal edge dislocation where the extra half plane of the material is above the dislocation slip plane, diagram c.) in Figure 2.17. In order to accommodate two balls in one well the surrounding balls must be pushed out of their minimum energy position at the bottom of their well.

The fact that in this model of graphite the springs are very stiff means that there are many atoms to each side of the dislocation which are displaced from their minimum energy position. This idea can be used to conclude that the core of a dislocation in
Figure 2.17.: Schematic diagrams of the Frenkel-Kontorova model of dislocations (represented by the gold T shapes) in graphite. a.) perfect graphite, atoms in the layer below are represented with an oscillating potential and the atoms in the layer are represented by a ball sitting in each potential well and connected to its neighbours with a stiff spring. b.) a basal edge dislocation in graphite showing a potential well without an atom and displaced atoms on either side of the dislocation core. c.) an oppositely signed basal edge dislocation where there are two atoms in the same potential well, again atoms to each side of the core are displaced to accommodate the dislocation.

Graphite must be very wide. In fact, Telling and Heggie estimate the core width to be just over 4 nm.\textsuperscript{61}

Despite the Frenkel-Kontorova model being quite historic in dislocation theory it is still held in high regard today as both a conceptual and a research tool. The model even forms the basis of papers which have been published as recently as 2015, for example to theorise on the propagation and interaction of edge dislocations (in particular kinks).\textsuperscript{66}

**Peierls-Nabarro model**

A proposal by Peierls in 1940\textsuperscript{67} and further work by Nabarro in 1947\textsuperscript{68} has led to the well accepted Peierls-Nabarro model of dislocations.

The Peierls-Nabarro model begins by assuming that the regions of the crystal above and below the glide plane can be modelled with classical elasticity theory. The region of the crystal where elasticity theory cannot be applied is localised to a single plane separating the two regions of continuum (see Figure 2.2 where the two regions of elasticity are separated by the glide plane, represented by the dashed black line).
From this theory Peierls developed an equation for the force required for a dislocation to move along its glide plane. The force required depends on the Burgers vector (size of the dislocation), the dislocation core width and the physical properties of the material; shear modulus, Poisson ratio and the lattice vectors of the crystal. The force required to move a dislocation is shown to be proportional to $e^{-2\pi W b}$, where $W$ is the width and $b$ is the Burgers vector, from this we can see that dislocations with a wide core are able to glide with a much lower force.

It is likely that the core of the basal edge dislocation in graphite will therefore be very wide as it is known that the dislocations are able to glide with virtually no applied force.\textsuperscript{61}

### 2.2.3. Effect of dislocations on the value of $C_{44}$ in graphite

Basal dislocations have an effect on the elasticity of the graphite, altering the value of $C_{44}$. The value of $C_{44}$ is seen to be an order of magnitude lower for unirradiated samples containing basal dislocations.\textsuperscript{61} This is thought to be due to the glide of basal dislocations within the crystal. These dislocations glide freely and as such their movement is reversible until the graphite is irradiated and a distribution of pinning points is introduced which prevents their glide.\textsuperscript{36}

### 2.3. Basal dislocation dipoles in bilayer graphene

As shown in Figure 2.5 a basal dislocation introduces a stacking fault into a graphite system. The stacking fault energy of AB stacked graphite has previously been investigated by Telling and Heggie.\textsuperscript{61} As the graphite is sheared in the armchair direction the stacking fault energy is seen to go through a maximum at a displacement of 0.071 nm and another larger maximum at 0.282 nm where the graphite is in AA stacking. An understanding of the stacking fault energy in bilayer graphene is useful to aid in understanding the energy stored in a basal dislocation. A basal dislocation causes a shift in stacking equal to its Burgers vector, in this case 0.142 nm, one bond length. This has the effect of translating the stacking of the bilayer from AB to AC. Figure 2.18 shows the difference between AB and AC stacking. Across the core of the dislocation the structure could be divided into small finite sections where the stacking
2.3.1. Review of dislocated bilayer graphene literature

There has been a lot of work in the early 2010s using molecular dynamics to investigate defected bilayer graphene. Defected bilayer graphene is a useful structure to consider as it will display similarities to defected graphite but with far fewer atoms. This allows for much faster computational times and will allow for a better understanding of basal dislocations to allow graphite systems to be constructed which are closer to their optimum energy positions, and hence should be faster to optimise.

Butz et al. have carried out molecular dynamics calculations on a dipole of 60° basal dislocations in bilayer graphene. The dislocations modelled have an edge component of their Burgers vector of half a lattice constant each and equal magnitude but oppositely signed screw components such that the net screw component is zero and the total slip across the cell is one lattice vector. These simulations contain of the order of ≈1500 atoms. The method used is a classical molecular dynamics with an additional registry dependent interatomic potential as described by Kolmogorov and Crespi (KC).

This registry-dependent interlayer potential was developed specifically for graphitic
Figure 2.19.: Graph of the stacking fault energy for AB graphite sheared in the armchair direction showing a maximum stacking fault energy of 7.25 meV Å$^{-2}$ at the point where the stacking is AA. Reproduced from Telling and Heggie$^{61}$
systems as existing potentials were insufficient. One method of modelling graphite is to add a Lennard-Jones (LJ) type interaction such as that used by Lee et al. in a study on carbon based structures\textsuperscript{74} to a reactive empirical bond order REBO) potential.\textsuperscript{75} The Lennard-Jones type potential alone does a good job of describing the interplane cohesion however cannot describe the variations in the alignment of the neighbouring planes. The REBO potential is another classical potential which attempts to model graphitic systems however there are no dispersion or non-bonded repulsion terms which means that the REBO potential is not ideal for graphitic systems.\textsuperscript{76}

A combination of LJ and REBO potentials have been implemented in the adaptive intermolecular reactive empirical bond order (AIREBO) potential\textsuperscript{76} however this leads to the measurement of $C_{44}$ being an order of magnitude too small. Zheng et al.\textsuperscript{77} reported a value of 0.1783 GPa compared to the experimental result of 4.5 GPa found by Kelly.\textsuperscript{36} Work by Kelly and others has shown that any interaction which was given only by a vector connecting two atoms could not simultaneously get the values of $C_{44}$ and $C_{33}$ correct.\textsuperscript{36}

The KC potential, used in the Butz work described here, in addition to classical molecular dynamics is much more accurate than a LJ potential.\textsuperscript{73} However, empirical potentials will always contain approximations and may not always behave as one would expect. It is therefore important to know the limitations of the potential in use when compared to results from density functional theory. Latham et al.\textsuperscript{78} have completed a comprehensive study comparing DFT results to a selection of empirical potentials, including AIREBO. Work such as this can be vital in interpreting the reliability of empirical results.

The authors simulate TEM images from their optimised structures and compare these to experimental TEM images of basal dislocations in bilayer graphene. From these TEM images the authors determine that the bilayer structure is buckled by the inclusion of basal dislocations and that this buckling acts to accommodate the strain introduced by the dislocations. The TEM images, both experimental and theoretical, have been reproduced in Figure 2.21 where TEM images for flat and buckled structures are compared to the experimental images to conclude that the experimental samples must be buckled. The magnitude of this buckling is measured to be 0.92 nm. Their image of the buckled bilayer can be seen in Figure 2.20
Figure 2.20: The buckled dislocated bilayer optimized using molecular dynamics by Butz et al. This image is reproduced from their 2013 paper. 

[Image of the buckled dislocated bilayer]
Figure 2.21.: This image reproduced from Butz et al. shows the comparison of theoretical and experimental TEM images of dislocations in bilayer graphene. The second differential of the TEM image is used to argue that the experimental bilayer must be buckled as a result of the basal edge dislocations.
Similar work on defected bilayer structures by Lin et al. measured the width of the stacking fault from AB to AC stacking. Large regions of AB and AC stacking are observed by TEM, a false colour image of these stacking regions can be seen in Figure 2.22 reproduced from their paper. Again this paper employs molecular dynamics to optimise their atomic structures and compares the result to experimental TEM images. This paper has found the width of the stacking transition, or basal dislocation, to be approximately 10 nm, as shown in Figure 2.23 from the same paper and again the authors observe delamination of the basal planes. This value for the core width of the dislocation is confirmed by Alden et al. who measure the width of the boundary between AB and AC stacking in dark field (DF) TEM images for both shear and tensile boundaries (screw and edge dislocations respectively). They measure the widths to be approximately 6 nm for the screw dislocation and 10 nm for the edge dislocation. However Gong et al. have studied stacking faults in few layer graphene using Raman spectroscopy and have estimated the width of a partial basal dislocation to be much larger, of the order of 40 nm, significantly wider than otherwise reported in the literature. They also report a partial dislocation separation distance of 35 nm giving a total width of the partial dislocation dipole and stacking fault region of 115 nm.

Figure 2.22.: A false colour microscopy image of AB and AC stacking regions in bilayer graphene where the sections of bilayer graphene are coloured in yellow and blue. This image is reproduced from Lin et al.
While these studies are informative, none used a full density functional theory calculation to measure the width of the dislocations and so there is room for a far more accurate calculation to be completed, such as the calculations reported in this thesis (see Chapter 4). It is also worth considering that in graphite the layers surrounding those which contain dislocations will act to hold the basal planes together and as such this layer buckling will be far more difficult.

### 2.4. Non-basal dislocations

There is also a potential for dislocations to be introduced within the planes of the graphite. These are non-basal dislocations and have a dislocation line perpendicular to the basal plane and Burgers vector parallel to the plane. These non-basal dislocations could manifest in defects such as the Stone-Thrower-Wales defect\(^{33,79}\) (where a bond rotation creates a pair of 5-7 rings) or more simply a dipole as a result of a reconstructed vacancy line. Research into non-basal dislocations in graphene has resulted in a huge number of publications over recent years, particularly notable is the work from Jamie Warner and colleagues.\(^{80-86}\)

Non-basal dislocations in the form of vacancy coalescence into vacancy lines in graphene have been of particular interest to other members of this research group. Dr Trevethan has led work to investigate the dynamics of vacancies in graphene. Further details of this research can be found in his papers.\(^{87,88}\)

Owing to the rotational symmetry of graphene, there are three identical glide
Figure 2.24.: These images show the six different vacancy lines which upon healing form the twelve different non basal dislocations. The dislocations are drawn as a dipole of oppositely signed dislocation. Diagrams a.-c. show the three orientations of $V_6$ armchair vacancy lines and diagrams d.-f. show the three orientations of $V_6$ zig-zag vacancy lines which collapse to form the dislocations indicated by the gold T shapes.

planes at $120^\circ$ to each other through the lattice for both zig-zag and armchair sheet orientations. This gives twelve possible non-basal edge dislocations in a graphene sheet. These twelve non-basal dislocations can be seen in their oppositely signed pairs in Figure 2.24.

These vacancy lines collapse into a lower energy reconstructed state where the core of the dislocations are 5-7 or 5-8 defects for the glide and shuffle dislocations respectively. The atomistic representation of the dislocations can be seen in Figure 2.25 reproduced from Ewels et al.\textsuperscript{89} The glide dipole moves through the sheet by the rotation of a carbon bond. The isolated dislocation core was not studied in the paper, but rather the formation of the Stone-Wales (SW) defect, which is an intimate glide dipole of non-basal dislocations. The activation energy required for this is reported to be quite high at 7.6 eV making it relatively immobile compared to the shuffle dislocation, which is 2.2 eV in the forward direction and 0.7 eV backwards, removing the SW defect.\textsuperscript{89}
2.5. Collective Behaviour of Dislocations

Dislocations in a system will interact with each other and their behaviour is affected by those around them. This section discusses the effects of a large number of dislocations on a material. This begins with the extreme cases when dislocation density is so high that the long range order of the crystal becomes lost, analogous to the crystal melting. The effect of highly mobile basal dislocations is then discussed followed by a discussion of basal and prismatic equivalence.

2.5.1. Crystal Melting

If the density of dislocations in a material becomes high enough that the introduction of a new dislocation dipole releases energy, rather than costing energy, the material becomes mechanically unstable. For each dipole which is introduced strain in the crystal increases (as can be seen by the Lehto-Oberg formula), this is analogous to the material yielding. However, the long understood limitation to this theory of melting, is that melting occurs when the free energy of the liquid and of the solid are equal. The implication of this is that a theory which ignores the liquid phase is unlikely to be correct. This mechanism has been explored and verified by Lin et al. who have carried out Monte Carlo simulations of two dimension melting.90

Kosterlitz and Thouless91,92 developed a theory of two dimensional melting in the 1970’s which stated that in a solid the disappearance of long range order represents a transition to a fluid. This work was based on an earlier theory of dislocation mediated melting by Nabarro in 1967.93 Halperin and others have since expanded on this concept stating that the long range order of a crystal is destroyed by a...
concentration of dislocations which tends to zero as the temperature tends to the melting temperature of the material.\textsuperscript{94–96} A more recent related work by Burakovsky et al.\textsuperscript{97} brought to light a proposal for dislocation mediated melting. In this case a material is considered melted when half of the atoms in the material are located within a dislocation core. They found that the point at which a material had melted could be related to the density ($\rho$) of dislocations with Burgers vector, $b$, as

$$\rho = \frac{0.6}{b^2}. \quad (2.17)$$

The authors have since published a paper stating that this equation is accurate for at least half of the periodic table.\textsuperscript{98} This equation predicts that two dimensional graphite containing partial prismatic dipoles with Burgers vector $b = 0.332 \text{ nm}$ (prismatic loops) should melt at a dislocation density of $5.4 \times 10^{18}$ dislocations per m$^2$.

### 2.5.2. Kink Bands

From the equations of force exerted on a dislocation by other dislocations in an elastic continuum discussed in Section 2.1.7 there are certain positions which have a lower overall total energy. For systems containing a large number of dislocations long range patterns become apparent in the positions of the dislocations. Frank and Stroh\textsuperscript{99} published the concept of kink-bands in 1952 where they describe a ‘thin plate of sheared material... bounded by opposite tilt walls of dislocations’. Since then more modern research has continued to look into kink bands, in particular Barsoum et al.\textsuperscript{100} describe the formation of kink bands specifically in damaged graphite. These are bands of basal dislocations which form alternating walls through the crystal. These walls of dislocations cause bending of the basal planes of the graphite as depicted by the schematic diagram shown in Figure 2.26.

Barsoum et al. subject single crystals of graphite to a load applied parallel to their $c$-axis and observe the formation of these bands of dislocations. The authors note that under extremely high stresses the dislocation walls are seen to be mobile. Their studies include microscopy images of the defected graphite, clearly showing the kink bands through the material. Figure 2.27 is reproduced from their paper\textsuperscript{100} and shows the bending of the basal planes.
Figure 2.26.: Schematic diagram of dislocation walls, “kinks”, such as those observed in the basal dislocation model of the 2D-DD program. The physical effect of these dislocation walls is a bending of the basal planes forming two distinct kink boundaries.

Figure 2.27.: This image shows the kink bands in indented graphite as reported by Barsoum et al.\textsuperscript{100}
These bands of basal dislocations have also been observed in theoretical modelling such as the two dimension dislocation dynamics work by Raabe. Raabe carried out two dimensional isotropic dislocation dynamics studies and has presented work showing clear walls of alternating dislocations such as those observed experimentally. A result from these two dimensional dislocation dynamics can be seen in Figure 2.28.

### 2.5.3. Basal and Prismatic Dislocation Equivalence

Basal edge dislocations in graphite are free to move along their glide planes (parallel to the graphite sheets) without resistance and interact similarly to the prismatic dislocations. Telling and Heggie described the motion of dislocations using the Peierls model, (discussed in Section 2.2) where a periodic potential opposes dislocation glide by lattice friction. The stress required to overcome this potential and move the dislocation is known as the Peierls stress which in graphite is effectively zero.

Basal dislocations on the same glide plane are able to interact constructively for same signed Burgers vectors and pile up or annihilate if their Burgers vectors are equal and oppositely signed. The piling up of same signed dislocations does require some applied stress as the dislocations will repel each other. It has been shown by
Boone\textsuperscript{102} that the in-plane stress caused by a pile up of same signed dislocations can be relieved by bending of the basal planes and delamination of the planes adjacent to the dislocation glide plane.

Recent interest in line defects in van der Waals materials has introduced the concept of \textit{ripplocations} which are line defects with both surface ripple and crystallographic dislocation character.\textsuperscript{103} Li \textit{et al.} have used empirical force fields to calculate the energy barrier of merging two of these ripplocations (Burgers vector $3\mathbf{b}$, where $\mathbf{b}$ is the lattice vector) in few layer MoS$_2$. The authors determine that same signed ripplocations are attractive, not replusive as dislocation theory predicts. The explanation for this discrepancy is given by the authors as being due to the different forms of elastic energy for few layered material in comparison to bulk materials. There is a possible explanation\textsuperscript{104} that these properties could be a result of strong core-core interactions rather than a new topological defect.

It is proposed that pileups of basal dislocations can cause defects in the crystal which result in a $c$-axis expansion analogous to the dilation observed in the standard model as a result of prismatic dislocations. From the equations for displacement due to the elastic strain of a dislocation it can be seen that for a pure edge dislocation, such as those in this program, there will be no displacement in the $c$-axis direction for dislocations with no $y$ component in their Burgers vector. This means that a single basal dislocation does not give any $c$-axis expansion according to classical elasticity theory. However if you consider the basic example of a section of bilayer graphene with fixed ends it is not difficult to imagine that if basal dislocations were added to the top layer such that their glide plane was between the layers, the extra material in the top sheet would need to be accommodated in some way. The most obvious solution for the top layer would be to buckle outwards such that the C-C bonds could remain at their fixed lowest energy bondlength as described in Heggie \textit{et al.}\textsuperscript{105} This would have the effect of increasing the thickness of the bilayer \textit{i.e.} effectively causing a $c$-axis dilation.

This simple concept could be applied to a large many layer crystal of graphite. Imagine a block of perfect single crystal graphite with fixed edges. Now introduce an increasing number of basal dislocations to a central layer. In this case the adjacent layers above and below the layer containing dislocations prevent any delamination of
the sheets however the extra material still needs to be accommodated. This is where the effect of rucking and tucking of layers described in Heggie et al. comes in.

The model proposed by Heggie et al. suggests that a high enough density of basal dislocations can result in a fold forming in the graphite. This fold occurs due to a number of small dislocations and can grow with addition of more dislocations. If the fold becomes wide enough that the rounded edges of the fold are small in relation to the width then we can approximate the fold as a ribbon of extra material. This fold can then be assumed to have the same effect on the dimensions of the crystal as a ribbon of equal width. This concept of being able to represent a defect in terms of an equivalent basal or prismatic dislocation arrangement is vital in being able to create a model of dimensional change in graphite due to basal dislocations. The equivalence of basal dislocation arrays with prismatic dislocation dipoles will be exploited in this program and the resulting c-axis expansion calculated.

Consider a hypothetical rectangular single crystal of graphite and make a horizontal cut in the centre of the block of width \(w\). Into this slit, insert a ribbon of material of equal width and height, \(h\), in the prismatic direction. One can assume that the depth of the single crystal and the ribbon of material tends to infinity. The most obvious dislocation description of this scenario is that there is a dipole of prismatic dislocations, separation \(w\) and Burgers vector \(h\) in the prismatic direction. A second description of this scenario is a dipole of superedge basal dislocations, separation \(h\) and Burgers vector \(w\) in the basal direction. This second scenario is less plausible than the prismatic description as the energy of a dislocation is proportional to the square of the energy. Despite this energy problem the second scenario can occur just from basal slip and so must also be a correct description.

An example of this basal and prismatic dislocation equivalence can be seen in Figure 2.29 where a system of basal dislocations arranged in an array on adjacent layers such that the extra material is equally well represented by a prismatic dislocation dipole. As described in an earlier thesis written by a member of this research group Dr Irene Suarez-Martinez a representation of a single basal dislocation dipole is usually ruled out as the energy of a dislocation is proportional to the square of its Burgers vector and so a single basal dislocation dipole would have an incredibly high energy due to the large Burgers vector. In order to introduce an equivalent amount of extra material
Figure 2.29.: A schematic diagram demonstrating the equivalence of basal and prismatic dislocations. 

- **a** shows a cut of width $w$ made in a block of graphite where a ribbon of material is inserted.
- **b** shows the same structure represented by a prismatic dislocation dipole, of Burgers vector $c$ and separation $w$. In these schematics dislocations are represented by the gold T shapes with the magnitude of their Burgers vector indicated by their relative size.
- **c** shows the structure in terms of an array of basal dislocations of Burgers vector magnitude $w/4$ which have moved into the material by basal slip.
it would be more realistic to consider an array of basal dislocations of smaller Burgers vector which would have an overall lower energy while still introducing the same amount of material.

In this basal dislocation model as the dislocations move and interact certain configurations can be replaced by prismatic dislocations. The paper by Heggie et al.,\textsuperscript{105} on the buckle, ruck and tuck of graphene planes, discusses in detail how it is hypothesised that basal dislocations could glide by defects and deposit extra material into these folds, causing the dilating defect to grow and the \textit{c}-axis to expand. A step by step diagram of this process can be seen in Figure 2.30. The program needs to replicate this process allowing folds to form where basal dislocations pile up. Once these folds form they should then be allowed to grow when basal dislocations glide past the defect. These basal dislocations can then climb to the next layer and continue gliding through the crystal.

These properties of dislocations can be combined into a dynamic dislocation model of irradiated graphite. The following section outlines the principle and applications of dislocation dynamics, in particular two dimensional models.
2.6. Dislocation Dynamics

The principle behind dislocation dynamics is rather like molecular dynamics where by a system of interacting bodies is considered as time evolves. In dislocation dynamics an array of dislocations in a material with given elastic properties is allowed to evolve by calculating the forces on dislocations and allowing the dislocations to move accordingly. The dislocations can be used to calculate any dimensional change of the overall material by considering the elastic strain fields generated by each dislocation and summing over all the dislocations in the system to calculate the overall displacement of the boundary of the material as a result of the dislocations.

2.6.1. Applications of Dislocation Dynamics

Two dimensional (2D) dislocation dynamics (DD) simulations using plane strain discrete dislocation plasticity have been carried out for many years and for many different aims. An early example is Ghoniem’s work in the 1980’s. Current dislocation dynamics by the same author have now advanced to simulating in three dimensions. However, there are many recent studies which still use the 2D model, for example Dickel et al., who describe dipole formation for gliding edge dislocations. There are a wide range of applications of 2D-DD. In particular thin films, single crystals under quasi-static loading and crack propagation studies. Many pieces of work assume isotropy of the crystal as a close enough approximation of the elastic strains. This cannot be the case in graphite. This work uses the anisotropic displacement equations in order to account for the vastly different elastic constants of the material; \( c_{33} = 36.5 \text{ GPa} \) whereas \( c_{11} = 1060 \text{ GPa} \). These values show that it is easier to expand in the \( c \) axis direction, separating the layers, than it is to expand along the basal plane, stretching the layers. This is not surprising given the strength of a carbon to carbon bond which is much greater than the bonds holding the layers together. For the explanation of the notation for the elastic constants \( c_{ij} \) please refer to Section 2.1.5 and the publication in Appendix B (page 119).

As previously discussed, dislocations are atomic displacements which experience a configurational force due to external stresses and internal Peach-Koehler (inter dislocation) interactions. However, this thesis does not consider that dislocations
also have an effective mass and are able to carry momentum, moving relativistically with respect to the speed of sound in the crystal.\textsuperscript{105,112,113} This effective mass effects the speed of the dislocation however this factor is not thought to be critical in understanding radiation damage processes and so the movement is treated as heavily damped and proportional to the second differential of the force on the dislocation.

The following chapter details the dislocation dynamic program which has been written to model both the standard model of dimensional change in irradiated graphite and the behaviour of basal dislocations and their potential to contribute to dimensional change.
3. Dislocation Dynamics

The theory of dislocations explained in Chapter 2 can be used to create a program which models the movement of dislocations in a system. In this case a program was written to model the evolution of a system of dislocations in graphite, with the aim of observing the dimensional changes and stored energy of the system.

This chapter explains the processes behind the program and results obtained for both a prismatic and basal dislocation model. It is useful to note that these 2D-DD models can be applied to any material with a simple substitution of elastic constants. This allows the models and concepts described here to be utilised to investigate any crystal regardless of its lattice type.

3.1. Prismatic Dislocation Model

Simulations based on a single crystal graphite rather than nuclear graphite for simplicity and proof of concept were carried out, with the aim of ensuring the program could be expanded to polycrystalline nuclear graphite with applied stress in the future. Calculations using anisotropic strain theory are not specific to individual defects and so can be applied to any dilating defect which can be represented using prismatic dislocations for example cracks or buckles. The method used is fully scalable and as such should allow large systems to be simulated comfortably with current levels of computing resources. Certain aspects of the calculations also lend themselves well to GPU (graphical processor unit) parallel programming which again strengthens the scalability of the dislocation dynamic approach.

In the current model, prismatic dislocation dipoles are introduced and the dimensional change calculated. As this is a 2D model the dislocation dipole can be considered as an infinite ribbon of extra material between the layers of graphite. It has been suggested that basal defects could be very significant in the mechanisms
of dimensional change. The hypothesis is that almost all structural change requires basal slip. This basal slip arises simply by the differential geometry between the planes of a stack of graphene layers which are bending. A simple real world example of differential geometry is where runners on an oval track are given a staggered start in order for all runners to cover the same length of track.

Basal dislocations can glide freely on their glide plane (parallel to the basal plane) with zero Peierls stress. Prismatic dislocations are more restricted, in fact they are normally sessile in graphite as their glide plane is normal to the basal plane and it has been found that the dangling bonds at the edges of the prismatic loop can form bonds to neighbouring layers further inhibiting motion, movement of the dislocations then requires the breaking of strong carbon to carbon bonds.

Despite this, loop formation does occur and does cause dimensional change, so it is worthwhile simulating the introduction of these prismatic loops, the basal slip mechanism could then act in addition to the standard model, further affecting the dimensions of the material. This arises because of the equivalence descriptions of basal defects. An example being the equivalent description of a ruck and tuck defect as a pile up of basal dislocations or a prismatic dislocation loop. Figure 3.1 shows schematics of the prismatic representations of ruck and tuck defect and a layer which has buckled into a wrinkle. As both defects can be represented using prismatic dislocations both defects will give a c-axis expansion when introduced into the two dimensional continuum.

It should be noted at this point that the energy of a dislocation is proportional to the Burgers vector squared and so the energy stored in dislocation structures may not be equivalent despite giving rise to equivalent dimensional changes. This will be covered in more depth in section 2.5.3.

Figure 3.1: Suggested schematics of the ruck and tuck defect and a wrinkled layer shown with prismatic dislocation representation with dislocations shown in navy.
It was therefore important to ensure that dislocation dynamics could produce results in agreement with the existing standard model of dimensional change using prismatic dipoles before moving on to a basal dislocation model.

3.1.1. Method

The program was written to follow the simple process illustrated in the flow diagram in Figure 3.2. It is written in C++ with a Qt user interface and CUDA for running in parallel on GPUs. The vast majority of the coding was completed during this PhD, however it start from an initial version of the program written by a previous PhD student in the group, Glen Sheehan. This preliminary version read in dislocation positions from a text file and output their positions to a new text file in addition to rendering a jpg image of the crystal. In order to increase the usability of the code a user interface was a high priority which would allow run parameters to be altered without recompiling the program. Initially input parameters are required such as how many dislocations to start with, how many iterations to carry out and how many dislocations should be added per iteration along with how many relaxation steps to allow per iteration. Following the input the program generates material boundaries and begins to randomly insert dislocations within these boundaries. There are an array of repeat cells to both the left and right side of the crystal which contain an exact copy of ‘ghost’ or image dislocations, used to prevent finite size effects. Then the force on each dislocation is calculated and the dislocation moved according to this force. An animation of the dislocations moving is displayed and a movie file can be generated and saved when the program reaches its end.

The simulation is infinite in two dimensions (along the dislocation line direction and along the basal plane) and finite in the prismatic c axis direction. Dislocations must be introduced as a dipole so that the net Burgers vector is zero. Whenever a new dipole of dislocations is introduced it interacts with other dislocations and the image dislocations in the periodic cells. This interaction is very long range, proportional to the log of the separation of the dislocations. This is analogous to the interaction of electrical charges.

The energies calculated by this dislocation dynamic program are summations of the energies of interactions over many repeat cells, it is known that these summations
Figure 3.2.: Flow diagram showing the flow of the programming steps implemented in the prismatic dislocation model.
Figure 3.3.: Schematic diagram showing the finite periodicity in $x$ and no periodicity in $y$. The boundary at the top and bottom is free to expand or contract as a result of the dislocations within the cell.

are not always convergent, they are known as conditionally convergent and has been discussed in depth in works such as Cai et al.,\textsuperscript{116} in which they use a method of taking expanding supercells containing fractional dislocations at their boundaries to give a net Burgers vector of zero. This method could be employed in future iterations of this program however for now the brute force method of fixing the net Burgers vector at zero by introducing dipoles and summing over a large number of repeat cells has been used.

**Dimensional Change**

The number of repeat cells influences the accuracy of the dimensional change where the higher the number of repeat cells the stronger the agreement of the expansion with that predicted by Lehto and Oberg.\textsuperscript{50} As discussed in Section 2.1.5 the expansion of a material due to the introduction of a prismatic dipole should be equal to $\frac{bW}{L}$, where $b$ is the Burgers vector of the dislocations, $W$ is the width of the dipole and $L$ is the width of the material. Owing to the program using a finite number of repeat cells the agreement of the $c$-expansion calculated with the program converges to the expansion predicted by the Lehto Oberg formula with increasing repeat cell number.

Figure 3.4 shows the percentage agreement of the calculated $c$-axis expansions. From this example one can see that a 99% agreement can be achieved using at least 15 repeat cells.
Figure 3.4.: The blue line shows convergence of the c-expansion for 80 dislocation dipoles calculated by the program with the expansion calculated using the formula from Lehto and Oberg. The red line shows the convergence of the energy of the system from its initial value to its minimal value with increasing repeat cell. Finally the dashed cyan line shows the time taken to calculate the expansion and energy of the system with increasing number of repeat cells.

Energy

The graph shown in Figure 3.4 also shows the convergence of the total energy of the system with increasing number of repeat cells. The simulation was carried out on a random distribution of 80 dislocations of Burgers vector 6.67 nm. This graph shows that the energy converges faster than the expansion and as such if sufficient repeat cells are used so that the dimensional change is converged the energy should also have reached convergence.

3.1.2. Computational time

The final piece of information plotted in Figure 3.4 is the time taken to compute the dimensional change and energy in seconds on a single core of a 2.93GHz Intel Core 2 Duo processor. The time taken is seen to increase linearly as would be expected as the number of dislocation images, and hence number of computations which are carried out increases linearly with number of repeat cells.
3.1.3. Relaxation by Dislocation climb

The prismatic dislocation dipoles will have a very high interaction energy if two loops are formed close together as the interaction energy is dependent on separation distance. As reported by Bacon and Warren,\textsuperscript{60} on the basis of x-ray diffraction patterns, prismatic loops in graphite are found to form at a large distance from all existing loops. As the dislocation loops in this program are introduced to the system in random positions it is possible that two dipoles are placed unphysically very close to each other. In this case the interaction energy will be unrealistically high and so to account for the loops being placed unphysically an artificial relaxation (i.e. geometry optimisation) of the dipoles has been introduced.

In this relaxation the dislocation dipoles are allowed to move in the basal direction only, appearing to slide parallel to the layers above and below it. This would correspond physically to conservative climb, which has been postulated to occur during the formation of prismatic loops.\textsuperscript{33} As the name suggests, conservative climb does not produce or lose any material so the width of the dipole will be fixed. This process is not likely to happen easily in graphite as loops are thought to be sessile and so this process is introduced in an attempt to alleviate computational errors rather than model a physical process. Alternatively, dislocations could move by prismatic slip, perpendicular to the basal planes. This process cannot be activated at reactor temperatures as it requires the breaking of strong carbon to carbon bonds, thus dislocations are considered sessile for prismatic slip. Conservative climb has been discussed here as a physical process however it is primarily a computational method to account for the observed pattern of loop nucleation which depends on kinetics of loop growth\textsuperscript{117} which are not accounted for by a random insertion method such as the one used in this program.

Initially, a force based relaxation technique was employed to minimise the system energy where-by the force on each of the dislocations in a pair, due to all other dislocations in the system, was calculated and the pair moved a distance proportional to the average force across it. This method was found to be very slow and so a more efficient Newton-Raphson method based on second derivatives was used, which should be exact for quadratic surfaces.

The equation for the change in position of a dislocation with an applied force is
Figure 3.5.: The gold line on this graph shows the energy of a system of 50 prismatic dislocation dipoles which were allowed to relax by calculating the average force on a dipole due to the others and moving the dipole proportionally. The navy line shows the percentage expansion of the crystal which is seen to be constant as no new dislocations are added.

given by:

\[ x' = x - \frac{dF}{dx} \]  

(3.1)

where \( x \) is the original position, \( x' \) is the new position and \( F \) force on the dipole.

From the equation for the force between two prismatic dislocations (equation 2.16) the differential \( \frac{dF}{dx} \) is given as:

\[
\frac{dF}{dx} = \frac{1}{(A6(x^2 + A2y^2) + A3y^2x^2)^2}
\left(\begin{array}{c}
(A1A4b_1b_2y^2 + 3A5x^2)(A6(x^2 + A2y^2)^2 + A3y^2x^2)

- (A1A4b_1b_2y^2x + A5x^3)(4A6x(x^2 + A2y^2) + 2A3y^2x)
\end{array}\right)
\]  

(3.2)

where the constants \( A1 \rightarrow A6 \) are defined as previously, see section 2.1.7 (page 23), \( b_1 \) and \( b_2 \) are the Burgers vectors of the two dislocations you are calculating between and \( x \) and \( y \) are the separation distances in each direction.

Calculating this differential between each dislocation and every other dislocation and adding the differentials linearly to the original position will move the dislocation towards the minimum energy. By using this method the optimisation should require fewer steps and reach a minimum. Figure 3.6 shows the updated flow diagram of
the program including the Newton-Raphson optimisation.

Newton-Raphson gives very fast convergence to local minima, however this method experiences problems when the energy profile is at a point of inflection and so this must be planned for in the programming. Figure 3.7, from Numerical Recipes, shows the situation where a point in the energy profile is found where the gradient is zero. The closer \( x \) is to the point of inflection the smaller the gradient of the line which causes the displacement to tend to infinity as the gradient tends to zero.

In order to avoid the situation where a dipole can be moved by a displacement tending to infinity, a maximum limit is put on the displacement of dislocation dipoles. This limit has been set to half the width of a dipole.

A comparison of the force based relaxation and the Newton-Raphson method can be seen in Figure 3.8, it is seen that the Newton-Raphson method provides a much faster energy optimisation which is also a lot smoother than the force relaxation.

\[ \text{3.1.4. Results} \]

As would be expected when prismatic dislocation dipoles were added to the system the boundaries were seen to expand in the \( c \)-direction and the energy of the system, due to the elastic strain from introducing dislocations is seen to increase. The dimensional change is linear in the \( c \)-axis as would be expected by adding an equal length of dislocation on each iteration. The expansion calculated agrees with the Lehto-Oberg equation where the expansion is equal to \( bW/L \) as discussed previously.

The energy of the system was seen to increase as the number of dipoles increased however it was observed that at very high densities of dislocation there was a reduction in the rate of the energy increase causing the total system energy to decrease for a short time before increasing again as the number of dipoles continued to increase. This energy behaviour can be seen in Figure 3.9 where the data has been fitted using a Bezier smoothing function to eliminate small fluctuations in energy. A Bezier curve follows a polynomial of \( n \) degrees where \( n \) is the number of data points and was calculated within gnuplot with a data point weighting of 1 such that all the data points are equally weighted in the polynomial.

The following series of images (Figures 3.10 to 3.14) are screen captures of the graph which is plotted by the 2D-DD program during runtime. The runs are all in material of
Figure 3.6.: Flow diagram showing the basic steps carried out by the prismatic dislocation dynamics program, where the number of iterations is the number of times dislocations should be added to the system and time steps are the number of relaxation steps carried out. The purple process blocks indicate the additional steps carried out with the Newton-Raphson optimisation in place.
Figure 3.7.: This figure is reproduced from Numerical Recipes and shows a pitfall of the Newton-Raphson optimisation whereby when the point where the gradient is equal to zero is reached the displacement tends to infinity. The numbers indicate the order in which the points are reached, so starting at point 1 the algorithm moves to point 2 which is a maxima (gradient=0) and then the displacement tends to $-\infty$.

Figure 3.8.: These graphs show the energy of a system of 40 dislocation dipoles which are allowed to relax by using the force method (top) and Newton-Raphson method (bottom) showing the much faster convergence for the Newton-Raphson method.
Figure 3.9.: The energy behaviour of a single crystal of graphite modelled using 2D-DD as the density of dislocations increases. The run parameters used are: 80×60 nm crystal, dislocations are added in iterations of 100 dipoles with a Burgers vector of 0.664 nm fitted using a Bezier smoothing function.

80×60 nm. In each case the dislocation dipoles are introduced in pairs (4 dislocations in total added per iteration) and are partial prismatic dislocations, b=0.33 nm. Each job was run for 100 iterations giving a total of 200 dislocation dipoles, in all cases this results in an expansion of 10.8%. Each job had a different number of relaxation steps applied between each iteration of 0, 1, 5, 10 and 20.

The resulting energies of these jobs are higher for the low degrees of relaxation and lower for 5 or more relaxation steps. This result is not surprising and matches the findings of a closed system where no new dislocations are added, such as the resulting energy graph shown earlier in Figure 3.8.

3.1.5. Discussion & Conclusion

In order to try to find an explanation for the energy behaviour observed two dimensional melting was considered such as the popular work by Kosterlitz and Thouless\textsuperscript{92} and work by Burakovsky \textit{et al.}\textsuperscript{97} as described in Section 2.5.1. The density at which the energy of the system decreased was seen to agree with the Burakovsky equation (Equation 2.17) which shows a density of dislocation mediated melting which is proportional to $1/b^2$. This is due to an increase in shielding between existing dislocations and newly introduced dislocations.
Figure 3.10.: The dimensional change (in black) and energy (in red) for a crystal 80 × 60 nm of an evolving system of partial prismatic dislocations of Burgers vector 0.332 nm, where 2 dipoles are introduced for 100 iterations with no relaxation between iterations.

Figure 3.11.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial prismatic dislocations of Burgers vector 0.332 nm, where 2 dipoles are introduced for 100 iterations with one relaxation step between iterations.

Figure 3.12.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial prismatic dislocations of Burgers vector 0.332 nm, where 2 dipoles are introduced for 100 iterations with 5 relaxation steps between iterations.
Figure 3.13.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial prismatic dislocations of Burgers vector 0.332 nm, where 2 dipoles are introduced for 100 iterations with 10 relaxation steps between iterations.

Figure 3.14.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial prismatic dislocations of Burgers vector 0.332 nm, where 2 dipoles are introduced for 100 iterations with 20 relaxation steps between iterations.
The program was executed with a range of Burgers vectors and the density at which the energy decreased was compared to the theoretical value proposed by the Burakovsky equation. Figure 3.15 shows the results obtained from this program compared to the density predicted by Burakovsky et al. for a range of Burgers vectors.

The error on these results comes from the width of the trough of Figure 3.9 and the difficulty in making a measurement from the graph. For larger Burgers vectors the transition occurs at a much lower density and so fewer iterations are required making it much easier to make an accurate measurement of the density at which the point of inflection occurs on the graph. To improve the accuracy of these readings an improvement would be to run the program several times at each Burgers vector and take an average reading. As well as helping reduce any human error this would also have the benefit of reducing the error due to the noise on the total energy. When dislocations are introduced to the crystal they are introduced randomly and so some may be placed artificially close together, although this is accounted for in allowing the prismatic loops to climb constructively the energy is still not completely smooth as dislocations cannot glide into adjacent planes meaning they are restricted to the plane they were introduced to. In addition to taking multiple readings it would be beneficial to look at the raw data rather than taking readings from a graph, an attempt could then be made to fit the data with a function to gain a more accurate reading of the density at which this behaviour occurs.

The density for dislocations of Burgers vector 0.664 nm (the Burgers vector of a perfect prismatic dislocation in graphite) at which the transition occurs in the 2D-DD program is $1.14 \times 10^{14}$ dislocations per square centimetre. This agrees very well with the theoretical prediction given by the Burakovsky equation of $1.36 \times 10^{14}$ dislocations per square centimetre.

The prismatic dislocation mode of this program has been shown to qualitatively model the dimensional change of irradiated graphite with respect to the c-axis expansion. This is essentially modelling the standard model of dimensional change as outlined in the preceding chapters (Section 1.1). A quantitative agreement with literature on two dimensional melting has also been achieved. From this point the program was developed further to include the basal dislocation in the hopes that it could be used as a proof of concept for the hypothesis that basal dislocations act
Figure 3.15.: The density of dislocations of various Burgers vectors 0.33Å to 2.33Å at which the energy is seen to reach a local maximum. The gold line represents the theoretical value of density calculated using the Burakovsky equation.
in addition to the standard point defect models, storing energy and contributing to dimensional change. The following section outlines the basal dislocation mode of the program and results obtained from it so far.

3.2. Basal Dislocation Model

Once the principles of prismatic dislocation dynamics had been finalised and confirmed a basal dislocation model was developed. As proposed by Heggie et al.\textsuperscript{105} the motion of basal dislocations can lead to interactions causing $c$-axis dilation. This section describes the basal dislocation model developed to assist in visualising and proving this concept and results obtained from this model. The key concept of basal and prismatic dislocation equivalence is exploited throughout this model. This concept has been described in Section 2.5.3.

3.2.1. Method

The method implemented in this basal dislocation model is very similar to the prismatic dislocation model. As far as possible the program has been written such that all the classes and methods can be applied to dislocations with any combination of $b_x$, $b_y$ and $b_z$. This avoids any duplication of code and helps prevent obsolete code remaining in the program. Writing the program in a way in which it is as generic as possible should make it very easy to apply to program to alternative systems of dislocations and materials as the field of research progresses.

In the same way as the prismatic model the material boundary is first mapped out using user input dimensions. The dislocations are then introduced within the dimensions of the material as dipoles. In this case the dipoles are climb dipoles, meaning that they are introduced directly above each other on adjacent planes. The dislocations were introduced in this way as they are very unstable in a glide dipole arrangement (where both dislocations are introduced on the same glide plane). This is because the basal dislocation in graphite glides extremely easily and has a very wide dislocation core. When dislocations are introduced as a glide dipole it was observed that they instantly collapse together and annihilate.

Once introduced the dislocations can then move according to the forces and second
differential of the forces on them using the same methods as the prismatic model. After each movement interactions are calculated for any dislocations within the core radius of another. The core radius in these simulations was approximated to the magnitude of the Burgers vector of the dislocation to each side of the dislocation in question. Despite the fact dislocations of the same sign Burgers vector repel there are still situations where same signed dislocations can come close enough together to interact. For high densities of dislocations the chance of a dislocation being introduced next to a dislocation of the same sign is intuitively higher. As the dislocation interactions add linearly it is also possible to overcome the repulsion of a same signed dislocation if the net forces due to other nearby dislocations act to push the dislocations together.

The interactions are calculated by a simple linear addition of Burgers vectors so that oppositely signed dislocations will result in a dislocation of zero burgers vector (i.e. annihilation) and dislocations of unequal or same signed Burgers vectors add up to give a dislocation with the net Burgers vector.

In order to exploit the basal and prismatic dislocation equivalence to give dimensional change in this basal model the program looks not only for dislocations on the same glide plane to react with, but also dislocations on adjacent glide planes. If the criteria for folding is met (basal dislocations on adjacent planes with large Burgers vectors of the order $3b$) then the basal dislocations are replaced by a prismatic dislocation dipole. The width of this dipole is dictated by the magnitude of the Burgers vectors of the reacting basal dislocations.

The relaxation of the dislocations is variable so that the user can chose how many iterations of relaxation to perform. A few simple test runs for the particular scenarios of interest can gauge an appropriate number of steps. A possible expansion to this program could be to allow the user to input a tolerance on the relaxation so that the relaxation loop is carried out until the maximum force on any dislocation is less than the tolerance.

### 3.2.2. Optimisation

To relax the system in the same way as the prismatic dislocation system, described in section 3.1.3, the second differentials for the force between two basal dislocations and between a basal and a prismatic dislocation were calculated. From equations 2.15
and 2.16 we have the following second differentials.

For the interaction between a prismatic dislocation and a basal dislocation:

\[
\frac{dF}{dx} = \frac{A_1A_7b_1b_2}{(x^2 + A_2y^2)^2 + A_3y^2x^2} \left[ -2yx\left((x^2 + A_2y^2)^2 + A_3y^2x^2\right) \right. \\
- \left. \left(4x(x^2 + A_2y^2) + 2A_3y^2x\right)(A_2y^3 - yx^2) \right] 
\]

(3.3)

and for the interaction between two basal dislocations:

\[
\frac{dF}{dx} = \frac{A_1A_7b_1b_2}{(x^2 + A_2y^2)^2 + A_3y^2x^2} \left[ (A_2y^2 - 3x^2)\left((x^2 + A_2y^2)^2 + A_3y^2x^2\right) \right. \\
- \left. \left(4x(x^2 + A_2y^2) + 2A_3y^2x\right)(A_2y^3 - x^3) \right] 
\]

(3.4)

where in both cases the constants \(A_1 \rightarrow A_7\) are as listed in section 2.1.7 (page 23), \(b_1\) and \(b_2\) are the Burgers vectors of the two dislocations you are calculating between and \(x\) and \(y\) are the separation distances in each direction.

### 3.2.3. Results

The behaviour of the graphite crystal has been studied, again in terms of dimensional change and energy of the system as well as qualitative behaviour of the dislocations.

#### Dislocation Behaviour

On running the program it quickly became apparent that there are low energy positions of basal dislocations which resemble walls of same signed dislocations running through the material. A schematic of this is shown in Figure 2.26. These walls occur in an alternating fashion so that adjacent walls are of opposite signed dislocations. Figure 3.16 shows such an output.

These basal dislocation walls have been referred seen in literature relating to other materials such as work by Raabe\(^{101}\) see Figure 2.28 which shows a resulting dislocation map from their 2D-DD simulations. This dislocation walls are generally known as kink bands. Kink bands in graphite have been discussed in depth by Barsoum et al.\(^{100}\) Figure 2.27 shows the kink bands observed in graphite by Barsoum et al. In this
Figure 3.16.: This screen capture shows the output of the program when basal dislocations are allowed to relax. The dislocations are seen to form walls of oppositely signed dislocations.
paper the authors subject single crystals of graphite to a load applied parallel to their c-axis and observe the formation of these bands of dislocations in the material. The authors note that under extremely high stresses the dislocation walls are seen to be mobile. The application of stress on the graphite in this dislocation dynamic model is discussed later (see Section 3.4).

**Dimensional Change**

As outlined above (Section 2.5.3) in the equations for the displacement of a boundary due to a dislocation within it, it can be easily predicted that the basal dislocation will have a negligible effect on the displacement of the boundary in the c-axis direction. Just as prismatic dislocations do not affect the boundaries of the material perpendicular to the c-axis. As displacement fields of dislocations add linearly there are no arrangements or combinations of basal dislocations which will give rise to a c-axis expansion using classical elasticity theory alone. Therefore, any dimensional change in this model must result from interactions of basal dislocations which can be represented by prismatic dislocations such as the proposed ruck and tuck defect.

The dimensional change is seen to increase with dislocation density, however this effect is not linear as in the case of prismatic dislocations. Figures 3.17, 3.18 and 3.19 are examples of screen shots of the 2D-DD program in basal dislocation mode. In all three cases partial basal dislocations \( b = \pm 0.142 \text{ nm} \), are introduced into a material \( 80 \times 60 \text{ nm} \), each job is run for 50 iterations with 20 relaxation steps between each iteration. The jobs have a varying number of dislocation dipoles added on each iteration of 100, 200 and 400 dislocations respectively.

The resulting dimensional changes are seen to be irregular and increase in a step fashion. This is due to the fact that the dimensional change must result from prismatic dislocations which occur when basal dislocations pile up in specific arrangements, in this case when a dislocation of at least \( 3b \) is found to be on an adjacent plane to a dislocation of at least \(-3b\), this array is then replaced by a perfect prismatic dislocation dipole \( b = 0.667 \text{ nm} \) with a separation distance proportional to the number of basal dislocations which formed it. The resulting expansions are seen to be approximately 5%, 10% and 12% for insertions of 100, 200 and 400 dipoles.
Figure 3.17.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial basal dislocations of Burgers vector 0.142 nm, where 100 dipoles are introduced for 50 iterations with 20 relaxation steps between iterations.

Figure 3.18.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial basal dislocations of Burgers vector 0.142 nm, where 200 dipoles are introduced for 50 iterations with 20 relaxation steps between iterations.

Figure 3.19.: The dimensional change and energy for a crystal 80×60 nm of an evolving system of partial basal dislocations of Burgers vector 0.142 nm, where 400 dipoles are introduced for 50 iterations with 20 relaxation steps between iterations.
Energy

There is an inconsistency in the prismatic and basal dislocation equivalence argument in the quantitative measurement of the energy of the system. The energy of a dislocation depends on the square of the Burgers vector of the dislocation. For a perfect prismatic dislocation the Burgers vector is almost five times that of a basal dislocation, 0.667 nm compared to 0.142 nm. With a $b^2$ dependence this makes the energy of the prismatic dislocation much larger than that of a basal dislocation for an isotropic material. The anisotropy of graphite does add a layer of complexity to this as different energy factors must be used for basal and prismatic dislocations to take into account the differing elastic constants of the material. Section 2.1.6 contains the equations for these energy factors (Equations 2.7 and 2.8). These equations give energy factors of $K_{ex} \approx 71$ GPa and $K_{ey} \approx 13$ GPa for the basal and prismatic dislocations respectively. Taking these energy factors into account we find a ratio of 1.4:5.8 for the self energies of basal and prismatic dislocations in graphite. When an array of basal dislocations are considered to be equivalent to a prismatic dislocation dipole the self energy of the basal dislocations may not equal the self energy of the prismatic dislocation dipole. This problem is currently not solved within the 2D-DD program, however it is hypothesised that an energy equivalence could be implemented by considering an additional terms to the interaction energy and the core energies of the dislocations involved in the representations. Addition of an adjustable core energy and an adjustable core-core interaction energy could be used to find a method of equating the energy of these representations. Introducing a solution to this inequality should be given the highest priority in the continuation of the development of this 2D-DD program. It is regrettable that implementation of a solution has fallen outside of the time constraints of this thesis.

3.2.4. Discussion & Conclusion

A basal dislocation model has been implemented using a similar procedure to the prismatic dislocation model. This model has been designed as a proof of concept for the importance of the basal dislocation in a new theory for the dimensional change or irradiated graphite. The program gives excellent qualitative agreement with similar work on basal dislocations, such as 2D-DD work by Raabe and experimental
observations of graphite subjected to high loads. The program relies on the ability to exploit a basal-prismatic dislocation equivalence. This has been shown to be well reasoned in terms of dimensional change due to additional material in the crystal. However, an inconsistency has been highlighted in the equivalence of energy stored in the dislocations and as such no energies have been presented here. A short term solution to this inequality could be to consider the energy of an arrangement of dislocations in terms of their basal representation, while determining their effect on the displacement of a boundary in terms of their prismatic representation. A consideration would have to be made as to which representation to use for calculation of the interaction forces between dislocations during the relaxation of the 2D-DD model.

### 3.3. Mapping the stresses and strains

A third mode developed for this 2D-DD program is a stress and strain mapping mode. This was introduced to gauge the magnitude of stress and strain variations. The strain could be compared to x-ray diffraction measurements on radiation damaged graphite. The strain variations could prove beneficial in investigations into vacancy diffusion. This mode allows a colour map of the stresses in the continuum to be produced. This was implemented in order to highlight the long range effect dislocations have on their system. The shape and intensity of the stresses can be used to qualitatively understand the way in which dislocations and their strain fields interact with each other.

#### 3.3.1. Method

The dislocation stress and strain mapping mode is an extension to the previous two modes. The program runs as usual depending on the user input parameters however in addition to the program rendering an image of the material showing the displacement of the boundary and the positions of the dislocations within that boundary, the material is also overlaid with a colour map showing the areas of maximum and minimum stress or strain using a graduated colour scheme. The stresses or strains are calculated by creating a mesh of points across the material. The stress or strain due to the array of dislocations within the material is then calculated.
at each point and stored in an array. The program then locates the maximum and minimum values of these stresses and sets those values as the extreme values on the colour scale. The remaining values are then sorted into one of eleven bins depending on their proportionality to the maximum values. The bins have been assigned a colour to represent them from dark orange through to white at the mid point to dark blue at the other extreme. When the dislocations and boundaries are rendered to the screen a 2x2 pixel image of the appropriate colour is rendered to the location of each point on the mesh. This results in a smooth graduation of high stress or strain areas in dark orange to low areas of negative stress or strain in blue, with areas of zero stress or strain in white. Again the equations for stress and strain have been programmed in such a way as to ensure that dislocations of any Burgers vector, \((b_x, b_y, b_z)\), can be mapped without any alterations to the code.

3.3.2. Basal and Prismatic dislocations

The simple case of a single basal dislocation has been mapped to validate this mode of the program with theory. The resulting stress maps can be seen in Figure 3.20. The theoretical stress maps can be seen in Figure 2.11 and are based on equations derived in Hirth and Lothe.\(^{47}\) These figures show an excellent agreement between theory and the output from this program. The ability to render stress maps of more complex systems is useful to aid in conceptualising how the dislocations may move in relation to each other due to the stresses in the material. A more complex example can be seen in Figure 3.21. In this simulation 100 dislocation dipoles (separation 12 nm) have been randomly inserted within a boundary of \(80 \times 60\) nm. The dislocations are perfect prismatic dislocations of Burgers vector 0.667 nm and they have been allowed to relax for 10 iterations of the relaxation cycle to prevent any unphysically high stresses being introduced. The stress which has been plotted here is \(\sigma_{yy}\).

3.3.3. Non-basal dislocations

Exploiting the generic implementation of the programming in this 2D-DD code allowed for a non basal dislocation model to be very quickly investigated. Non basal dislocations are dislocations within the sheet of graphene. These could be defects such as lines of vacancies or the Stone-Wales-Thrower defect, along with many
Figure 3.20.: These diagrams show the stress map for a single basal dislocation in graphite as rendered by the 2D-DD program. These diagrams can be directly compared to the theory shown in Figure 2.11.
Figure 3.21.: The 2D-DD program output stress map for the stress in the graphite continuum due to 100 prismatic loops of Burgers vector 0.667 nm in an area of 80 × 60 nm.

other dislocation arrangements. As described in Section 2.4 non-basal dislocations are currently highly topical, particularly as manufacturing large sheets of perfect graphene is difficult. Another member of this research group, Dr T. Trevethan has performed extensive analysis of the coalescence of vacancies in graphene and the stresses in the sheet as a result of these non basal dislocations.87 His work has involved a huge number of ab initio calculations to create a stress map around particular defects. It was hoped that in using my program to map the stresses of non-basal dislocations additional evidence to support his work could be obtained, the strength of this work being its speed. A stress map of a particular arrangement of non-basal dislocations could be produced in seconds rather than as a culmination of several tens of ab initio calculations, each taking both human input time and computational run time.

The only alterations needed to this program to allow for a non-basal dislocation model were to change the elastic constants of the material and implement additional glide planes in the material. Owing to the symmetry of the graphene sheet there are three glide plane directions for zig-zag type vacancy lines and three for armchair
type vacancy lines. There are therefore twelve different configurations of non basal dislocation. Figure 2.24 shows the atomic representations of these twelve dislocations. By implementing these additional glide planes this non basal mode can be used not only for stress and strain mapping but also as a fully dynamic model of the non basal dislocations in an elastic continuum.

A resulting stress map for a static dipole in this 2D-DD program can be seen in Figure 3.22 along side the stress map calculated using \textit{ab initio} calculations by Trevethan \textit{et al.} These figures show a strong correlation of stress mapping between both the methods. There is a slight asymmetry in the \textit{ab initio} case which could stem from relaxation to a low energy state of a dipole where the dislocations are at 45° to one another (as in Figure 2.8 earlier in this thesis - see page 2.8).

3.4. Dislocation Dynamics with an Applied Stress

In order to consider creep, it was important to allow the program to run with an applied stress on the system. The applied stress will result in an additional force on
the dislocations as well as the force due to the other dislocations in the system.

As discussed in Section 2.1.8, an applied stress is considered to act on all dislocations within the boundary and remains in place for the duration of the simulation. The force exerted by this stress is given by, \( F = \sigma b \) where \( \sigma \) is the stress in Pascals and \( b \) is the Burgers vector of the dislocation in meters.

It was hypothesised that applying a stress to the system will result in more dislocation motion and hence pileups and a greater \( c \)-axis expansion.

### 3.4.1. Method and Optimisation

The method used in this version of the dislocation dynamics is the same as in the previous basal dislocation model with the exception of the additional force which is added onto the dislocations due to the applied stress. As derived previously (Section 2.1.8) only specific components of stress will contribute to an additional force on the dislocations in question. This additional force is noted to act in opposite directions depending on the sign of the Burgers vector of the dislocation. Dislocations of opposite signed Burgers vectors will give forces of opposite sign. These opposing stresses will result in dislocations of opposite sign moving in opposite directions.

The optimisation of the dislocations is carried out in the same way as previously described in section 3.2.

### 3.4.2. Validation

Initially simulations were carried out on single dislocation dipoles in a small area of elastic continuum (20 nm \( \times \) 20 nm). These simulations were carried out on a single crystal with no periodicity in order to ensure that the dislocation was acting as expected in the simplest case possible.

Figure 3.23 shows a graph of the force felt by a basal dislocation, \( \mathbf{b} = b[100] \), or a prismatic dislocation, \( \mathbf{b} = b[010] \), for a range of applied stresses. The components of the force, \( F_x \) and \( F_y \) are plotted for \( \sigma_{xx} \) and \( \sigma_{xy} \) and \( \sigma_{yy} \) all other components of stress are confirmed to have no effect on the net force of either dislocation. For a basal dislocation, \( \sigma_{xy} \) gives only a force component in the \( x \) direction, along the glide plane and \( \sigma_{xx} \) gives only a component of force in the \( y \) direction, perpendicular to the glide plane. For a prismatic dislocation, \( \sigma_{xy} \) gives a component of force in the \( x \)
direction and $\sigma_{yy}$ gives a force in the $y$ direction.

The force on a partial prismatic dislocation ($b=0.335\,\text{nm}$) is seen to be greater than the force on a basal dislocation ($b=0.142\,\text{nm}$) by a factor of 2.4 for the same applied stress. However, as previously discussed the nature of the bonding in graphite means that prismatic dislocations are held very strongly in place and as such are unlikely to move even with a large net force acting upon it.

### 3.4.3. Discussion & Conclusion

The applied stress mode of the program has confirmed the expected outcome, predicted by the mathematical derivations outlined above, for the case of a single dislocation. Although the mathematical ability to run the program in the prismatic model under applied stress is implemented, these dislocations are sessile and so there is little potential for interesting science in these models so they have not been investigated in this thesis. The focus here has been predominantly on the basal dislocation. Despite this, as usual for completeness the equations have been fully implemented in the code in case of future expansions.

### 3.5. Summary

This chapter has outlined the 2D-DD program which has been written to investigate concepts in the theory of irradiation damage in single crystal graphite. The program has confirmed the standard model behaviour using prismatic dislocations - two dimensional ribbons which model a cross section through a dislocation loop. A basal dislocation model has been implemented to illustrate the potential of a basal dislocation centred model of dimensional change in graphite. The functionality to quickly map stresses and strains in a continuum as a result of a complex system of dislocations has been outlined. Finally, an attempt has been made to expand the program to study creep in defected graphite under an applied stress. The possibilities for expansion of this program are extensive and where possible it has been designed with future expansion in mind so that minimal maintenance would be required on existing classes. Some aspects of the program use educated estimations for physical quantities such as the width of the dislocation core. The 2D-DD program also lacks
Figure 3.23.: These graphs show the force on a single dislocation as a result of an applied stress. The force is split into the x and y components represented by the navy and gold lines. Figures a, b, and c show the force on a basal dislocation as a result of stress applied in $\sigma_{xx}$, $\sigma_{xy}$ and $\sigma_{yy}$ respectively. Figures d, e, and f show the net force on a prismatic dislocation as a result of the same applied stresses.
a contribution of energy for the core of the dislocation. Core energies cannot be measured using classical elasticity theory as the structure of the dislocation core is complex and not well replicated with elasticity theory. The next chapters outline the work which has been carried out to use \textit{ab initio} calculations to establish accurate values for some of these quantities.
4. Density Functional Theory (DFT) and the AIMPRO code

The following chapters outline atomistic calculations which have been carried out to aid in understanding the atomic level processes and structures of dislocations in graphite. The calculations were predominantly carried out using AIMPRO, \textit{ab initio} Modelling PROgram, a density functional theory (DFT) code currently developed by Patrick Briddon and Mark Rayson (both at Newcastle University). Details of the code can be found in a number of publications by the authors.\textsuperscript{121–124} In order to understand the implications of these results it is beneficial to consider DFT from a fundamental level.

4.1. Theoretical Background

This chapter describes the history and evolution of quantum chemical theories and their implementation in AIMPRO, beginning with the notorious Schrödinger equation and progressing through a range of approximations which are employed to solve it.

4.1.1. The Schrödinger equation

The Schrödinger equation,

\[ \hat{H}\Psi = E\Psi \] (4.1)

is a time independent, non-relativistic, equation which describes the ground state of a many body system, where \( \hat{H} \) is the Hamiltonian operator, \( E \) is the energy of the system and \( \Psi \) is the wavefunction of the system.

The Hamiltonian consists of a sum of the kinetic and potential energies of the
particles in the system, both electrons ($e$) and nuclei ($N$).

\[
\hat{H} = \hat{T} + \hat{U} = T_e + T_N + V_{ee} + V_{NN} + V_{Ne}
\]  

(4.2)

where $\hat{T}$ is the kinetic energy operator and $\hat{U}$ is the potential energy operator. These operators can be taken as the sum of the kinetic energy of the electrons, $T_e$, the nuclei, $T_N$ and the potential energy of the interaction between the electrons, $V_{ee}$, nuclei, $V_{NN}$ and nuclei with electrons, $V_{Ne}$.

Solving the Schrödinger equation for a system allows a host of properties to be established for example geometry, defect energies, migration energies and diffusion pathways. However, solving the Schrödinger equation numerically is very difficult for systems with more than a couple of atoms and essentially impossible for the large systems investigated in this thesis. Even the He atom has so far not been solved exactly. In order to obtain a good estimate of the atomistic properties it is possible to simplify the Schrödinger equation by making approximations.

### 4.1.2. Born-Oppenheimer

The Born-Oppenheimer approximation\textsuperscript{125} was published in 1927 and considers that the mass of a nucleus and the mass of an electron are orders of magnitude different. The mass of an electron is approximately $\frac{1}{1836}^{th}$ of the mass of a proton. Because of this it is possible to assume that the nuclei are stationary with respect to the fast moving electrons, and so their kinetic energy is zero and their potential energy due to other nuclei is constant. As the nuclei are considered stationary it is now much easier to consider that the electrons are moving in the fixed fields of the nuclei.

The Hamiltonian then only contains an electronic component,

\[
\hat{H} = T_e + V_{ee} + V_{Ne}
\]

(4.3)

where the quantities are as described in Equation 4.2.

While this provides some simplification the solutions are still not easy for many body problems, particularly the electron electron interaction term, $V_{ee}$.
The nature of electrons is that their movements are not independent of each other. Not only do electrons follow the usual conditions of electrostatic repulsion of same signed charged particles but they also obey the Pauli exclusion principle where two electrons cannot occupy the same state. This problem has led to further approximations. The two most popular methods to get around this issue are Hartree-Fock and DFT. While Hartree-Fock can be useful for small systems with few electrons, large systems with a large numbers of electrons require density functional theory to attempt to find a solution.

### 4.1.3. DFT

In order to simplify the many body problem further it is possible to consider the electronic charge density $n(r)$ instead of the wavefunction. This idea was published in 1964 by Hohenberg and Kohn\textsuperscript{126} and expanded on shortly after by Kohn and Sham in 1965\textsuperscript{127} with a set of self-consistent equations, known as the Kohn-Sham equations.

Hohenberg and Kohn’s paper\textsuperscript{126} proves that the electron charge density uniquely determines the wavefunction. The benefit is that the electron density simplifies the calculation considerably. The density is always three dimensional unlike the wavefunction which is proportional to the number of electrons in the system and their spins which means only the smallest of systems can be studied using full wavefunction methods.

The Kohn-Sham equations follow on from the theory outlined by Hohenberg and Kohn and have been developed to describe inhomogeneous systems. The Kohn-Sham equations provide an approximation of the exchange and correlation effects using the chemical potential, $\mu_n(n)$, of a homogeneous interacting electron gas.\textsuperscript{127}

The Kohn-Sham equations are as follows:

\begin{align*}
\varepsilon_i\Psi_i(r) &= \left( T_e + V_{eff} \right) \Psi_i(r) \\
&= \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right] \Psi_i(r)
\end{align*}

(4.4)
where

\[ V_{\text{eff}}(r) = V_{Ne}(r) + E_C(r) + E_{XC}(r) \] (4.5)

\( T_e \) is the non interacting kinetic energy of the electrons as defined previously, \( \Psi_i \) is the wavefunction, \( V_{Ne} \) is the potential between the electrons and nuclei, \( E_c \) is the Coulomb component of the electron-electron interaction, \( E_{XC} \) is the exchange-correlation term and \( V_{\text{eff}} \) is the effective potential. The final charge density equation is

\[ n(r) = \sum_i |\Psi_i(r)|^2 \] (4.6)

where the charge density, \( n(r) \) is given by the sum of all the wavefunctions squared.

As the effective potential, \( V_{\text{eff}} \) depends on \( n(r) \) which in turn depends on \( \Psi(r) \) solving the Kohn-Sham equations are iterative. Initially, a guess is made for the density which is then used to calculate the effective potential and solve the Kohn-Sham equation to obtain the wavefunctions. These wavefunctions are then used to calculate a new density and the result is compared to the previous density until the calculation is self consistent.

The solution can then be used to find useful properties such as the total energy of the ground state, forces on the atoms, charge density, band structures, density of states and vibrational modes. It is important to consider that DFT is unlikely to give a reasonable solution for excited states and only the ground state is considered to be correct.

### 4.1.4. Local Density Approximation (LDA)

The exchange-correlation energy, \( E_{XC} \), in Equation 4.5 is another term which cannot be expressed analytically. There are a number of different approximations which can be made to solve this problem. The local density approximation (LDA) is one such approximation which is widely used in DFT.

LDA builds \( E_{XC} \) from the exchange correlation energy per particle of a homogeneous electron gas with the same electron density. \( E_{XC} \) is given by

\[ E_{XC}[n] = \int n(r)e_{XC}[n(r)]dr \] (4.7)
where $\epsilon_{\text{XC}}$ is the exchange-correlation energy density at $r$, is equivalent to that of a homogeneous electron gas of electron density $n$.

LDA is a good approximation however it does generally overestimate binding energies and underestimate ground state energies. There are also methods to approximate $\epsilon_{\text{XC}}$ based on gradient corrections (e.g. the Generalised Gradient Approximation (GGA)) which are usually better at optimising geometries; these can be slightly more computationally expensive. The problem with GGA in graphite is that the equilibrium value of the interlayer separation is hugely overestimated and so the separation must be fixed at experimental values.\textsuperscript{128}

Throughout this thesis LDA has been chosen rather than GGA as it has been shown that LDA performs far better than GGA in calculation of the interlayer binding energy for graphite systems.\textsuperscript{31}

4.1.5. Pseudopotentials, Basis Sets and k-point Sampling

Pseudopotentials

The AIMPRO code uses pseudopotentials to further reduce the complexity of the calculation. Core electrons are tightly bound to the nucleus and so do not impact the bonding of atoms the way that valence electrons do. The influence of the core electrons can be taken into account in a more simple way by incorporating their effect into the nuclear potential. This is known as a pseudopotential.

There is a database of pseudopotentials for AIMPRO, based on the potentials by Hartwigsen, Goedecker and Hutter,\textsuperscript{129} for all atoms from H to Rn and of varying accuracy. The accuracy of the pseudopotential is dependent on the radius considered as the core region. The larger the cutoff radius the lower the accuracy, however the calculation can be completed more quickly. There is therefore a trade off between accuracy and computational speed.

The core radius is the distance from the nucleus beyond which the pseudo wave function matches the electron wave function. The philosophy is to replace the kinetic energy functions with an artificial potential energy. The pseudo wave function has fewer nodes (and hence lower KE than the all electron valence wave function. The benefit of using a pseudopotential is that the core basis functions are eliminated, reducing the size, $N$, of the Hamiltonian. Since time to solution generally scales as
N^3, so this drastically speeds up the compute time.

**Basis Sets**

The valence electrons are not included in the pseudopotential, unlike the core electrons. The valence electron wavefunction, \( \Psi_\lambda(r) \), is therefore written in terms of the basis set, \( \Phi_i \), and the expansion coefficients, \( c_i^\lambda \), as follows

\[
\Phi_\lambda(r) = \sum_i c_i^\lambda \Psi_i(r)
\]  

(4.8)

Throughout this work the AIMPRO calculations have used Gaussian functions rather than the alternative method of plane waves as the basis set has far fewer functions per atom and so is computationally cheaper to run. The Gaussian shells are centred on the nuclei in the structure and have s, p or d symmetries.

The charge density which is specified in the AIMPRO input data file can be one of two types; either a simple Gaussian fit or a modified Gaussian. In this thesis a modified Gaussian fitted charge density is used to improve the rate of convergence of the calculation. The charge density basis is a set of exponents which are used to give a spherically symmetrical initial charge density for each atom. These exponents are used to calculate an initial charge density for the structure.

As with the pseudopotentials the charge density and wavefunction basis sets used by AIMPRO are available from the AIMPRO website.\(^{130}\)

**k-point Sampling**

For supercell calculations, such as those in this thesis, periodic boundary conditions are applied to the system and the Kohn-Sham equations are solved in reciprocal space. Periodic boundary conditions prevent finite size effects of cluster calculations. A supercell calculation is one where the input structure is surrounded by identical image cells, infinite in each lattice dimension. The infinite nature of the supercell calculation also removes the effect of interactions of the studied defect with the surface of the crystal.

Reciprocal space is the Fourier transform of real space, *i.e.* the inverse of the real
space such that

\[ \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (4.9) \]

where \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are the real basis lattice vectors, \( \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3 \) are the reciprocal lattice vectors and \( \delta_{ij} \) is the Kronecker delta function (0 if \( i \neq j \), 1 if \( i = j \)).

In reciprocal space a wave is described by its wave vector, \( \mathbf{k} \). This can be translated into the wavelength of a wave by

\[ |\mathbf{k}| = \frac{2\pi}{\lambda} \quad (4.10) \]

In AIMPRO the Kohn-Sham equations are solved for a mesh of \( \mathbf{k} \)-points in the Brillouin Zone (the region in reciprocal space where all electron eigenstates are represented). It is important to consider the density of \( \mathbf{k} \)-points such that an approximately uniform density of points is chosen. The inverse proportionality of \( \mathbf{k} \)-space means that in a supercell which has unequal cell dimensions, there should be more \( \mathbf{k} \)-points in the smaller dimensions and fewer points in the larger dimensions.

In the AIMPRO calculations described in this thesis a Monkhorst-Pack sampling system has been used.\(^{131}\) This is a system which chooses a set of \( \mathbf{k} \)-points equally distributed in each direction of the reciprocal lattice.

The number of \( \mathbf{k} \)-points is related to the accuracy of the calculation such that the higher the number of \( \mathbf{k} \) points the more accurate the calculation. It is important to use enough \( \mathbf{k} \)-points that the results are converged but not so many that the calculation takes an excessively long time. Smaller supercells will in general require more \( \mathbf{k} \)-points to achieve convergence than a larger supercell however it is more efficient to increase the \( \mathbf{k} \)-points than use an unnecessarily large supercell. The time scales linearly with the number of \( \mathbf{k} \)-points, but is proportional to \( N^3 \) where \( N \) is the number of atoms in the structure.

Each of the \( \mathbf{k} \)-points in the system has a wavefunction, \( \Psi_k \), and an associated eigenvalue \( E_k \) which is used to give a solution to the Kohn-Sham equations which gives the minimum energy of the system.
4.2. The AIMPRO code

The AIMPRO code is a self consistent local density functional code which incorporates the theory outlined in the previous section to calculate properties of structures input by the user.

AIMPRO was first developed at Exeter University in the late 1990’s by R. Jones and P.R. Briddon\textsuperscript{132} but is now used by a wider community around the world. The code is currently maintained and developed by P.R. Briddon and M.J. Rayson at the University of Newcastle.

This section outlines the user input to AIMPRO and a description of the ‘filtration’ algorithm.

4.2.1. Data input

In order to use the AIMPRO code the user needs to create a data input file which contains all the relevant information about the calculation they wish to perform. The basic components of the input file are the atom types and positions including pseudopotentials and basis sets, the lattice type and parameters, k-point sampling type and number of points, the filling of the Kohn-Sham levels and the type of job (e.g. optimisation, lattice optimisation or analysis such as bandstructure calculations). Detailed information on the data file components and job types can be found in the documentation on the AIMPRO website.\textsuperscript{130}

An example of a data file can be found in Appendix A.

4.2.2. Filtration

In recent years there have been significant developments to the AIMPRO code, the most notable being the use of a filtered basis set which allows AIMPRO to be used for tens of thousands of atoms instead of a couple of hundred.\textsuperscript{123,124,133,134}

An uncontracted basis with shells of four Gaussian orbitals typically has about 16-40 functions per atom, whereas this contracted basis set uses a linear combination of four functions per atom. The filtration algorithm as implemented in AIMPRO discards the part of the space of the functions which span the unoccupied orbitals leaving only the functions which contribute to the total energy.
In order to take advantage of this filtered basis set the AIMPRO code needs additional information about the species of atom. This requires the user to construct a *species* and *dat.filt* file.

The use of filtration will be vital in this project as graphite structures containing dislocations will require a very large number of atoms due to the wide core width of dislocations in graphite.
5. Density Functional Theory Calculations in Bilayer Graphene and Graphite

The next stage of this project was to carry out density function theory (DFT) calculations on dislocation structures in bilayer graphene and graphite. Previously calculations of dislocations in graphite have not been possible using DFT due to the large number of atoms required and the computational limitations of such systems. With recent advances in DFT it is now possible to run calculations on such structures. This chapter discusses structural and energy calculations of graphene and graphite structures using density functional theory (DFT).

The DFT code which is used is the Ab Initio Modelling PROgram (AIMPRO) as described in the preceding chapter. This code allows the user to specify initial identity and positions of atoms, a wave function basis set, charge density basis set and electron configuration and then calculates the relaxed positions of the atoms and the energy of the structure. The energy given should then be compared to a perfect structure to find the net change in energy due to any defects present.

Details of the theoretical concepts implemented in AIMPRO have been discussed in Chapter 4 and further information can be found in papers written by the code authors.121–124,132–134

5.1. Bilayer Graphene

Owing to the limitations on the number of atoms when carrying out a full density functional calculation initial calculations have been carried out on bilayer graphene. These preliminary results could then be used to gain a more accurate expectation of the behaviour of dislocations in graphite, with the hope of reducing computational time by starting a full graphite calculation on a structure which is as close as possible to the
expected optimised structure. The focus of this work will be to look at the behaviour of the basal dislocation dipole, in particular the dipole separation distance, width of the core of the basal dislocation and the energy per unit length of the dislocation, expanding this to basal dislocations in graphite using the filtration method as described by Briddon and Rayson.\textsuperscript{124}

Initially calculations were performed looking at the stacking fault energy and interlayer separation distance in pristine bilayer graphene (discussed in section 5.1.1) as well as calculations of a basal dislocation dipole in bilayer graphene (discussed in 5.1.2).

**5.1.1. Shear of bilayer graphene**

The introduction of a basal dislocation in bilayer graphene creates a stacking fault where the layer order is translated from AB to AC stacking. This concept is discussed in Section 2.3 and forms the basis of the initial DFT calculations carried out for this thesis.

In order to measure the stacking fault energy in bilayer graphene a series of 8 atom unit cells with a large vacuum gap above the bilayer were created. The top layer was sheared increasing increments away from AB stacking until the atoms had been sheared by 0.426 nm, a full unit cell width, returning the structure to AB stacking.

Figure 5.1 shows the 8 atom starting cell used for these calculations. The $x$ and $y$ dimensions are 0.426 and 1.23 nm respectively. A series of cells were created with the top layer sheared in the $+x$ direction until the structure returned to its initial structure at shear=0.426 nm.

The structure was optimised using AIMPRO and the resulting energy compared to the perfect AB stacked bilayer.

The resulting energy change of each sheared cell from the AB stacked cell could then be used to calculate the stacking fault energy per unit area of the fault. A graph of the resulting energies can be seen in Figure 5.2. It can be seen that the results agree with those published by Telling and Heggie\textsuperscript{61} (see their graph which has been reproduced in Figure 2.19) in that there is a maximum energy at 0.071 nm and a much larger maximum at 0.282 nm where the atoms are stacked directly above on another, AA stacking.
A point of comparison between the data obtained by Telling and the data obtained in these calculations is that the stacking energy in graphite is higher per unit area in his calculations than in the bilayer systems reported here. Telling and Heggie report a maximum stacking fault energy of $7.25 \text{ meV } \text{Å}^{-2}$, compared to these calculations which give a maximum energy of $5.82 \text{ meV } \text{Å}^{-2}$. It is believed this could be attributed to the slightly different methods used, however it could also be a result of the different physical situations. Telling’s calculations were a one shot energy calculation on graphite with no relaxation, whereas in these bilayer calculations the atomic structure has been allowed to relax so that the total energy of the system is likely to be slightly lower.

The interlayer spacing of the sheared bilayer has also been investigated and calculations show that the average interlayer spacing follows the same trend as the energy whereby the interlayer spacing is at a minimum (0.331 nm) when the bilayer is in AB stacking (shears of 0 nm, 0.142 nm and 0.426 nm) with a larger separation distance at a shear of 0.071 nm and a maximum (0.349 nm) where the layers are in an AA configuration (shear 0.284 nm). A graph of these results can be seen in Figure 5.3 where the data mirror that of the energy. It is noted that one of the points on the curve looks artificially lower than it would be for a symmetrical curve, it is likely that there is a mistake in this data point, either during the analysis or the job did not converge successfully.
Figure 5.2.: Fault energy of bilayer graphene sheared in the armchair direction. The shear and energy is measured in Å for ease of comparison with figure 2.19.

Figure 5.3.: The average interlayer separation distance of a sheared bilayer.
These structures were optimised using a k-point mesh of $16 \times 16 \times 4$ at a Fermi temperature of $kT = 0.04\,\text{eV}$. The pseudopotential used was graphite-pdddp.

### 5.1.2. Bilayer graphene with basal dislocations

Following on from the work on bilayer graphene with shear a program was written which creates bilayer graphene cells of any length containing a basal dislocation dipoles. There has been a lot of work since 2013 on defected bilayer graphene\(^{69-72}\) (as discussed in Section 2.3.1) however the only atomistic simulations have been carried out using classical interatomic potential methods.\(^{70,72}\) With recent advancements in AIMPRO we have the ability to carry out density functional theory calculations on these large systems, with the aim to measure the core width of the basal dislocation and investigate dislocation energies, comparing these to dislocation theory.

The structures are more challenging to optimise than the previous 8 atom shear unit cells as the number of atoms is much higher and the cell has a large aspect ratio, being small in the $y$ and $z$ dimensions and very long in the $x$ direction. The structures are one lattice vector thick in the $y$ direction and $3c$ thick in the $z$ direction (about 2\,nm) to allow for a vacuum gap between the periodically repeated bilayers. The dislocations are inserted on the glide plane between the bilayers and separated in $x$. This was done by writing a C program which generates any width cell of AB stacked bilayer graphene and then maps the displacement fields of a dipole of dislocations using Equations 2.2 and 2.3.

The dislocations are partial basal edge dislocations and are aligned such that the dislocation line runs parallel to $y$ with equal and opposite Burgers vectors of $\pm 0.142\,\text{nm}$, the C-C bond length. Viewing the structures from above clearly shows the transition from AB stacking to AC stacking at the location of the first dislocation and then from AC back to AB stacking at the location of the second dislocation. Figure 5.4 shows an example of the change in stacking due to the basal edge dislocation dipole.

Calculations have been completed in a range of cell sizes from as small as $4.26\,\text{nm}$ (80 atoms) up to $17\,\text{nm}$ (320 atoms) where the dislocations always annihilate on structural optimisation. This is not surprising as the dislocation core of a basal dislocation in graphite is known to be very wide. Overlapping dislocation cores are likely to annihilate on relaxation.
A series of calculations has been carried out to investigate the effect of changing the lattice parameter and number of k-points of a 160 atom structure containing a dislocation dipole. The structure was optimised with two pinning points to hold the basal dislocations in place. These were two pairs of alpha atoms, one at the edge of the cell and a pair in the centre of the cell between the dislocations. By fixing these atoms in the x direction the slip in the centre of the structure is held and so the dislocations cannot annihilate. A range of x direction lattice parameters were calculated from 8.387 to 8.599 nm. The energy of these optimised structures can be seen in Figure 5.5. The energy of these structures is shown per atom and is relative to the energy of the lowest calculated energy structure, lattice parameter 8.467 nm. These values can be used to find the optimum lattice parameter, 8.452 nm, which was obtained by quadratic interpolation of the obtained values. The energies can also be seen in Table 5.1.2.

The number of k-points was also investigated with the 160 atom bilayer being optimised with k-point grids of $1 \times 2 \times 1$, $1 \times 4 \times 1$, $1 \times 8 \times 1$, $1 \times 16 \times 1$, $1 \times 32 \times 1$, $1 \times 64 \times 1$ and $1 \times 128 \times 1$. In general it is best to use a k-point mesh which is uniform in all directions. In this case a 1:40 ratio of k-points would be approximately uniform. However this uniformity becomes impractical for cells with a very large aspect ratio such as the long thin cells in this thesis. The energy of these structures can be seen in Figure 5.6 and Table 5.1.2 where the energy is relative to the converged energy per atom. However the time taken for the calculation increases linearly with the number
Figure 5.5.: This graph shows the energy per atom of a dislocated 160 atom bilayer structure for a range of x axis lattice parameters. The dipole is fixed in place by the use of two pairs of pinned alpha atoms, one at $x = 0$ and one at $x = L/2$.

<table>
<thead>
<tr>
<th>x dimension (nm)</th>
<th>Relative Energy (×10^{-5}eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.387</td>
<td>176.11</td>
</tr>
<tr>
<td>8.414</td>
<td>64.58</td>
</tr>
<tr>
<td>8.440</td>
<td>5.27</td>
</tr>
<tr>
<td>8.467</td>
<td>0.00</td>
</tr>
<tr>
<td>8.493</td>
<td>48.47</td>
</tr>
<tr>
<td>8.520</td>
<td>150.51</td>
</tr>
<tr>
<td>8.546</td>
<td>302.22</td>
</tr>
<tr>
<td>8.573</td>
<td>509.87</td>
</tr>
<tr>
<td>8.599</td>
<td>772.80</td>
</tr>
</tbody>
</table>

Table 5.1.: The relative energies of a range of bilayer graphene systems containing a dislocation dipole for a range of x-axis lattice parameters.

of k-points used and so increasing the number of k-points can very quickly increase the length of time taken to optimise the structure.

A cell 25.6 nm long (1480 atoms) has also been optimised and was the first cell where the dislocations are still present after relaxation. In order to make a measurement of the core width of the dislocation the dipole needs to be sufficiently well separated that there is no overlap in displaced atoms. In this case the dislocations were found to be too close together for the core width to be accurately measured however it puts
Figure 5.6.: This graph shows the energy per atom of a dislocated 160 atom bilayer structure for a range of $y$ dimension k-points. Again the dipole is fixed in place by the use of two pairs of pinned alpha atoms, one at $x = 0$ and one at $x = L/2$.

Table 5.2.: The relative energies of a range of bilayer graphene systems containing a dislocation dipole for an increasing number of k-points in the $y$ dimension.

<table>
<thead>
<tr>
<th>k-points</th>
<th>Relative Energy ($\times 10^{-5}$eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x2x1</td>
<td>19920.53</td>
</tr>
<tr>
<td>1x4x1</td>
<td>733.52</td>
</tr>
<tr>
<td>1x8x1</td>
<td>222.79</td>
</tr>
<tr>
<td>1x16x1</td>
<td>5.36</td>
</tr>
<tr>
<td>1x32x1</td>
<td>3.06</td>
</tr>
<tr>
<td>1x64x1</td>
<td>0.85</td>
</tr>
<tr>
<td>1x128x1</td>
<td>0.00</td>
</tr>
</tbody>
</table>

an upper limit on the core width of 13nm. Figure 5.7 shows the slip across the cell and its second derivative. It can also be noted that the maximum slip in the centre of the cell and the minimum slip at the edge of the cell are not quite at 0 and 1.42nm and so perfect AB stacking is not achieved in these regions.

Following on from these small calculations longer cells were created and optimised until a structure was found to be long enough in the $x$ dimension to contain two well separated stable basal dislocations. This structure contained 1800 atoms and was approximately 96nm long. Once these structures had been optimised a script was
Figure 5.7.: The navy line shows the shear of the layer stacking in the \( x \) direction along the cell. The cyan line shows the second differential of this shear, the FWHM of this second differential is equal to the width of the core of the dislocation however the cores are not sufficiently well separated to accurately measure this width.

written to accurately measure the core width using the final atomic positions given by AIMPRO.

The core width is defined by the width of the region across which the slip is equal to \( b/2 \). This can easily be measured by plotting a graph of the slip between the two layers of the bilayer across the \( x \) dimension of the cell. From this the second differential of the slip can be calculated which has the appearance of two well defined peaks. The full width at half of the maximum of these peaks is the core width of the dislocation. An example of the graph plotted by the core width measuring script can be seen in Figure 5.8.

The interlayer separation distance has also been measured and it is seen that the distance is lowest in regions of AB and AC stacking and increases in regions containing a stacking fault. Figure 5.9 shows an example of the interlayer distance measured across a bilayer containing a 90° partial dislocation dipole.

The core width was found to be 10.65±0.05 nm. This is in agreement with literature values of similar structures of the order of 10 nm,\(^{70,71}\) however as far as we are aware is the first full DFT calculation of the 90° basal dislocation in bilayer graphene. The energy of the dislocated structure was compared to the energy of a perfect AB stacked bilayer of equal size. This gave an energy per unit length of the dipole of 1.45 eV/nm.

All structures are optimised using HGH pseudopotential 6-C-4, with charge basis
Figure 5.8.: The navy line shows the shear of the layer stacking in the $x$ direction along the cell. The cyan line shows the second differential of this shear, the FWHM of this second differential is equal to the width of the core of the dislocation.

Figure 5.9.: This graph shows the increase in interlayer separation distance across the dipole. The location of the cores of the dislocations are shaded in grey and the navy line shows a clear increase in the distance between the layers at the dislocation cores.
atom-1-5xs and a wavefunction basis set for graphite-pdpp. These pseudopotentials are all available on the aimpro website. The calculations were run with a k-point mesh of $1 \times 32 \times 1$ which was chosen as it was sufficiently dense to ensure the energies are well converged without prolonging the computational time. The number of k-points in each dimension is inversely proportional to the lattice parameter such that the longest dimensions have fewest k-points.

Owing to the huge aspect ratio of some of these cells it was not always possible to use a mesh which was exactly uniform as the calculation speed becomes unpractical when a mesh containing hundreds of k-points is used. In all cases the number of k-points in the $x$ and $z$ direction was 1. The calculations were run with Fermi smearing and a Fermi temperature of $kT = 0.05\text{eV}$.

In these initial bilayer calculations the lattice parameters are not optimised and as such the layers are held flat. This is likely to be the case for single dislocation dipoles in graphite systems as the neighbouring layers could act to hold the layers flat and prevent any delamination. However, this may not be the case in bilayer graphene as discussed in section 2.3.1.

A recent paper by Butz et al.\textsuperscript{72} has observed buckling of almost 1 nm of a bilayer of graphene containing a basal dislocation dipole which they explain occurs to release strain energy of the dislocations. This should not be surprising given the strength of the carbon to carbon bond and the energy it would take to stretch or compress these bonds. In a flat bilayer structure a very large number of bonds would have to be stretched or compressed to accommodate a basal dislocation even over a very wide core. If the layers were allowed to bend and buckle out of their flat planes the bond length variation could be reduced and so less energy would be stored in the dislocated structure.

For very large structures it was found to be beneficial to use classical potentials to pre-optimise the structures. This allowed a very fast computationally cheap calculation to be run on the initial structures to find a better starting point for AIMPRO to work from. This has proved very worthwhile as DFT calculations can be incredibly slow on large systems. Most of the structures optimised were over 1000 atoms and so even with access to the UK national supercomputer, ARCHER,\textsuperscript{135} only 20-30 optimisation iterations could be performed in 24 hours. Therefore, if several tens of cycles could
be avoided by providing a better starting structure it vastly speeds up the processing time for each structure.

The structures were pre-optimised with assistance from Dr T. Trevethan using the LAMMPS\textsuperscript{136} package with an AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) potential.\textsuperscript{76} This potential generally performs well\textsuperscript{78} but does not reproduce $C_{44}$ well and so requires atoms to be artificially fixed between the dislocations of the dipole to avoid unphysical annihilation. In AIREBO $C_{44}$ is known to be around ten times too small and so in order to prevent annihilation of a basal dislocation dipole the cell would need to be around ten times longer than reality. This means that the core width of the dislocation would also be approximately 10 times too large. For these reasons it was decided that molecular dynamics would be useful to pre-optimise the structures by introducing pinning points to hold the dislocations in, but it would still be essential to complete the optimisation using DFT to obtain the most accurate result.

It may be worth considering that the structures reported here contain a pure edge dislocation dipole (the armchair direction runs parallel to the $x$ axis and the dislocation line runs perpendicular to this) in this case a 90° partial edge dislocation, whereas Butz et al. have performed their optimisation on a mixed edge and screw type, 60° partial dislocation dipole (the zig-zag direction runs parallel to the $x$ axis and the dislocation is a contains edge and screw character such that the dislocation line has an $x$ and $y$ component). Alden et al.\textsuperscript{71} have shown that these boundaries have different properties. For example, from dark-field TEM, the FWHM of the boundary between AB and BA stacking is measured to be $6.2 \pm 0.6$ nm in the case of a shear boundary (screw type dislocation) and $10.1 \pm 1.4$ nm in the tensile boundary (edge type dislocation).

In order to provide a comparison for the methods used here to data published in the literature, the structure described in the work by Butz\textsuperscript{72} has also been replicated for optimisation using AIMPRO. Unfortunately there have been difficulties in optimising this structure using AIMPRO due to the large aspect ratio. It is hoped that this structure will be optimised using AIMPRO in the very near future with assistance from one of the code author, Dr Mark Rayson. Butz et al. do not make a measurement of the stored energy of the dislocation in the bilayer but their values of buckle amplitude and core width can will be used to validate further calculations.
In addition to the 90° partial and the Butz structure (60° partial), calculations have been prepared for defected graphite structures. These are discussed in the following section.

### 5.2. Graphite

The main challenge with extending the bilayer graphene work to graphite systems is the huge increase in the number of atoms. In order to meet the requirements of periodic boundary conditions it is no longer sufficient to build a structure containing a single dislocation dipole as there will be a discontinuity at the boundary of the periodic cell. Therefore a quadrupole of dislocations must be used to ensure that there are no discontinuities at the boundaries. A schematic diagram showing the alignment of dislocations in the quadrupole can be seen in Figure 5.10.

The number of atoms required to build this quadrupole is very large, mostly due to the larger core width of the basal dislocation in graphite. A simple way to half the number of atoms in a structure is to use a monoclinic lattice instead of the orthorhombic lattice used in the bilayer calculations reported in this thesis. A monoclinic cell allows the cell to be canted at an angle such that each dislocation is positioned below an oppositely signed dislocation in a neighbouring cell. This ensures that the periodic boundary conditions are upheld. A schematic diagram showing the monoclinic lattice can be seen in Figure 5.11. By halving the number of atoms in the structure in this
Figure 5.11.: This schematic shows the arrangement of dislocations in a cell of graphite. The cell is canted such that the dislocations are aligned with dislocations in neighbouring cells allowing a quadroupole to be created with the fewest possible atoms.

way it is possible to carry out calculations on dipoles of larger separation distances or separated by a larger number of layers.

Another program was written to quickly build dislocation structures in monoclinic graphite cells. This mapping of theoretical elastic strains onto the optimised perfect atom positions over a core width equal to that found in the work on basal dislocations in bilayer graphene allowed for a structure to be built as close as possible to the optimised structure.

A structure containing 3600 atoms (30 layers, 12.7 nm long) canted an at angle of 0.566 radians was created containing two basal dislocations of opposing Burgers vector, ±0.142 nm on the central glide plane. This structure was intended to be optimised using AIMPRO with a pinning point between the dislocations in order to hold the dislocations in place. However, owing to time and computational constraints this structure has not been optimised. The width of the structure required to create a stable dislocation dipole is likely to be the same as the width of a bilayer, this means that a structure big enough to hold a stable dislocation dipole would require over 10,000 atoms. Current DFT technologies and computer power means that a calculation this large is likely to be easily within our capabilities in the very near future, but not within the time frame of this thesis.

A much smaller cell containing 256 atoms (8 layers, each 3.4 nm) was optimised
using a k-point mesh $3 \times 6 \times 3$ and a Fermi temperature of $kT=0.01$eV. It was verified that the basal dislocation dipole also annihilates when the cores are overlapping, leaving perfect AB stacked graphite.

5.3. Summary

This chapter has described DFT calculations of dislocations in both bilayer graphene and graphite using the AIMPRO package. Structures containing both $60^\circ$ and $90^\circ$ partial edge dislocations in graphene have been created and their core widths measured and compared to literature values from theoretical and experimental papers. These calculations are the first full DFT calculations of dislocations in bilayer graphene and have only been made possible by the recent advances in filtration methods of AIMPRO and the support of its authors. Structures containing a dipole of $90^\circ$ partial edge dislocations in graphite have also been built and the behaviour of dislocations with overlapping cores has been confirmed to match that of dislocations in a bilayer. Unfortunately, it has not been possible to optimise a graphite cell wide enough to theoretically contain a stable dislocation dipole however it is expected that the dislocations will behave in the same manner as those in a flat graphene bilayer. These results can directly feed back into the 2D-DD modelling program to improve the quantitative results it provides.
6. Conclusion

The focus of this thesis has been dislocations in graphite, investigated using both 2D dislocations dynamics and density functional theory. Despite many decades of research there are still many areas of graphite science which have unanswered questions. This thesis has employed classical elasticity theory to simulate the standard model of dimensional change in graphite and a basal dislocation model. The expansion of the single crystal in the \( c \) direction was confirmed to agree with the expansion predicted theoretically by Lehto and Oberg.\(^{50}\) A further confirmation of the validity of this program is the agreement with the theory of two dimensional melting which was first discussed by Kosterlitz and Thouless in the 1970’s.\(^{91,92}\)

The energy stored in dislocation systems was found to be very large; in principle large enough to explain the Wigner energy peak at 200°C.\(^ {49}\) Explanations for this energy release have previously been incomplete; this suggestion of energy being stored in the dislocations in the graphite could prove very important in developing a complete theory of stored energy in irradiated graphite.

Observations of the motion of basal dislocations in a single crystal of graphite show that the dislocations glide freely into low energy configurations, namely kink bands. The formation of kink bands is not only theoretical and agrees with bands which have been produced experimentally.\(^ {100}\) The reaction of basal dislocations has also been implemented such that when basal dislocations in the same glide plane pile up they are replaced by a prismatic dislocation dipole. However, the question of the equivalence of energy of a basal dislocation configuration with a prismatic dislocation configuration has remained unanswered in this thesis. This is a large topic which needs to be explored and there are several ways this could be approached. One suggestion would be to add an energy term to the core of the dislocation which is dependent on the type of dislocation so that the basal and prismatic dislocation
representations are equivalent. This energy term would likely need to be dependent on the Burgers vector of the dislocation and the separation distances of the dipole. The core energies of dislocations could also be investigated to assist with formulating this core energy term using density functional theory to look at potential core structures and establish which arrangements of core atoms are most likely to occur.

The 2D-DD program was expanded to study related topics such as dislocations under an applied stress and a mode to map the internal stresses of a continuum containing dislocations. Stresses can be mapped for prismatic, basal and non-basal dislocations. The stress mapping function qualitatively reproduces the stresses mapped by Trevethan et al. using 

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The second area of research in this thesis employed the density functional theory program AIMPRO. Initial calculations were run on bilayer graphene systems containing basal dislocation dipoles. Calculations such as these have been carried out using molecular dynamics and are well documented in the literature however a full density functional theory calculation of dislocations in bilayer graphene had not been completed until this point. This is largely due to the number of atoms needed in the system to contain a stable basal dislocation dipole. Basal dislocations in graphite are known to glide freely and so a dipole will annihilate readily if the separation is not larger than the core of the dislocation. This is particularly problematic in graphite systems as the basal dislocation core is known to be very wide. Advances in AIMPRO have proved invaluable in allowing these calculations to be completed. Filtration algorithms have allowed system sizes orders of magnitude bigger than standard DFT limits.

The calculations within this thesis have confirmed that the width of the basal dislocation core in graphite is very wide and our measurement agrees with the estimates given in the literature by other modelling methods and experimental measurements. These calculations provide information which can be used to aid the construction of a dislocated graphite cell. The core width measurement can be fed back into the program which has been written to create these atomistic dislocation models to allow a structure to be produced which is as close as possible to the optimised structure. This will make the optimisation much faster and computationally less expensive.
An area of this thesis which has potential for further work is the simulation of basal dislocations in both the bilayer graphene and graphite cells. In the very near future it will be possible to carry out DFT calculations such as these on an average desktop computer. Several structures of different orientations of dislocations have been built and are just waiting for the computational ability to run the optimisation. A large area which could be investigated is the buckling of bilayer structures with dislocations of different magnitude Burgers vectors.

These DFT results can be fed back into the 2D-DD program to dictate the laws of reactions of the dislocations in the continuum, allowing for a more scientifically accurate evolution model. The obvious advantage being that modelling dislocations in a continuum is far faster than quantum based computational methods. A possible direction of future research for this 2D-DD program would be to take the output dislocation arrangements and simulate microscopy methods such as TEM for comparison to the wealth of microscopy imagery in the literature. The wider implication of this being that likely dislocation structures could be produced which explain well documented observations. This could help with the development of new models of dimensional change in irradiated graphite.

An additional area which could be explored is the potential to match these resulting structures up with other experimental evidence. For example the 2D-DD output could be used as an input for a TEM simulation which could then be compared to the extensive data in the literature.

The field of irradiated graphite research remains extremely broad and there are many avenues of investigation which need to be pursued before we have a complete picture of exactly what happens to graphite bombarded with neutrons inside the nuclear reactor. One of the greatest challenges is the difficulty of real time monitoring of the graphite during reactor cycles and of course just how black the material is - which makes microscopy experiments extremely tricky. This means theoretical modelling techniques are extremely valuable to provide likely scenarios and rule out unphysical mechanisms. As modelling methods advance this area will only become more and more powerful and it is only a matter of time before huge advances in graphite research are made as a result of these efforts.
A. AIMPRO

A.1. The data input file, *dat*

An example of the format used in the *dat* file used to submit a job to AIMPRO is as follows (Comments are denoted by ‘!’):

```
begin{data}
begin{title}
Unitcell for armchair bilayer system.
end{title}
filespace{.}

! lattice specification, including type of lattice and the lattice parameters, measured in atomic units
lattice{type=ort-p, params=8.050232711 4.648725932 12.604472344}
sampling{type=mp,grid=6 12 4,shift=0.5 0.5 0.5}
filling{smear=fermi,kT=0.01,metallic}
selfcon{tol=1.0E-5}
parameter{ecut=248.8}
parameter{use_kpar=TRUE}

! Job type
optimise{atoms=all}

! Specification of psudeopotentials and basis sets
begin{hghpseudo}
lib{.}
species{pot=6-C-4,cdbas=atom-1-5xs,wfbas=graphite-pdpp}
end{hghpseudo}
```

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Specification of the atoms and their position in the supercell. In this case the positions are described in internal co-ordinates relative to the lattice parameters described in the lattice(...)

\begin{verbatim}
1 1 0 0 0 0 0.000000 0.500000 0.000000
2 1 0 0 0 0 0.166565 0.000000 0.000000
3 1 0 0 0 0 0.499899 0.000000 0.000000
4 1 0 0 0 0 0.666431 0.500000 0.000000
5 1 0 0 0 0 0.000000 0.500000 0.500000
6 1 0 0 0 0 0.499882 0.000000 0.500000
7 1 0 0 0 0 0.333333 0.500000 0.500000
8 1 0 0 0 0 0.833098 0.000000 0.500000
\end{verbatim}
B. List of Publications and Presentations

B.1. Presentations

- **EDS2012** Thessaloniki, Greece. June 2012. *Dislocation theory for the mechanics of radiation damage in graphite*

- **INGSM13** Meitingen, Germany. September 2012. *Dislocation theory for the mechanics of radiation damage in graphite*

- **FunGraph Consortium meeting** Leeds, UK. January 2013 *Dislocation theory for the mechanics of radiation damage in graphite*

- **EDF Graphite Research Meeting** Manchester, UK. April 2013 *Radiation Damage in Graphite: Line Defects and Processes*

- **AIMPRO.2013** Guildford, UK. June 2013 *Dislocation theory for the mechanics of radiation damage in graphite*

- **INGSM14** Seattle, USA. September 2013. *Dislocation theory for the mechanics of radiation damage in graphite*

- **Chemistry department seminar** Guildford, UK. March 2014. *Dislocations in graphite and bilayer graphene*

B.2. Poster Presentations

- **CCP5 Summer School** Cardiff University, Cardiff. July 2012. *A 2D Dislocation Dynamic Model for Dimensional Change in Irradiated Graphite*

- **NanoteC12** University of Sussex, Brighton. August 2012. *A 2D Dislocation Dynamic Model for Dimensional Change in Irradiated Graphite*
• NanoteC13 University of Surrey, Guildford. August 2013. *A 2D Dislocation Dynamic Model for Dimensional Change in Irradiated Graphite*


B.3. Publications


The following paper, published in the special edition of Physica Status Solidi c for the proceedings of the Extended Defects in Semiconductors conference (EDS 2012), contains further details on the displacement and energy equations implemented in the 2D-DD program.
A 2D dislocation dynamic approach to simulating dimensional change in irradiated graphite using anisotropic strain theory

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Keywords anisotropic elasticity, 2D dislocation dynamics, graphite, irradiation damage

A program using two-dimensional dislocation dynamics with anisotropic strain equations has been written to simulate the dimensional change and stored elastic energy of irradiated graphite. A dislocation based model is put forward as a vehicle for both the long-standing atomic displacement model for dimensional change in irradiated graphite and a new model based on basal slip.

As expected the introduction of prismatic dislocation loops (climb dipoles in 2D) results in the expansion of the graphite crystal in the c-axis direction. Interestingly the stored elastic energy of the system was found to increase with number of dislocation dipoles and reached a maximum at the density which Burakovsky et al. (Phys. Rev. B 61, 15011–15018 (2000) [1]) predicted for melting.

1 Introduction

Graphite has been used as a neutron moderator in nuclear reactors in the UK and around the world for many decades [2]. As such there has been extensive research into the properties of the material and yet many questions remain unanswered. In particular the current standard model for dimensional change of irradiated graphite does not completely characterise the experimentally observed behaviour [3].

The standard model for irradiated graphite explains the dimensional change by migration of point defects into interstitial loops [4] which cause c-axis expansion. Formation of vacancy lines which can collapse and heal has been reported as the mechanism for basal contraction [5]. It is also worth noting that the contraction of the basal planes by this vacancy line healing prevents the annihilation of interstitial-vacancy pairs which would allow the material to return to perfect lattice over time [6]. However this point defect model does not predict nearly enough c-axis expansion as is observed [7]. At reactor temperatures the dimensional change in irradiated graphite with increasing fluence is linear in expansion parallel to the c-axis and linear in contraction along the axis normal to the c-axis [8]. There is a roughly 2:1 ratio of c-axis expansion to basal contraction as the basal contraction occurs over both the a-axis and b-axis.

The internal energy in a crystal of graphite will increase as defects are introduced to the material. The standard model attributes this internal energy to point defects such as interstitials which upon annealing move to more stable states and therefore release stored energy. The energy releases at different annealing temperatures can be used to interpret the defect which may have been present however it has been pointed out by Heggie et al. [3] that there are peaks in the energy release on annealing which cannot be explained by a point defect model.

Dislocations also introduce energy to the crystal and it is proposed that investigation of dislocation energies could answer questions posed by the unexplained energy release peaks of the point defect standard model [3]. The energy of the dislocation is an integral from the centre of the dis-
location to infinity and as the energy diverges at both these limits we can take the energy to be the integral between a small cylinder, with radius \(r_a\) and a large cylinder, radius \(r_a\), which are both concentric about the core of the dislocation [9].

It is hoped that the work presented here may assist in producing a model of the dimensional change in irradiated graphite based on dislocation theory additional to the current standard point defect model. If a model can be developed which explains the dimensional change of the graphite and the behaviour of the stored energy using a unified theory then this model could be far more satisfactory than the current model.

Two dimensional dislocation dynamics simulations using plane strain discrete dislocation plasticity have been carried out for many years and for many different aims. An early example is Ghoniem’s work in the 1980’s [10]. Current dislocation dynamics by the same author have now advanced to simulating in three dimensions [11]. However there are many recent studies which still use the two-dimensional model, in particular for applications to thin films [12], single crystals under quasi-static loading [13] and crack propagation studies [14]. Many pieces of work assume isotropy of the crystal as a close enough approximation of the elastic strains. This cannot be the case in graphite. This work uses the anisotropic displacement approximation of the elastic strains. This cannot be the case in graphite and the behaviour of the stored energy using a unified theory then this model could be far more satisfactory than the current model.

Two dimensional dislocation dynamics simulations using plane strain discrete dislocation plasticity have been carried out for many years and for many different aims. An early example is Ghoniem’s work in the 1980’s [10]. Current dislocation dynamics by the same author have now advanced to simulating in three dimensions [11]. However there are many recent studies which still use the two-dimensional model, in particular for applications to thin films [12], single crystals under quasi-static loading [13] and crack propagation studies [14]. Many pieces of work assume isotropy of the crystal as a close enough approximation of the elastic strains. This cannot be the case in graphite. This work uses the anisotropic displacement approximation of the elastic strains. This cannot be the case in graphite and the behaviour of the stored energy using a unified theory then this model could be far more satisfactory than the current model.

Dislocations and elasticity theory Introducing dislocations into a material introduces stresses which will result in atoms in the crystal being displaced from their original crystallographic positions. The elastic strain fields of dislocations have been studied in great detail and theory is based on the generalised Hooke’s law, \(\sigma_{ij} = C_{ijkl}\varepsilon_{kl}\) where stress, \(\sigma\), is related to strain, \(\varepsilon\), by a stiffness tensor \(C_{ijkl}\). We follow the usual convention of replacing the stiffness tensor with a \(6 \times 6\) matrix of stiffness constants \(c_{mn}\) where \(ij, kl\) to \(m, n\) in the following way (11 \(\rightarrow\) 1, 22 \(\rightarrow\) 2, 33 \(\rightarrow\) 3, 12 \(\rightarrow\) 6, 23 \(\rightarrow\) 4, 31 \(\rightarrow\) 5).

\[ \begin{align*}
&\text{displacement in } x, \\
&u_x = -\frac{b_x}{4\pi} \left( \tan^{-1} \frac{2xy\lambda \sin \phi}{x^2 - \lambda^2 y^2} + \frac{\varepsilon^2_1 - \varepsilon^2_2}{2C_{11}C_{16} \sin 2\phi} \ln \frac{q}{t} \right), \\
&\text{displacement in } y, \\
&u_y = \frac{\lambda b_y}{4\pi C_{11} \sin 2\phi} \left( (\varepsilon^2_1 - \varepsilon^2_2) \cos \phi \ln q t \\
&- (\varepsilon^2_1 + \varepsilon^2_2) \sin \phi \frac{1}{x^2 - \lambda^2 y^2} \ln \frac{q}{t} \right), \\
&\text{displacement in } z, \\
&u_z = 0.
\end{align*} \]

where in both equations \(b_x\) and \(b_y\) are the \(x\) and \(y\) components of the Burgers vector of the dislocation, \(x\) and \(y\) are distances from the dislocation axis and \(\varepsilon_{ij}\) values are elastic constants where \(i\) and \(j\) denote the crystal direction along which the constant is measured. The prime indicates that the constants used are oriented such that the \(3\) direction coincides with the dislocation axis. The rotated elastic constants used are obtained using equations from Hirth and Lothe [19] and values of the unrotated constants from Cousins [15], where \(C_{11} = 1060\) GPa, \(C_{22} = 36.5\) GPa, \(C_{12} = C_{13} = 7.9\) GPa and...
\[ c'_{11} = c'_{44} = c_{44} = 5.05 \text{ GPa}. \]

\[ \bar{c}_{ij} \] is the average elastic constant along the basal plane, given by the equation

\[ \bar{c}_{ij} = \left( c_{11}'c_{22}' \right)^{1/2} = 107 \text{ GPa}. \]

\( q \) and \( t \) are given by the relations

\[ q^2 = x^2 + y^2 \lambda^2 + 2 \right. \sinh \delta \text{ and } t^2 = x^2 + y^2 \lambda^2 - 2 \sinh \delta \]

and the remaining quantities are given as follows:

\[ \Lambda = \left( \frac{a^*}{c^*} \right)^{1/4} = 2.3, \quad \cosh 2\delta = \frac{c'_{11} - c_{11}'}{2c_{11}'}, \quad \cosh 2\lambda = 19.4 \]

and

\[ \phi = \frac{1}{2} \cos^{-1} \left( \frac{c'_{11} - c_{11}'}{c_{11}'} \right), \]

which is imaginary.

Since \( 2c'_{11} + c_{12}' - c_{11}' < 0 \), in this case \(-179\) GPa, the angle \( \phi \) evaluates to a complex angle and therefore the following substitutions must be made\[19\] in order for equations 1 and 2 to be used:

\[ \cos \theta = i \sin \delta, \quad \cos 2\phi = -\cosh 2\delta, \]

\[ \sin \phi = \cosh \delta \] and \( \sin 2\phi = i \sinh 2\delta, \]

where \( \delta \) is as defined previously. The complex components reduce to real expressions which are easily calculated.

These strain equations can be applied to each element of the boundary of a material in turn to find the displacement of that boundary due to a dislocation. Each subsequent dislocation which is added will add its own contribution to the displacement of each boundary element. If these displacements are summed the resulting shape of the material can be determined as a result of the strains of all the dislocations present.

### 2.2 Method and boundary conditions

Dislocation dipoles are added to the material, one dipole at a time, by generating a random \( x \) position and random \( y \) position quantised to account for the interlayer separation of graphite sheets. These dipoles are introduced with a fixed \( x \) separation of 80 Å and all have the same initial Burgers vector and are not allowed to be generated in a position which is already occupied by another dislocation, within one Burgers vector, in this case 6.64 Å.

In order to avoid finite size effects a periodic array of cells have been used along the \( z \)-axis, such that each cell holds an identical arrangement of dislocations. Each cell is populated with dislocations after which all dislocations in all cells are used to calculate the displacement of the edges due to Eqs. (1) and (2) described previously. The new positions of the edges are then used to calculate the mean expansion of the material which is plotted on a graph of expansion vs number of dislocations.

The program repeats this process of adding dipoles, calculating the boundary displacements and plotting the result until the requested number of iterations have been completed.

### 3 Energy

The energy of the system has also been calculated and is given as the sum of the self energies of the dislocations in the origin cell and the interaction energy of these dislocations with all dislocations in all repeat cells.

The core energy is set to zero.

#### 3.1 Self energy

The self energy of each dislocation per unit length is calculated as:

\[ E_{\text{self}} = \frac{K_e b^2}{4\pi} \left( \ln \frac{R_b}{R_e} - 1 \right) \]

where \( K_e \) is the energy coefficient which depends on the elastic constants of the material, \( b \) is the Burgers vector of the dislocation, \( R_b \) is the core radius of the dislocation and \( R_e \) is the radius within which the energy is calculated.

#### 3.2 Interaction energy

Interaction energy per unit length between two dislocations is given by:

\[ E_{12} = \frac{K_e}{2\pi} b_1 b_2 \left( \ln \frac{R}{R_b} - \cos^2 \theta \right) \]

where in this case \( b_1 \) and \( b_2 \) are the Burgers vectors of each dislocation, \( R \) is the separation between the dislocations \( \theta \) is the angle subtended between the line connecting the dislocations and one of their glide planes.

#### 3.2.1 Energy coefficients

The anisotropy of graphite is taken into account using the energy coefficients, \( K_{e_x} \) and \( K_{e_y} \) for the \( x \) and \( y \) directions respectively. These coefficients are given by:

\[ K_{e_x} = \frac{\left( c'_{11} + c'_{12} \right) \left[ c_{44} (c'_{11} - c'_{12}) \right]}{c_{22}' \left( c_{11} + c_{12} + 2c_{44}' \right)} \]

\[ K_{e_y} = \frac{\left( c'_{11} + c'_{12} \right) \left[ c_{44} (c'_{11} - c'_{12}) \right]}{c_{11}' \left( c'_{11} + c_{12} + 2c_{44}' \right)} \]

where the \( c_{ij}' \) values are elastic constants from Section 2.1, again transformed so that the line direction (in a basal direction) is \( z \). In the case of graphite \( K_{e_x} \approx 71 \text{ GPa} \) and \( K_{e_y} \approx 13 \text{ GPa} \).

### 4 Results

Prismatic dislocation dipoles are introduced into a 2D elastic continuum with the boundary mapped out as described in Section 2.2.
The program shows a linear expansion in c-axis with the introduction of prismatic dipoles. The energy of the system is also calculated with increasing dislocation concentration and the response of energy can be seen in Fig. 2. It was found that the energy of the system increases with number of dislocations, as would be expected, before reaching a peak energy when the density of dislocations is high.

![Figure 2](image_url)

**Figure 2** Program output showing the energy per cubic meter of the system for a material $(8 \times 12) \times 10^{-6}$ m with from 0 to 24000 dislocations $(b_n = 6.64 \times 10^{-10}$m). Red line: total energy of system. Black line: c-axis expansion.

As the self energy of the dislocations will always act to increase the total energy of the system the interaction energy must be causing the energy to decrease. The energy required to add a dipole of dislocations to the system can be negative when the magnitude of the interaction energy is greater than the magnitude of the self energies of both dislocations in the dipole. This effect of the system energy has been previously described by Cotterill as the transition point between a 2D solid and a 2D liquid [20].

The melting point of a 2D solid containing dislocations has been calculated by Burakovsky in terms of the density of dislocations as $\rho = (0.01 \pm 0.02)b^{-2}$ [1]. Our results agree with this prediction of the dislocation density at the observed energy peak as can be seen in Figure 2 where the Burakovsky formula predicts melting at $3320 \pm 110$ dislocations with Burger’s vector $6.64 \times 10^{-10}$m. The total energy of the system is seen to reach a maximum (approximately 11000 dislocations, 1.3 GJ m$^{-3}$). The stored energy at the peak corresponds to approximately 650 Jg$^{-1}$ for relatively dense (2.0 Mg m$^{-3}$) nuclear graphite.

Given that perfect prismatic dislocations were assumed and the dipole separation was arbitrary, and also that optimisation of dipole position after insertion was not allowed, it is very encouraging that this stored energy is of the same order of magnitude as the value of 420 Jg$^{-1}$ for the 200 °C peak inferred from the stored energy plot in Bollmann [21] for graphite irradiation at 30 °C.

**5 Conclusions** A two dimensional dislocation dynamic program has been written for graphite with anisotropic strain equations derived by Hirth and Lothe [19]. Random introduction of climb dipoles of prismatic dislocations gives large c-axis expansion as experimentally observed. The dipoles can represent any centre of c-axis dilation, either the prismatic interstitial loops of the standard model, or the new structures arising from basal slip, figure 1. Basal contraction is not accounted for at this stage. Phenomena related to the dislocation theory of melting are observed, with the stored energy decreasing after peaked [20, 1] and being similar in magnitude to experimental values [21].

In order to examine the possibility that basal slip affects dimensional change through the defects in Fig. 1, a version of this 2D-DD program based on basal dislocations is being developed.

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